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Graphene Oxide-Thermoplastic Nanocomposites: Fabrication and Properties

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GRAPHENE OXIDE-THERMOPLASTIC NANOCOMPOSITES: FABRICATION AND PROPERTIES

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Materials Science and Engineering

by
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ABSTRACT

Polymer nanocomposites are used for a wide variety of applications. These nanocomposites can have a number of important characteristics depending on the nature of the nanomaterial, its size, volume fraction, its distribution, and interactions within the host polymer. Mechanical strength, thermal and electrical conductivity are some of these materials' most focused and studied features. Besides the positive influences of the reinforcements, nanomaterials also might have some adverse impacts on the polymer matrix. These issues could arise from the aggregation of the fillers and the poor interfacial interactions of the components. Several approaches are introduced to modify the nanofillers and enhance their dispersion in polymer materials, leading to better performance of these composites. Graphene oxide (GO) is a relatively new carbonaceous material that is a good candidate for incorporation in polymers owing to its two-dimensional structure composed of sheets of sp² bonded carbon atoms.

The study presented in this dissertation is dedicated to fabricating polymer/graphene oxide nanocomposites with added functionality without deteriorating their properties. The first part of this dissertation is devoted to preparing polypropylene (PP)/graphene oxide nanocomposites based on PP short fibers through a combination of solution and melt mixing methods. Incorporating the nanoplates into the matrix is challenging because hydrophilic GO sheets tend to aggregate in the hydrophobic polypropylene matrix. Hence, GO sheets are modified to reach a good dispersion and adhesion of the filler to the matrix. For this purpose a reactive bottle brush copolymer called poly(Oligo Ethylene Glycol
methyl ether Methacrylate [OEGMA]- Glycidyl Methacrylate [GMA]- Lauryl Methacrylate [LMA]) containing reactive, hydrophobic, and hydrophilic parts is synthesized. This copolymer that can chemically bond to the GO sheets is developed to perform as a compatibilizer between hydrophilic GO and hydrophobic polymeric matrices. The GO nanoplates are covered with the copolymer from a water suspension. It is worth mentioning that no organic solvents are used for GO modification and deposition, and all fabrication is done using water. The chemical attachment of the copolymer chains to GO sheets is examined through different characterization methods. An extensive study on the adsorption of GO sheets on the surface of PP fibers is conducted to realize and confirm the attachment of the two components. The PP fibers covered with GO/copolymer sheets are then melt-processed to obtain the bulk PP/GO nanocomposites. The thermal and mechanical properties of the composites are characterized to examine the effect of GO and modified GO on the PP matrix. It is found that the addition of GO nanosheets does not significantly change the mechanical properties of polypropylene since the copolymer shell shields the nanomaterial inside the polymer matrix.

The second part of the dissertation is focused on employing the obtained functional nanocomposites for joining polymer parts via microwave heating. The heat generated by GO due to microwave absorption causes the melting of the polymer chains in the vicinity of the nanosheets and diffusing them into each other. Composites containing modified GO sheets heat up at a higher rate than those containing neat GO. These composites are used for assembling and dissembling polymeric parts, especially 3-D printed products. The 3D
printed parts are first mechanically investigated and compared with the similar pressed samples and then are exposed to microwave radiation.

Finally, the copolymer-modified graphene oxide is used as a compatibilizer for immiscible polystyrene (PS)/polypropylene (PP) blends. The copolymer containing hydrophobic and hydrophilic side chains attached to the GO sheets and pushed them to the blend interface. The PS/PP/GO blend composites are fabricated through a combination of solution mixing and melt processing methods. GO is either premixed with PS or PP in the materials’ processing stage. The influence of GO modification and the mixing order on the morphological and mechanical properties of the blends is studied. Based on thermodynamical predictions and morphological observations, it can be seen that modified GO sheets tend to go to the interface of PS/PP. Also, the order of mixing influences the morphology and properties of the composites.
DEDICATION

I dedicate this dissertation to my family, who always supported me and provided me with encouragement, guidance, and help throughout my life and my studies: my parents, Ebrahim Seyedi and Ameneh Seyedi, my brother and sisters Reza, Maedeh, Mahshid, and Sheida.

I would like to give special dedication to my dear husband, Mehrdad Yousefi, who always was there to help me. This step of my journey was not possible without his unconditional support, help, and caring.
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CHAPTER ONE

INTRODUCTION

Graphene is a two-dimensional sheet of sp² bonded carbon atoms with a honeycomb structure.¹ Its high intrinsic mechanical properties,² electrical,³ and thermal⁴ conductivity, have made it a suitable candidate for many applications. Graphene oxide (GO) is a derivative of graphene that has hydroxyl, carboxyl, and epoxy groups,⁵-⁶ making it more chemically active. In essence, oxidation of graphite to obtain GO makes the nanomaterial more wettable and prone to chemical bonding.⁷

Embedding GO in polymers to fabricate polymer/GO composites has received significant attention in the past decade due to the composites' exceptional mechanical, electrical, and thermal properties. If the host polymer is compatible with GO, the mechanical and thermal properties of the fabricated nanocomposite can be enhanced significantly.⁵, ⁸-¹⁰ Besides mechanical purposes, polymer/GO nanocomposites can be used for a number of advanced applications. For instance, due to the dielectric properties of graphene oxide sheets, their polymer composites can absorb electromagnetic waves.¹¹-¹² Such materials could be used in stealth applications where an object is required not to be detectable.¹³ Also, by shielding against electromagnetic waves, these nanocomposites can be exploited in electronic devices to protect the parts from electromagnetic interference and elevate the efficiency of the systems.¹⁹ Furthermore, polymer composites containing graphene oxide nanoplates can be heated up through microwave heating.¹⁴ The fact is that the dissipation of electric and electromagnetic energies and transforming them to heat by the nanosheets increases the
temperature of the surrounding polymer chains. This effect can be used to elevate the mechanical properties of 3D printed polymeric parts by improving the adhesion of the different printed layers. Another important application would be welding polymeric parts under microwave radiation. Polymers cannot be heated up without flow through traditional heating methods. Microwave heating on contact line is a suitable alternative that allows heating molded and 3D printed parts to assemble and disassemble them.

Considering all the mentioned advantages of GO-embedded polymers, the focus of this study is to fabricate polymer/GO composites and investigate the influence of GO on the mechanical and thermal properties of the polymers. Afterward, the nanocomposites are exposed to microwave radiation to explore their microwave absorption behavior.

However, there are some challenges with preparing polymer/GO composites. First of all, in the nanocomposites processing step, GO should be mixed with the polymer. Among the three most common methods of processing composites, including melt mixing, solution mixing and in situ polymerization, \(^{15}\) considering the economic and industrial criteria, melt blending is the most popular fabrication method. \(^{16-17}\) Because in this method, there is no need to use a solvent and the time of the process is shorter compared to the two other approaches. Furthermore, the required equipment is available in most of the industrial units. \(^{18}\)

However, producing polymer/GO nanocomposites via melt processing is a major challenge because of the difficulty in handling dry GO, the arrangement of GO in polymer matrices, and the weak matrix/filler adhesion, which results in poor mechanical properties. \(^{16}\) To ease working with GO, we propose to deposit GO on PP fibers from an aqueous GO solution.
before melt processing. The outcome of this process will be PP fibers wrapped by the GO sheets, which can be used to produce mechanically robust composites, Figure 1.1. Solution mixing followed by melt processing has been reported for HIPS/PE/GO blends. But in that research, the solution mixing part of the procedure is done in a THF solution, while here, we employ water as the only dispersing media.

Figure 1.1 SEM images of a) pristine PP fiber, b) PP fiber immersed in a 0.5mg/ml GO solution, obtained for this research.

Another critical challenge in achieving enhanced properties of the nanocomposites is dispersing individual GO sheets in the polymer matrix. Overcoming this issue will result in a uniform dispersion of the nanofillers and strong interfacial adhesion between the GO nanoparticles and the host polymer. Functionalizing GO or using a surface-active compatibilizer are some of the methods to solve this problem. An alternative approach is to use polymer chains to modify the surface of GO through “grafting-to” or “grafting-from” techniques. Despite the “grafting-from” method in which polymerization initiates from the surface of the GO sheets, in the “grafting-to” approach, we can synthesize the polymer
chains in a highly controlled manner and then attach them to GO. In this research work, we have planned to synthesize an amphiphilic bottlebrush copolymer via conventional radical polymerization with control over molecular weight and the ratio between hydrophobic and hydrophilic parts and then graft it to the GO nanoplates. This water-soluble copolymer can interact with both GO and PP and improve the adhesion between the two components, which can lead to a composite with improved mechanical characteristics.

The nanocomposite fabrication method used here includes the following steps: a) synthesis of a bottlebrush copolymer to be used as a compatibilizer, b) modification of the GO sheets with the macromolecules to obtain a stable aqueous suspension, c) covering PP fibers with the modified GO nanolayers from the water suspension, and d) melt processing of the dried PP fibers to obtain the nanocomposites. The general scheme of this material fabrication method is shown in Figure 1.2.

It must be mentioned that this strategy and methodology can be applied to different thermoplastic polymers.
The ultimate goal of this dissertation was fabrication, characterization, and understanding of structure-property relationships of polymer nanocomposites containing graphene oxide sheets modified with bottlebrush copolymers. After characterizing the fabricated nanocomposites, they have been used as microwave absorber materials and were implemented as binders for welding molded and 3D printed polymeric parts.

Figure 1.2 Schematic representation of the fabrication of PP/GO-copolymer nanocomposites.
Furthermore, when we have the sheets modified, we could use them for compatibilizing immiscible polymer blends. Virgin and modified with the bottlebrush copolymer GO sheets were used in all the experiments, and the results were compared and contrasted. In essence, the impact of this copolymer on the thermal, mechanical, and microwave absorption behaviors of the nanocomposites is studied.

The work was conducted as follows. First, a bottlebrush copolymer called poly(Oligo Ethylene Glycol methyl ether Methacrylate [OEGMA]- Glycidyl Methacrylate [GMA]-Lauryl Methacrylate [LMA]) containing reactive, hydrophobic, and hydrophilic parts was synthesized. This copolymer was meant to perform as a compatibilizer between hydrophilic GO and hydrophobic polymeric matrices. Next, the GO nanoplates were covered with the copolymer from a water suspension. Different characterization techniques such as AFM, FTIR, DSC, and TGA were performed to confirm the chemical attachment of the copolymer chains to GO sheets. UV-Vis measurements were conducted to analyze the stability of GO and GO/copolymer suspensions and also to find the optimum ratio between the two components to obtain the best dispersion of the nanoflakes in the suspension. Virgin GO and the GO sheets enveloped with the copolymer were introduced to PP fiber and PS powder dispersed in water to obtain PP/GO and PS/GO composites. The thermal and mechanical properties of the nanocomposites reinforced with pristine and modified GO were analyzed.

This dissertation is structured as follows:

- Chapter 2 of this dissertation gives a literature review of graphene oxide and its properties, GO functionalization, and the methods for fabricating
polymers and their structure-property relationship. It also discusses the characteristics of graphene oxide as a microwave absorber and its application in electronics. Moreover, utilizing GO as a compatibilizing agent in different polymeric blends is reviewed.

- **Chapter 3** describes the synthesis and characterization of POEGMA-GMA-LMA copolymer through a solution radical polymerization technique. The obtained copolymer is used to encapsulate GO nanoplates. Different characterization techniques are utilized to investigate the copolymer's attachment to GO and understand the modification's impact on the sheets’ properties.

- **Chapter 4** focuses on preparing PP/GO and PP/GO-copolymer nanocomposites and examining the properties of the obtained materials. This chapter aims to see how the presence of copolymer chains will change the morphological, rheological, thermal, and mechanical behaviors of the composites.

- **Chapter 5** is devoted to the 3D printed PP/GO composites. These materials are fabricated polypropylene pellet. The mechanical and thermal behavior of the printed samples are measured and compared with those of the compression molded samples.

- **Chapter 6** investigates the microwave absorption behavior of PP/GO composites. The impact of GO modification on the absorption is studied. In addition, the microwave heating approach is exploited to attach and detach pressed and printed parts.
• **Chapter 7** examines the utilization of GO and GO/copolymer to compatibilize immiscible PS and PP matrices. Different orders of compounding are taken in the nanocomposite blend preparation step, and the morphology and location of the pristine and modified sheets are realized through different morphological and physical techniques.

• **Chapter 8** concludes and summarizes the findings of this dissertation.

**References**


19. Guimont, A.; Beyou, E.; Alcouffe, P.; Cassagnau, P.; Serghei, A.; Martin, G.; Sonntag, P., Pentadecane functionalized graphite oxide sheets as a tool for the preparation


CHAPTER TWO
LITERATURE REVIEW

2.1. Introduction

This chapter is devoted to reviewing the scientific concepts important for this research work. Firstly, graphene oxide is examined as one of the base materials used here. Understanding its structure and behavior would help us exploit its properties for the targeted applications. One of the key areas of using GO is in polymer nanocomposites, which gives them a variety of characteristics depending on the nanoplates treatment and incorporation method. Reviewing the literature, especially research on polypropylene/GO nanocomposites, could enable us to anticipate the properties of the fabricated materials. Moreover, the challenges of 3D printing of polymer/GO nanocomposites are reviewed since this technique would be used as a method of composite parts fabrication. Finally, two important applications of functionalizing polymers with GO are studied. Using microwave radiation to heat the polymer/GO composites is one of the essential aspects of this research, and its basics are explained in this chapter. Furthermore, the compatibilizing effect of GO on polymer blends is explored in the literature to see if this nanomaterial can positively influence the characteristics of the immiscible blends.

2.2. Graphene and graphene oxide

Since its discovery in 2004\(^1\) graphene (GR) has been the subject of many researches because of its outstanding properties. A single layer of graphene oxide has a tensile strength of 130GPa and Young’s modulus of 1TPa. This new class of two-dimensional carbon nano-
structure with its excellent characteristics such as high electrical\textsuperscript{2} and thermal conductivity,\textsuperscript{3} transparency,\textsuperscript{4} elasticity,\textsuperscript{5} and impermeability\textsuperscript{6} can be exploited in a number of applications. These features, along with the high aspect ratio and the cost efficiency of graphene, make it an effective filler in polymer composites comparable to carbon nanotubes. Incorporating a small amount of graphene significantly elevates the mechanical\textsuperscript{7}, thermal\textsuperscript{8}, and electrical\textsuperscript{9} properties of the host polymer.

Different methods have been established to synthesize GR, such as micromechanical cleavage of graphite,\textsuperscript{1} chemical vapor deposition (CVD),\textsuperscript{10} chemical synthesis,\textsuperscript{11} and chemical\textsuperscript{12} or thermal\textsuperscript{13} reduction of graphene oxide. Among these methods, the reduction of GO is currently the most used method since it has a low cost, produces large amounts of GR, and is easy to realize in industrial units\textsuperscript{14}, Figure 2.1.
Figure 2.1 Physicochemical method for preparing graphene oxide and reduced graphene oxide sheets from graphite stack.\textsuperscript{15-16}

GO is an electrical insulator material due to the presence of the functional groups. These groups break the conjugated structure and result in the localization of $\pi$-electrons.\textsuperscript{17} Furthermore, the defects present on the surface of GO decrease its mechanical properties.\textsuperscript{17} GO has an amphiphilic structure composed of hydrophobic carbon hexagons containing epoxide and hydroxyl groups\textsuperscript{18} on the basal plane and hydrophilic carbonyl and carboxyl groups on the edges.\textsuperscript{19}

2.3. Mechanisms of GO adsorption on surfaces
The adsorption isotherms are studied to understand the interaction between adsorbate and adsorbent. By investigating the equilibrium adsorption isotherms, one can understand the interaction between GO and the absorbent surface and the process of GO adsorption from solution to the surfaces. The equilibrium time can be obtained from the adsorption kinetics data. Among different isotherm equations describing the adsorption of a solute onto a solid surface, two important ones include two models governing adsorption to homogenous and heterogeneous surfaces, respectively. Langmuir model describes adsorption to a homogenous surface with energetically identical adsorbing spots. This model predicts a saturation concentration after which no more solute can be adsorbed by the solid surface, resulting in formation of a monolayer over the surface:

$$q_e = \frac{X_m a_L C_e}{1 + a_L C_e}$$

(2.1)

where $q_e$ is the equilibrium amount of GO per unit weight of the dry adsorbent (mg/g), $C_e$ is the equilibrium concentration of the GO solution (mg/l), $X_m$ represents the maximum adsorption capacity, and $a_L$ is the Langmuir constant describing the affinity of adsorbate to adsorbent.

The second model is Freundlich isotherm, which can be applied to adsorption of a multilayer on a heterogeneous surface. Based on this empirical model, first, stronger binding sites are occupied, and by completion of the adsorption procedure, the adsorption energy decreases exponentially:

$$q_e = K_F C_e^{1/n_F}$$

(2.2)
where \( K_F \) represents the adsorption capacity of the adsorbent and \( n_F \) describes the heterogeneity and adsorption intensity of the adsorbate.\(^{20}\) A low \( n_F \) value represents the minimal adsorbent heterogeneity, close to be homogeneous. Therefore, a surface with very small \( n_F \) will be a uniform and homogenous one following the Langmuir model. On the other hand, a large \( n_F \) indicates the deviation of adsorption from linear isotherm. If \( n_F \) is in the range of 2-10, it shows strong adsorption, and the range of 1–2 implies relatively difficult adsorption. Poor adsorption is indicated by the values of \( n_F \) lower 1.\(^{23}\) By finding the governing equation on GO adsorption; one can predict if there is a saturation time when the adsorbate can adsorb no more GO.

### 2.4. Polymer/ graphene oxide nanocomposites

GO has an extended \( \pi \)-conjugated structure, making it an excellent candidate to perform as a reinforcing agent to enhance the properties of polymer composites.\(^{24}\) Moreover, the oxygen-containing functional groups on the surface of GO improve the interfacial interaction between various polymers and the GO sheets\(^{25}\), Figure 2.2.

![Figure 2.2 Chemical structure of graphene oxide containing different functional groups.\(^{26}\)](image)

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### 2.4. Polymer/ graphene oxide nanocomposites

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![Figure 2.2 Chemical structure of graphene oxide containing different functional groups.\(^{26}\)](image)
The two main factors determining the properties of the final composite material are the level of dispersion of GO in the matrix and the interfacial adhesion between the two components. The strong π-π interactions causing stacking of GO sheets can prevent their fine dispersion in the host matrix and accordingly deteriorate the mechanical properties of the composites. In essence, GO agglomeration deteriorates the adhesion of these sheets to the matrix, resulting in a lower tensile modulus.

Graphene oxide is more compatible with most of polymers than graphene, resulting in a better dispersion in the host matrix. Due to their polar nature, GO nanoplates are incompatible with many non-polar polymer matrices leading to poor mechanical properties of their composites. In other words, GO still does not have a strong interfacial interaction with most of the polymers, and consequently, its application in fabricating composites is limited.

Strong bonding between GO and polymer matrix is required to exploit the ultrahigh mechanical properties of the fillers. The interaction of the filler and the matrix determines the tensile strength of the composites. These interfacial interactions between GO and polymer at the molecular level can be strengthened by functionalization of GO or using a surface-active compatibilizer which prevents the restacking of the nanoplates during compounding with polymer and results in enhanced dispersion of GO in the matrix. Consequently, mechanical characteristics of the composite such as strength, stiffness, toughness, and brittleness can be improved. An alternative approach is to use polymer chains to modify the surface of GO through “grafting-to” or “grafting-from” techniques. Despite the “grafting-from” method in which polymerization initiates from the surface of...
the GO sheets, in the “grafting-to” approach, one can synthesize the polymer chains in a highly controlled manner and then attach them to GO.\textsuperscript{35}

GO has two opposite effects on the dynamic of the polymer chains. It can be increased free volume around the GO sheets for the polymer chains to move. On the other hand, GO functional groups' hydrogen bonding with polymer chains can restrict their movement. In total, the presence of GO often causes a higher Tg of the composites because hydrogen bonding is stronger than Vander Waals bonding.\textsuperscript{17} GO sheets can also perform as nucleation agents for crystallization and increase the crystallinity of the composites,\textsuperscript{19} which can lead to improved mechanical properties.

Polymer/GO composites have been fabricated through different methods, including melt blending, solution mixing, and in-situ polymerization. It is reported that melt blending leads to poor distribution of nanofillers in most cases.\textsuperscript{36} Melt compounding of GO and polymers has been done for elastomers\textsuperscript{25} and plastics.\textsuperscript{37} Comparing melt blending and solution blending of GO with polymers shows a better dispersion of GO in the solution-processed nanocomposites.\textsuperscript{25} There is no research reporting a better result for compounding via polymerization than the two other methods.

2.5. Polypropylene/GO nanocomposites

Polypropylene (PP) is a thermoplastic polymer with high chemical resistance,\textsuperscript{38} good melt processability,\textsuperscript{39} good thermal and mechanical properties,\textsuperscript{40} and low cost.\textsuperscript{41} These parameters make this polymer suitable for many practical applications including automobiles,\textsuperscript{42} electronics,\textsuperscript{43} and packaging.\textsuperscript{40} Enhancement of PP properties and
introducing new features to PP materials are possible by adding an active dispersed phase. To this end, compounding PP with reinforcing and functional materials, especially nanomaterials, has been suggested and realized by many researchers with positive results.\textsuperscript{44} For instance, carbon nanotubes (CNT) and graphene-based carbon nanomaterials were used to improve PP-based materials.\textsuperscript{15} The degree of improvement is a function of geometrical parameters of the fillers (size, surface area, and aspect ratio), dispersion and orientation of the nanofillers in the matrix, and the interaction between particles and the matrix.\textsuperscript{45} It has been shown that GR provides more advantages than CNT and offers enhanced mechanical properties to a higher degree.\textsuperscript{46} This observation is attributed to the 2D structure of GR\textsuperscript{47}, which leads to more efficient load transfer inside the polymer composite.

The incorporation of GO in different polymers like poly(methyl methacrylate) (PMMA)\textsuperscript{48} and epoxy\textsuperscript{7} has shown a significant improvement in the mechanical properties of the nanocomposites. However, a limited number of research works focus on PP/GO nanocomposites and investigate their rheological,\textsuperscript{49} mechanical,\textsuperscript{39} thermal\textsuperscript{50}, and electrical\textsuperscript{51} properties. The main concern in most research works is the poor adhesion between polypropylene and graphene oxide due to the incompatibility and low thermodynamical interaction between these non-polar and polar components.\textsuperscript{52} Therefore, different approaches have been employed to increase their compatibility, such as in-situ polymerization of PP in the presence of GO,\textsuperscript{53-54} using a compatibilizing agent,\textsuperscript{31, 55} functionalizing GO,\textsuperscript{14} and modification of GO with polymer chains before mixing.\textsuperscript{56} By utilizing characteristics of well-controlled synthesized polymers, the last method offers
more advantages over the others. The two main methods for anchoring polymer chains to a substrate are “grafting to” and “grafting from”, Figure 2.3. Attachment of readily synthesized polymers to the surface through the chemical reaction between functional groups of the guest polymer and the host substrate is known as the “grafting to” method. In this approach, the polymer chains can be characterized and optimized precisely before grafting, to result in the desired grafted layer on the surface. On the other hand, in the "grafting from" technique, polymerization starts from the host surface's initiating groups, which will guarantee dense attachment of polymer chains to the surface. This method requires functionalization of the GO sheets before polymerizations, which can vary between different batches, causing non-uniform coatings.

To quantify the dispersion of GO in the PP matrix, rheological measurements can be conducted. In this regard, it can be assumed that the GO nanosheets have a random
orientation in the matrix. However, the rheological behaviors are a function of the flow orientation of the embedded nanoparticles\textsuperscript{59} and this assumption can be unrealistic. Formation of the solid-like network is identified when elastic modulus starts to be independent of frequency.\textsuperscript{60} Also, It has been reported that strong interaction between PP and GO increases the viscosity of the nanocomposite\textsuperscript{61}, which can be attributed to restricting movements of the PP chains by GO nanoparticles.

Since we needed to evaluate the mechanical characteristics of PP/GO composites in this research, we have compared the research works investigating the effect of GO on the mechanical properties of the PP matrix, Table 2.1. As it can be observed, the most used method is melt mixing due to its applicability in an industrial setting. Also, in all cases, GO is either reduced or functionalized in organic solvents and compatibilized to enhance the properties of the composites.
Table 2.1 Mechanical properties of PP/GO composites reported in the literature.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Compatibilizer</th>
<th>Fabrication method</th>
<th>GO wt.%</th>
<th>Young’s Modulus change%</th>
<th>Tensile strength change%</th>
<th>Elongation at break change%</th>
<th>Storage modulus change%</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/GR</td>
<td>-</td>
<td>In situ polymerization</td>
<td>2</td>
<td>14.8</td>
<td>18.2</td>
<td>-13.8</td>
<td>-</td>
<td>54</td>
</tr>
<tr>
<td>PP/GO-alkyl</td>
<td>-</td>
<td>Solution mixing</td>
<td>1</td>
<td>92.3</td>
<td>-9.7</td>
<td>-</td>
<td>-</td>
<td>18</td>
</tr>
<tr>
<td>PP/GO</td>
<td>amine- alcohol grafted polypropylene</td>
<td>Melt mixing</td>
<td>1</td>
<td>23.5</td>
<td>5.1</td>
<td>-</td>
<td>-</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solution mixing</td>
<td>1</td>
<td>32.5</td>
<td>7.4</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PP/GO</td>
<td>-</td>
<td>Melt mixing</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-152 at 25°C</td>
<td>41</td>
</tr>
<tr>
<td>PPGO</td>
<td>maleic anhydride-grafted PP</td>
<td>Melt mixing</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-152 at 25°C</td>
<td></td>
</tr>
<tr>
<td>PP/GO-H3PO3</td>
<td>-</td>
<td>Melt mixing</td>
<td>0.3</td>
<td>-</td>
<td>14.3</td>
<td>-</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>PP/GO-p-phenylenediamine</td>
<td>amine- alcohol grafted polypropylene</td>
<td>melt mixing</td>
<td>1</td>
<td>0</td>
<td>-</td>
<td>-91.7</td>
<td>-7.2 at 30°C</td>
<td>52</td>
</tr>
<tr>
<td>PP/GR</td>
<td>-</td>
<td>Melt mixing</td>
<td>1</td>
<td>19.3</td>
<td>-10.6</td>
<td>-96.3</td>
<td>-</td>
<td>63</td>
</tr>
<tr>
<td>PP/reduced GO</td>
<td>maleic anhydride-grafted PP</td>
<td>Melt mixing</td>
<td>1</td>
<td>54.6</td>
<td>29.3</td>
<td>-90.3</td>
<td>-</td>
<td>64</td>
</tr>
<tr>
<td>PP/GO-alkyl-amine</td>
<td>-</td>
<td>Melt mixing</td>
<td>1</td>
<td>47</td>
<td>29.4</td>
<td>-</td>
<td>-</td>
<td>65</td>
</tr>
</tbody>
</table>

2.6. 3D printing of polymer/GO nanocomposites

3D printing, also known as additive manufacturing, is a relatively novel method for 3D parts production by joining materials in a layer-by-layer fashion. 66 3D printed structures
can be extremely complex compared to the conventionally fabricated ones, resulting in greater design flexibility and precision. Moreover, the amount of wasted material through the 3D printing technique is much lesser than that for conventional part fabrication methods.

Additive manufacturing approaches include but are not limited to fused deposition modeling (FDM), selective laser sintering, inkjet 3D printing, stereolithography, and 3D plotting. FDM is the most used approach in household, educational, and industrial settings, Figure 2.4. In this technique, thermoplastic polymer filaments are fed to the 3D printer according to a specific pattern, and their temperature is increased above the glass transition temperature. A moveable nozzle extrudes the filaments in an X-Y plane to print successive layers resulting in a 3D structure.

![Figure 2.4 Schematic representation of a typical FDM setup.](image)

Figure 2.4 Schematic representation of a typical FDM setup.
Operational parameters such as the printing temperature, speed, time, and bed temperature should also be optimized to reach printability. One of the most important factors is the printing temperature. The viscosity of the melted material should be low enough to enable the extrusion process and, on the other hand, high enough to provide mechanical support for the successive printed layers. A high temperature will result in the deformed shape of the printed structure when the low viscosity melted material spreads and covers the previously printed layers. On the other hand, reducing the temperature to increase viscosity can cause nozzle jam and consequently decrease the printing resolution.

Pure polymers such as polylactic acid (PLA), polyethylene terephthalate glycol (PETG), and acrylonitrile butadiene styrene (ABS) are the materials mainly used for 3D printing for general purposes. However, the 3D printed pure polymers usually do not have the desired strength and functionality, restricting their wide industrial application. Therefore, printing using polymer blends and polymer composites is growing dramatically. 3D parts fabricated using specific functional materials can be used in different applications such as conductive composites, sensors, electrochemical devices, and membranes. The raw functional materials to fabricate multifunctional 3D printed parts can be obtained through embedding micro and nanomaterials like silicate, graphene, and CNT in polymers. However, printing nanocomposites involves some challenges. The first one is the agglomeration of the nanofillers, causing nozzle jam, which reduces the printability and results in a rough surface of the printed material. Therefore, the size of the nanofillers and their distribution in the matrix play an essential role in the printability of the composite.
The addition of nanofillers usually decreases the flexibility of the materials; nonetheless, their flexibility should be maintained to an extent to get spooled during the filament collection process after melt mixing without breaking.\textsuperscript{68} Obviously, the selected polymer matrix and the nanofiller should be thermally stable enough to withstand the high temperatures of extrusion and printing steps. The temperature and the time length of the printing process cannot be too high since it will cause degradation of the materials and the introduction of voids in the printed part.\textsuperscript{78} Moreover, it has been shown that embedding metal particles can prevent the distortion of the printed parts.\textsuperscript{79}

Another issue associated with printing composite materials is the wearing of the printing nozzle. With et al. reported that after printing polybutylene terephthalate (PBT)/CNT and PBPT/graphene composites, they found that the brass printing nozzle (0.4 mm diameter) was abraded on the inside surface and the front surface touching the printed material, Figure 2.5. They have contributed this effect to the exceptionally high specific Young’s modulus of CNTs and graphene.\textsuperscript{68} The material printed with this degraded nozzle has a rough surface and irregular edges, resulting in a lower printing resolution and causing undesirable properties. For this reason, using nozzles made of harder materials -such as silicon carbide- is advised for printing abrasive polymer composites.
Figure 2.5 Optical micrographs showing the surface of a 3D printing nozzle before and after printing. (a) Unused nozzle. (b) Nozzle after printing ∼10 cm of PBT/G. (c) Nozzle after printing ∼1.5 m of PBT/CNT. (d) SEM image of PBT/G composite printed with an abraded nozzle.68

2.7. Microwave absorption of polymer/GO nanocomposites

Sometimes, it is needed to join different thermoplastic or thermoset parts in the polymers industry to make parts of sufficient complexity. An efficient welding technique could result in joints with mechanical properties close to bulk materials.80 The traditional jointing approaches of polymeric composites are mechanical fastening and adhesive bonding.81 However, these methods may need some pretreatments (such as surface treatment for adhesive bonding) or impose mechanical damage on the final pieces.82

As an alternative approach, thermal welding can address the issue of welding thermoplastic composite materials.83 Resistance welding is an example of thermal welding at which a
resistive element is placed on the surface of the parts. Then an electric current is applied through the elements to heat and melt the composites to bond them.\textsuperscript{82} This method has been reported for several graphite-reinforced thermoplastics.\textsuperscript{84}

Using microwave radiation as the source of heating for thermal welding is a new and fast-growing technique.\textsuperscript{85} In this method, a microwave absorber material heats up under microwave exposure and welds the polymeric parts, Figure 2.6.

![Figure 2.6 Welding polymeric parts using a microwave absorber material under microwave irradiation.\textsuperscript{85}](image)

Microwaves are electromagnetic waves in the frequency range of 300MHz to 300GHz\textsuperscript{80}, Figure 2.7. Commercial ovens produce 2450MHz microwaves.
Depending on their reaction with the microwaves, materials can be either transparent or absorbent to the microwave. The materials' electrical conductivity and dielectric properties indicate if they absorb microwave or not. Dielectric constant or electric permittivity ($\varepsilon'$) is the ability of a material to store an electric charge, so it would be a representative of the polarity of materials’ molecules in the electric field. On the other hand, dielectric loss or dissipation factor ($\varepsilon''$) indicates the amount of field energy dissipated by a material through dielectric mobility or polarization. A material with a high dielectric loss will have a low output field energy, which results in higher microwave absorption. Complex permittivity describes the loss mechanism, Equation 2.3:

$$\varepsilon^* = \varepsilon' \pm j \varepsilon''$$  \hspace{1cm} (2.3)
Complex permittivity represents the interaction of the material and the microwave radiation, and consequently, the amount of generated heat. In the case of multicomponent materials, when the electric field passes through the interface, the difference in electrical conductivities results in accumulated surface charges, which induces energy dissipation. Accordingly, loss tangent is defined as the ability of a material to absorb electromagnetic energy and convert it to heat energy:

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]  

(2.4)

A material is called a high microwave absorber if its \( \tan \delta > 0.5 \). By exposing to an alternating electromagnetic field, dielectric materials with permanent dipoles are forced to orient their dipoles in the direction of the alternating electric or magnetic fields, Figure 2.8. However, these dipoles will not quickly conform to the high-speed reversals in the field, and there would be a phase lag with the field. Consequently, the resistance to this rearrangement generates heat.\(^{87}\) Some of the advantages of microwave heating over the traditional heating methods are fast and selective heating, the use of a remote source, heating uniformity, clean energy and spreading in the vacuum, and high heating efficiency with negligible energy loss.\(^{17, 80, 86-87}\)
Lambert’s law expresses the microwave energy absorbed by a dielectric material. According to this equation, heat generation in a material is a function of the strength of the electric field, frequency, and dielectric loss properties of the material:

\[
Q = \sigma |\vec{E}|^2 = 2\pi f \varepsilon_0 \varepsilon (\tan \delta) \vec{E}^2
\]

(2.5)

where \( Q \) is the microwave energy density (W/m\(^3\)), \( \sigma \) is the electrical conductivity, \( \vec{E} \) is the electric field strength (V/m), \( f \) is the frequency of the microwave (Hz), \( \varepsilon_0 \) is the permittivity of free space (8.8514×10\(^{-12}\) F/m), \( \varepsilon \) is the dielectric constant that quantifies the stored and transmitted energy from the material, and \( \tan \delta \) is the loss tangent coefficient.

Therefore, by putting different materials under the same microwave irradiation, those with a higher dielectric loss will generate a higher amount of heat. The loss factor depends on
the frequency and temperature. For instance, the highest microwave absorption by water occurs at 18GHz.

The amount of heat generated by the material exposed to microwave radiation can be calculated experimentally, equation 2.6:

\[ Q = mc\Delta T \]  \hspace{1cm} (2.6)

Where \( m \) is the mass of the material, \( c \) is the specific heat capacity, and \( \Delta T \) is the temperature change. Consequently, the actual power of the microwave instrument, \( P_{actual} \), can be calculated using equation 2.7:

\[ P_{actual} = \frac{Q}{t} \]  \hspace{1cm} (2.7)

Where \( t \) is the radiation time. Then the heating efficiency can be obtained using equation 2.8:

\[ \eta = \frac{P_{actual}}{P_{nominal}} \]  \hspace{1cm} (2.8)

where \( P_{nominal} \) is the power attributed to the microwave instrument.

Most polymers are transparent to microwaves due to their low intrinsic dielectric loss. The addition of conductive, magnetic, or polar fillers could result in polymer composites with microwave absorption ability. Various carbon allotropes like graphite\(^{88}\), carbon black\(^{89}\), carbon nanofibers\(^{90}\), and carbon nanotubes(CNT)\(^{91}\) have been incorporated into polymers to improve their microwave absorption. The microwave absorption of the obtained material is a function of the filler-matrix interactions and the filler properties such as the intrinsic
electromagnetic properties, geometry, distribution and morphology, and the amount of the filler. Furthermore, the thickness of the sample plays an essential role in the exposure of different parts of the piece to microwave radiation. Since the microwave penetration depends on the thickness of the exposed material, its intensity decreases as it goes through the sample. In this regard, the penetration depth term is defined as it indicates the impact of radiation on the different depths of the piece. Penetration depth is the depth from the surface where the resulting temperature change is half of the surface or where the power density decreases to $1/e$ or 37% of its initial value.

$$D = \frac{3.31 \times 10^7}{f \sqrt{\varepsilon_r \times \tan \delta}}$$

(2.9)

where $D$ is the penetration depth, $f$ is the frequency, $\varepsilon_r$ is the relative permittivity and $\tan \delta$ is the dielectric loss angle. Therefore, the penetration depth decreases as the dielectric loss factor increases. So, a good microwave absorber material should possess an optimum dielectric loss amount to be microwave dissipating enough on the one hand, and on the other hand, allow the incident wave to go through its thickness. Moreover, the thickness of the samples should be designed considering the penetration depth to ensure that the whole piece is almost uniformly exposed to the waves.

Light-weight polymer-filler composites are excellent candidates for microwave absorption since they have low surface reflection (good impedance matching with the medium) and high loss properties (high electric or magnetic loss or a combination of both). Park et al. fabricated a multilayer microwave absorber material which at each layer had a different microwave absorption to maximize the overall absorption of the system. The front layer
prevents reflection, the middle layer absorbs microwave, and the substrate layer reflects the escaped waves to the middle layer.

Microwave absorptions of polymer composites containing different nanomaterials are examined and used for various applications. In a pioneer research, Green et al. used microwave radiation to weld 3D-printed thermoplastic interfaces using intense localized heating of carbon nanotubes\textsuperscript{94}, Figure 2.9. They reported a 275\% improvement in weld fracture strength after microwave irradiation.

Galindo et al. investigated the effect of carbon nanotubes and multilayer graphene on microwave absorption characteristics of PP composites.\textsuperscript{86} In virtue of the differences in electrical conductivity and dielectric properties of CNT and graphene; their microwave absorption behaviors are different.\textsuperscript{86} CNT composites perform as conductor materials, and they reach the melting temperature of PP quickly during microwave exposure. In contrast,
PP-graphene composites show a capacitance behavior and cannot be melted in the microwave oven even with 10% graphene loading and have a lower heating efficiency than the PP-CNT composites. PP-graphene composites show uniform heating inside the microwave oven, but due to the presence of CNT agglomerates, PP-CNT composites show hot spots when heated in the microwave, and some parts of the samples are burned. Zhu et al. used the microwave absorption ability of graphite oxide to exfoliate and reduce it to graphene.

GO is not a good conductor of electricity, so it does not absorb microwave as much as intact graphene. However, it has been shown that the interfacial interaction between polyvinyl alcohol (PVA) and GO has reduced after reduction of oxygen-containing functional groups of GO. This finding confirms that GO sheets absorb microwave, heat up, and release their oxygen atoms. Based on this, Li et al. fabricated polyurethane/GO composites and used their microwave absorption ability to apply in healable flexible electronics. The microwave absorption characteristic of GO is well reported previously, for instance the dissipation of the microwave and converting it to heat has been employed to GO reduction, which is a fast and material selective method of GO reduction.

When the GO sheet heats up, it causes the surrounding polymer chains to melt, and they will stick closer to the sheet surface; consequently, there will be less free volume at the GO/polymer interface. This will increase the glass transition temperature of the composite material. Also, these sheets with polymer chains stuck to them will be more rigid than the GO sheets. These isolated GO-polymer clusters will be more effective in bear loading;
therefore, the modulus will increase. But they restrict the deformation of the material so decrease the toughness.\textsuperscript{17}

The experimental observations have shown that a short time of microwave radiation results in a lower length of chains after the microwave treatment; therefore, the chains can align easier, and the crystallinity percent increases. However, a longer radiation time will result in degradation and lower crystallinity percent.\textsuperscript{97} In the same way, short microwaving time increases thermal stability due to cross-linking and better graphene dispersion, but longer times result in degradation and lower thermal stability.\textsuperscript{97}

In different literatures, microwave heating has been mentioned as a volumetric heating tool. However, several reports have shown that there are some factors that prevent the homogenous heating of a material exposed to microwave radiation. Some of these parameters are as explained following: 1) Thermal conductivity of the material: A material with low thermal conductivity retards the heat transfer through it. Therefore, the different parts of a sample can experience a variation of temperature, and the heat buildup in some parts may cause hot spots. Besides, the dielectric properties and the material's thermal conductivity might change during the heating process. The occurrence of chemical reactions and the mentioned factor can cause a non-uniform heat distribution in the material under microwave radiation.\textsuperscript{87} 2) Microwave shielding: This issue happens in filled materials at which the presence of the filler increases the microwave loss due to interface polarization. Consequently, a significant amount of the radiation is lost by passing through these fillers, so the parts beyond them will not be affected by the waves due to the reduction
of the penetration depth. Obviously, the extent of this parameter will be a function of the sample thickness and the filler content and morphology.

Hot spots could be avoided by applying different approaches such as rotating the specimens on a turntable stage, using mode stirrers that can change the distribution of the electromagnetic field inside the microwave cavity, using multiple magnetrons to obtain a more uniform field distribution using microwaves having multiple frequencies.

2.8. Using GO for compatibilizing immiscible polymer blends

Polymer blending is a straightforward and inexpensive method to combine the unique properties of different components to obtain new multiphase materials with necessary characteristics. Besides, polymer blends play a significant role in developing practical recycling. The intrinsic properties of each component and the ultimate structural morphology will affect the blends' properties. Nevertheless, the positive mixing enthalpy usually results in unfavorable mixing, and separated phases with high interfacial tension and poor interfacial adhesion are formed. The low interfacial adhesion decreases the final properties of the material, dramatically. Therefore, using a compatibilizer, like inorganic additives, or copolymers, which are compatible with both phases and can localize at the interface, is required to lessen the interfacial tension.

Polystyrene (PS) and polypropylene are commodity polymers extensively used in a wide variety of applications. PP is a thermoplastic polymer with good melt processability, and PS is a transparent rigid polymer. These two polymers are immiscible due to their high interfacial tension, which leads to a positive Gibbs free energy of mixing. Different
copolymers have been utilized to increase the thermodynamic affinity of this pair. For instance, a research work has reported the compatibilization of polystyrene/polypropylene blends using styrene-ethylene/butylene-styrene block copolymer (SEBS), which has concluded in a finer dispersed phase in the blend.\textsuperscript{102} However, these copolymers, which might not be easy to synthesize, are soft materials and deteriorate the mechanical properties of the blends. Using carbonaceous fillers is another compatibilization method since these fillers mostly contain the same elemental composition as the polymers do and can reinforce the blends in addition to the compatibilizing effect. Especially graphene oxide has a large $\pi$-conjugated system, making it compatible with several polymers. It can also be employed as a reinforcing agent to enhance the mechanical strength of the composites.\textsuperscript{24} The oxygen-containing functional groups of GO can form physical or chemical bonding with polymer chains. GO has been used to compatibilize an immiscible blend of 90\% polyamide (PA)/10\% polyethylene oxide (PEO), which led to the higher ductility of the composite blends and one order of magnitude reduction in the size of the dispersed phase.\textsuperscript{98} In another research work, reduced graphene oxide was used as a compatibilizing agent for polystyrene/polylactic acid (PLA) blends to be localized at the interface. The obtained morphology concluded in an enhanced electrical conductivity and a lower electrical percolation threshold.\textsuperscript{103}

Although GO has been widely used to enhance the affinity of different polymers, it is not functional for non-polar materials. Because the strongly polar GO\textsuperscript{18} is not compatible and dispersible in polyolefins, some GO surface modifications are required to make them compatible. Different approaches have been practiced to increase their compatibility, such
as GO functionalizing\textsuperscript{14} and modification of GO with polymer chains before mixing.\textsuperscript{56} You et al. grafted PP chains onto reduced GO nanosheets and used these modified sheets to compatibilize 70PP/30PS blends.\textsuperscript{104} This approach resulted in a smaller size of the minor dispersed phase and the elevation of tensile strength and elongation to break of the blends.

The high surface energy of GO sheets gives them a strong tendency to restack in the polymer matrix. On the other hand, an important parameter determining the final properties of the composites is the level of nanofiller distribution in the matrix polymer. Therefore, the processing method displays an essential effect on the dispersion of these nanosheets and the final properties of the composites. In this regard, different mixing sequences could be taken to incorporate GO in the polymer blends. It has been observed that premixing alkylated-grafted-GO with PS phase and then adding pure PP to the PS/GO masterbatch results in the nanoplates localization at the 30PS/70PP interface, which is the most desired morphology with improved mechanical properties.\textsuperscript{105} While the reversed mixing order concluded to deteriorated mechanical characteristics.

Graphene oxide nanoplates are capable of changing their localization during melt processing. Their localization would depend on their thermodynamical affinity to the polymer components. Therefore, if these nanosheets have enough time during the blending in the melt state, they can migrate to the interphase or another phase. Nagata et al. have reported that they first mixed GO with the less thermodynamically favorable PP phase.
After blending with the PE phase, some of the sheets migrated to the PE phase, and some others were localized at the PP/PE interphase,\textsuperscript{99} Figure 2.10.

![Figure 2.10 Localization of graphene sheets from the polypropylene (PP) phase to the polyethylene (PE) phase during melt blending, as well as the graphene sheets located at the PE/PP blend interface in the (graphene/PP)/PE composite.\textsuperscript{99}](image)

### 2.9. Conclusions

The review in this chapter demonstrates that:

- Graphene oxide is 2D nanocarbon material with strong mechanical, thermal, and dielectric properties.
- GO has been added to different polymers to obtain nanocomposites with various properties.
- GO usually needs to be modified before being added to polypropylene since these two materials are not compatible.
• Polymer nanocomposites can be 3D-printed to obtain complex functional structures. Process parameters should be optimized to address the challenges of printing these materials.

• Polymer/GO composites can perform as microwave absorber materials and be heated up under exposure. Based on this ability of GO nanocomposites, they could be used for welding polymeric parts by applying microwave radiation.

• Graphene oxide can be used as a compatibilizer in immiscible polymer blends.

2.10. References


19. Amani, M.; Sharif, M.; Kashkooli, A.; Rahnama, N.; Fazli, A., Effect of mixing conditions on the selective localization of graphite oxide and the properties of


79. Hwang, S.; Reyes, E. I.; Moon, K.-s.; Rumpf, R. C.; Kim, N. S., Thermo-mechanical Characterization of Metal/Polymer Composite Filaments and Printing


CHAPTER THREE
SURFACE MODIFICATION OF GRAPHENE OXIDE WITH COPOLYMER

3.1: Introduction

This chapter is devoted to i) characterization of the as received graphene oxide, ii) synthesis and characterization of the POEGMA-GMA-LMA copolymer, and iii) preparation and characterization of GO sheets modified with the copolymer.

The water-soluble, surface-active copolymer can chemically attach to GO to make it compatible with polar and non-polar materials. Upon modification, the nanolayer of copolymer envelopes the GO sheets, which could improve the dispersion of GO in the polymer matrix. It also yields physical bonding between the modified GO sheets and the surrounding matrix, which will improve the load transfer and consequently the mechanical properties of the composites. Furthermore, this nanolayer could shield the nanomaterial inside the polymeric matrixes. It is worth mentioning that all the modification process here is conducted in a water environment, and no organic solvents are used for these experiments.

3.2: Experimental

3.2.1: Materials

Graphene oxide (thickness=0.7-1.2 nm, Purity ~ 99%) synthesized by the Hummers method\(^1\) was purchased from Goographene company. 2-butanolone (MEK) solvent was
purchased from VWR International. Glycidyl methacrylate (GMA, 97%), oligo (ethylene glycol) methyl ether methacrylate (OEGMA, average Mn 950), lauryl methacrylate (LMA), azoisobutyronitrile (AIBN) initiator, and inhibitor removers (replacement packing for removing hydroquinone and MEHQ and replacement packing for removing tert-butylcatechol) were all purchased from Sigma Aldrich.

Silicon wafer was purchased from University Wafer with a resistance of 1–10 Ohm·cm and a thickness of 500 µm. Hydrogen peroxide and sulfuric acid were purchased from Sigma Aldrich.

3.2.2: Preparation of graphene oxide

The received graphene oxide was a suspension with a concentration of 5mg/ml GO in water. The dimensions of this nanomaterial as being mentioned by the company were several hundred nanometers up to several micrometers in XY plane and 0.7-1.2 nm in thickness. This suspension was diluted with DI water to obtain different concentrations at each step of the experiments. A TEM grid was dip-coated in the GO suspension and then dried at room temperature. The morphology of the nanosheets on the grid was observed using TEM (Hitachi HT7800, 120kV), Figure 3.1. The thin individual layers of GO could be clearly seen. Moreover, the crumpled surface of the sheets is observable at higher magnifications which is due to the high flexibility and large aspect ratio of this nanomaterial.²
3.2.3: Synthesizing the copolymer

Poly (oligo (ethylene glycol) methyl ether methacrylate-glycidyl methacrylate- lauryl methacrylate) or P(OEGMA-GMA-LMA) which is denoted as POGL was synthesized by solution free-radical polymerization,\(^3\) Figure 3.2. The molar ratio of the feed OEGMA:GMA:LMA monomers was 60:20:20. The monomers were mixed with the inhibitor removers for 30 minutes. 0.2463 g of AIBN, 88 ml of OEGMA, 1 ml of GMA, and 2.2 ml of LMA were added to 58.8ml MEK in a 250ml flask and stirred for 45minutes at room temperature. The nitrogen stream was connected to remove oxygen form the solution. Then the flask was transferred to a water bath with a temperate of 50°C and stirred for 90 more minutes. The resultant polymer was purified three times through precipitating in diethyl ether and dissolving in MEK to remove unreacted monomers and initiator.
3.2.4: Chemical analysis of the copolymer

The synthesized copolymer was analyzed via Nuclear magnetic resonance (NMR, Bruker AVANCE-300 spectrometer, TopSpin 1.3 PL4,) to calculate the ratio of OEGMA, GMA, and LMA parts; and Delta 5.0.4 software was used to analyze the spectra. The obtained molar ratio of OEGMA:GMA:LMA was calculated to be 66:15:19. Considering the densities and molecular weights of the homopolymers as following: $\rho_{\text{OEGMA}} = 1.08 \text{g/cm}^3$, $\rho_{\text{GMA}} = 1.075 \text{g/cm}^3$, $\rho_{\text{LMA}} = 0.868 \text{g/cm}^3$, $M_{\text{W OEGMA}} = 950 \text{g/mol}$, $M_{\text{W GMA}} = 142.15 \text{g/mol}$, and $M_{\text{W LMA}} = 254.1 \text{g/mol}$, the volumetric and weight ratios could be calculated, which are summarized in Table 3.1.

Table 3.1 Molar, volumetric, and weight ratios of parts of the copolymer.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>OEGMA</th>
<th>GMA</th>
<th>LMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar</td>
<td>66</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>Volumetric</td>
<td>88.5</td>
<td>3</td>
<td>8.5</td>
</tr>
<tr>
<td>Weight</td>
<td>90</td>
<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>
The chemical structure of the synthesized copolymer was further investigated via a Thermo Nicolet Magna 550 Fourier transform infrared (FTIR) spectrometer with the Thermo-Spectra Tech Endurance Foundation Series Diamond Attenuated Total Reflectance accessory. Sixteen scans were averaged for the copolymer sample. Dynamic light scattering (DLS, Malvern Zetasizer ZS) measurements were conducted to estimate the molecular weight of the copolymer. Polystyrene (PS) standards with known molecular weights were dissolved in methyl ethyl ketone (MEK), and their size was measured to build the calibration plot of molecular weight versus the size of the polymer. The copolymer was dissolved in MEK, and the hydrodynamic size of the coils was about 34nm. Therefore, based on the calibration plots, a molecular weight of 3000kg/mol was calculated for the copolymer.

3.2.5: Functionalizing GO with the copolymer

The industrially available GO suspension (5mg/ml) and the copolymer were mixed in a 1:2.5 mass ratio in an aqueous environment. The GO suspension was added to the POGL solution dropwise to inhibit stacking of GO sheets by bridging one POGL chain with multiple sheets. The mixture was vigorously shaken for 15 min and stirred for at least four hours to give enough time for POGL chains to attach to the GO sheets. The method of GO modification is illustrated in Figure 3.3.
We needed to remove the free POGL chains in the GO/POGL suspensions to obtain more accurate material characterization based on the morphological, chemical, and thermal analysis of the GO/POGL suspensions. The GO/POGL suspension was centrifuged and rinsed with water three times to remove the unattached POGL chains. The suspension was poured in 2ml centrifugation tubes and centrifuged (Mini Spin Plus, Eppendorf) at 15000 rpm for 5 min. The top portion of the suspension containing POGL free chains in each tube was removed. The precipitated solid part was mixed with water and was shaken for 5 minutes and centrifuged again. This process was repeated three times. Then the suspension was collected and centrifuged in a 45ml test tube at 1500 rpm (Prexision 100 Durafuge) for 10 minutes to separate any possible coagulated GO clusters. The top part of the mixture was pipetted out and saved for the next steps of the experiments. The sheets modified with GO are denoted as GOP from now on.

3.2.6: Morphological analysis of GO and GO/POGL

Atomic force microscopy (AFM, Dimension 3100, Veeco Digital Instruments, Inc.) was used in tapping mode to investigate the morphology of the GO sheets. The samples for
AFM were prepared via dip-coating of a silicon wafer in GO and GOP suspensions. For this purpose, silicon wafers were cut into 1cm*4cm pieces and rinsed with deionized (DI) water. Then they were placed in test tubes poured with DI water and sonicated (VWR, 97043-992) for 90 minutes at 60°C. After one more rinsing with DI water, the wafers were immersed in a piranha solution consisting of 25% hydrogen peroxide and 75% sulfuric acid for at least 2 hours. Then they were rinsed with DI water three times and dried using ultra-high purity nitrogen. The GO suspension was diluted with DI water to obtain a 0.5mg/ml mixture. The cleaned wafers were dip-coated using a dip-coater D-3400 (Mayer Feintechnik) in GO and GOP suspensions, and then were allowed to dry at room temperature. The samples were scanned using AFM silicon tips with a spring constant of 50 N m⁻¹ and a scanning rate of 1Hz. The wafers were analyzed via AFM to evaluate the structure and the thickness of the sheets before and after modification with the copolymer. The obtained AFM images were analyzed using Gwyddion version 2.55.

3.2.7: Chemical analysis of GO and GO/POGL

The chemical compositions of GO and GOP sheets were studied by FTIR. A Thermo Nicolet 6700 FTIR spectrometer equipped with a transmission base plate and a “Continuum” microscope was used to analyze these sheets. The samples used for this test were silicon wafers coated with GO, POGL, and GOP materials prepared the same way they were made for the AFM analysis. 256 scans were averaged during background and sample collection steps to achieve a high signal-to-noise ratio.
3.2.8: Thermal analysis of GO and GOP

Thermogravimetric analysis (TGA): Thermogravimetric analysis was conducted to evaluate the thermal stability of the materials and the amount of anchored POGL. These experiments were performed using a Q-5000 TA Instruments and AutoTGA 2950HR V5.4A under nitrogen gas from room temperature to 600 °C at a ramp rate of 10 °C min⁻¹.

Differential scanning calorimetry (DSC): The GO, POGL and GOP suspensions were dried at room temperature and then were placed in a vacuum oven for overnight to dry completely. Thermal properties of the powder samples were analyzed by differential scanning calorimetry (DSC) (2920; TA Instruments) at a heating/cooling rate of 20 °C/min and a temperature range of -100 °C to 120 °C. About 5mg of the materials were used for the thermal experiments.

3.2.9: Optical analysis of GO and GOP

Ultraviolet-visible (UV-Vis) spectroscopy: A valuable tool to measure the concentration of the solutions is UV-Vis measurements. According to the Beer-Lambert law, there is a linear relationship between the concentration and the absorbance of solutions:

\[ A = \alpha l c \] (3.1)

where A is the absorbance, \( \alpha \) is the unit absorptivity, l is the sample path length, and c is the concentration. In essence, in the case of graphene sheets, attenuation of light is due to both absorption and scattering of light. In this situation, the constant of the beer lambert law is called the extinction factor. The absorbance of the solutions was recorded using UV-Vis spectroscopy (UV3600; Shimadzu).
3.3: Results and discussions

3.3.1: Synthesizing the compatibilizing copolymer

Different approaches have been employed to increase the compatibility of polypropylene and graphene oxide, such as in-situ polymerization of PP in the presence of GO, using a compatibilizing agent, functionalizing GO, and modification of GO with polymer chains before mixing. By utilizing characteristics of well-controlled synthesized polymers, the last method offers more advantages over the others. In this research, an amphiphilic copolymer is synthesized to functionalize GO sheets and introduce them to the PP matrix. This copolymer improves the dispersion of GO nanosheets in the polymer matrix and forms a strong interfacial bonding between the filler and the host polymer.

At the synthesis step, we could determine the relationship between the polymerization parameters and polymer composition. For this purpose, we should specify the requirements that the polymer should meet. Since the GO modification process will occur in a water solution, the synthesized macromolecule needs to be water-soluble. Also, it should be stable during the melt processing stage. Another requirement for this polymer is to have a low surface energy component to allow adsorption of the modified GO on the surface of the non-polar polymer fibers from water. The last needed feature as a compatibilizer agent is to form covalent bonding with the GO sheets to coat the surface.

Considering all the mentioned requirements, we have synthesized a methacrylate random copolymer containing reactive, polar, and non-polar monomeric units through a radical polymerization method in a solution environment. Poly (oligo (ethylene glycol) methyl
ether methacrylate-glycidyl methacrylate- lauryl methacrylate) or P(OEGMA-GMA-LMA) is a cross-linkable amphiphilic copolymer that can form a covalent bonding with surfaces.

The polar monomer of OEGMA ensures the water solubility of the molecule. GMA is insoluble in water and performs as the reactive part and reacts with the functional groups of GO through its epoxy groups. LMA is a hydrophobic monomer that is used to balance the hydrophilic/hydrophobic characteristic of the copolymer and will allow the modified GO sheets to interact with the non-polar polypropylene.

3.3.2: Functionalizing GO with the copolymer

POGL molecules were grafted to the surface of GO nanosheets via the “grafting-to” approach. The reaction between functional groups of GO, including hydroxyl, carboxyl, and epoxy groups, and epoxy groups of GMA, results in a nanoshell of copolymer covering the GO sheets, Figure 3.4. This layer was hypothesized to decrease the coagulation of the GO sheets and increase the interfacial interaction between GO and polymer matrix. There are multiple epoxy reactive groups along each copolymer chain that form chemical bonding with the GO sheets and will ensure the complete enveloping of the sheets.
3.3.3: Morphological analysis of GO and GOP sheets

AFM visualizes the attachment of POGL molecules onto the basal planes of GO sheets and their effect on the thickness and morphology of GO. GO and GOP solutions were deposited on a silicon wafer and scanned with AFM in tapping mode, Figure 3.5. The thickness of neat GO nanoplates is 1.1nm, corresponding to a fully exfoliated single layer of GO.\textsuperscript{18} The \textasciitilde3.1nm increase in thickness of the sheets reveals the uniform attachment of the copolymer to the sheets. Assuming that the copolymer is uniformly grafted to both sides of the GO sheets, the thickness of the covering layer could be estimated as about 1.5 nm. The measured value for the thickness of the modified GO is slightly higher than that reported in another research work of Dr. Luzinov’s group,\textsuperscript{19} which can be attributed to the higher molecular weight of the copolymer.

Figure 3.4 Reactions of GMA epoxy groups of the copolymer with functional groups of GO.
3.3.4: Chemical analysis of GO and GOP

The attachment of the copolymer to the GO sheets was further investigated via FTIR. The FTIR spectra of GO, POGL and GOP materials were collected by Dr. Mykhailo Savchak in Dr. Luzinov’s group, Figure 3.6. The distinctive broad peak of neat GO at 3320 cm\(^{-1}\) is originated by the stretching and bending vibrations of the alcoholic hydroxyl (O-H) groups.\(^2\) Two narrow peaks evidenced at 1720 cm\(^{-1}\) and 1610 cm\(^{-1}\) correspond to the carboxylic acid groups (-C=O) stretching and the stretching vibrations of the GO skeleton (C=C), respectively.\(^{20}\) Also, the ether and epoxy groups peaks appear in the range of 1000-1280 cm\(^{-1}\). The spectrum of neat POGL shows the peak for the alkyl (C-H) stretching group.
at 2879 cm⁻¹. The peaks at 1725, 1250, 1111 cm⁻¹ are originated by the carbonyl (C=O), epoxy (C-O-C) and ether (C-O) stretching vibrations of this copolymer.

In the spectrum of GOP sheets the C-H, C=O and C-O-C groups of the grafted copolymer result in the peaks at 2873, 1732 and 1250 cm⁻¹. The drastic reduction of the oxygen-containing groups in GOP comparing to GO implies the attachment of POGL chains to the GO sheets through the functional groups of GO’s surface. These observations confirm the successful attachment of the POGL chains to the GO sheets.

**Figure 3.6 FTIR spectra of GO, POGL, and GOP materials.**

### 3.3.5: Thermal analysis of GO and GOP

**TGA:** Thermal stability of GO, POGL, and GOP materials was examined based on thermogravimetric analysis, Figure 3.7, a. The powder samples were heated up from room temperature to 600°C at a rate of 20°C/min under a nitrogen atmosphere. GO shows a two-
step degradation behavior. The first step takes place from 40°C to 150°C due to the evaporation of the water up-taken by GO. The next degradation step occurring from 200°C to 300°C is because of decomposition of the oxygen-containing groups of GO. The overall weight loss of GO is about 49.7%. The pure copolymer starts degradation after 300°C, and it completely decomposes at 600°C. The degradation of the GOP nanoplates takes place in two steps. First, the functional groups of GO decompose to CO, CO$_2$, and H$_2$O steam at around 200°C, and then the degradation of the attached copolymer starts. Mass loss of GOP is 68.9% at 600°C. The onset degradation temperature of GOP is higher than that of neat GO, which could be attributed to the removal of stored water from GO’s π-stacked structure.

In order to estimate the amount of POGL copolymer attached to GO, we took the first derivative of the GOP curve with respect to temperature, Figure 3.7.b. The only distinctive mass loss of POGL occurring between 233°C and 436 °C was integrated to obtain the area under the peak. The area under the GO peak at the mentioned temperature range was also obtained. By comparing these numbers and the integration of the GOP plot, it was concluded that the GOP material is composed of ~47% GO and ~53%POGL. The TGA results confirm that the POGL molecules are permanently attached to the GO sheets. This data also correlates well with the amount of anchored POGL estimated with AFM.
**DSC:** DSC analyses were carried out to assess the thermal transitions of POGL and GOP, Figure 3.8. The thermal properties of the homopolymers composing the POGL copolymer are shown in Table 3.2. Based on the DSC plots, the glass transition of the neat copolymer occurs at -32°C that is between the Tg of POEGMA/PLMA and that of PGMA. However, this transition vanishes for the GOP material. Moreover, the melting point of POGL reduces from 35°C to 27°C, and the area under the endothermic melting peak decreases dramatically. Therefore, it could be inferred that the POGL side chains cannot find each other to form crystals on the GO surface, and the POGL structure is a brush structure. In fact, the mobility of OEGMA segments in POGL copolymer is restricted by the surface anchoring that inhibits crystalization. Furthermore, based on the AFM images analysis, the thickness of the POGL layer on the GO surface is about 1.5 nm. However, the hydrodynamic diameter of the POGL coils was 34 nm based on the DLS measurement. This implies that the POGL chains do not retain their coil conformation when attached to the
GO sheets. Consequently, it could be concluded that the POGL layer is uniformly flattened on the GO sheet, and no clustering takes place, Figures 3.9 and 3.10.

![Figure 3.8 DSC plots of a) POGL, b) GOP, and c) overlay of POGL and GOP plots.](image)

**Table 3.2 Thermal properties of the homopolymers constituting POGL.**

<table>
<thead>
<tr>
<th>Homopolymer</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POEGMA</td>
<td>-60</td>
<td>26</td>
</tr>
<tr>
<td>PGMA</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>LMA</td>
<td>-50</td>
<td>-26</td>
</tr>
</tbody>
</table>
We hypothesized that the GMA parts of the chains are chemically attached to the sheets, and the OEGMA and LMA are exposing out of the surface and make the modified sheets compatible with hydrophilic and hydrophilic materials, respectively.

3.3.6: Optical analysis of GO and GOP

3.3.6.1: UV-Vis plots of GO and GOP

Materials with different chemical bonding absorb electromagnetic waves of different wavelengths. During a UV-Vis spectroscopy measurements, the materials are exposed to waves in the range of visible and ultraviolet wavelengths. A chemical with a stronger bonding gets excited when it is exposed to a wave with a shorter wavelength. It is known that GO sheets absorb light in the wavelength of 230 nm, which is due to the $\pi -$
\( \pi^* \) transitions of aromatic C=C bonds.\(^2\) Therefore, GO shows an absorbance peak at 230 nm when tested via UV-Vis experiment, which could be utilized for obtaining some information regarding the electronic conjugations of the sheets.\(^2\) The intensity of the absorbance peak depends on the concentration of the suspension and the level of sheets dispersion. A more exfoliated structure of the graphene oxide will lead to the availability of more UV-Vis absorbing GO surfaces.

In this research, GO and GOP suspensions of different concentrations are exposed to light in the wavelength range of 700nm-190nm, and the absorbance versus wavelength is recorded, Figure 3.11. The suspensions were poured in quartz cuvettes with a path length of 1cm. DI water was used as the reference material for all the experiments.

As expected, the absorbance peak of the GO and GOP suspensions occurs at 230nm. The addition of POGL to the GO sheets does not shift the position of the absorbance peak. However, the intensity of the peak is higher for the GO sheets decorated with POGL chains. It implies that the sheets encapsulated by the copolymer have a lower tendency to stacking, resulting in a larger GO surface absorbing the light. It has been stated before that a better dispersion of the GO sheets will lead to a higher absorption peak intensity at a constant concentration. Based on these findings, it could be concluded that the GOP sheets are more exfoliated rather than the neat GO sheets.
Figure 3.11 UV-Vis spectra of a) GO and b) GOP suspensions of different concentrations. 

It should be mentioned that the absorbance of pure copolymer solutions was examined to see if the higher peak intensity of the GOP suspensions is caused by POGL or not, Figure 3.12. Based on the linear relationship between absorbance and concentration, we have generated a linear equation to calculate the absorbance of the POGL suspensions at each concentration:

$$A_{\text{POGL}} = 0.33C_{\text{POGL}} \quad (3.2)$$

The concentration of POGL used for each GOP suspension is 2.5 times of the GO concentration. Therefore, for a GOP suspension with a GO concentration of 0.0833 mg/ml, the POGL concentration is about 0.21 mg/ml. Based on the linear equation, the contribution of POGL to the absorbance of this suspension could be 0.069. However, the difference between the absorbance of 0.0833 mg/ml GO suspension and that of the 0.0833 mg/ml GOP suspension is 1.25, which is much larger than the amount of absorption that POGL could originate at this concentration of the GOP suspension.
Attachment of POGL molecules to the GO sheets will increase the thickness of the sheets, resulting in a higher inter-layer distance between the GO sheets. It has been stated that the effect of van der Waals forces increases as the materials' structure enters the nanoscale regime. According to Equation (3.3), this larger distance will decrease the van der Waals attraction forces between the modified GO sheets comparing to the unmodified GO sheets:

\[ \Phi_{p,VDW} = -\frac{A}{12\pi h^2} \] (3.3)

where \( \Phi_{p,VDW} \) is the van der Waals attraction per unit area of the sheets, \( A \) is the Hamaker constant, and \( h \) is the distance between the GO sheets. Therefore, we can suggest that successful coverage of the GO sheets by the copolymer molecules is preventing aggregation of the nanosheets and result in their better dispersion.

Figure 3.12 UV-Vis spectra POGL suspensions of different concentrations.

3.3.6.2: UV-Vis calibration plots

We need to determine the concentration of the GO and GOP suspensions at all stages of the experiments to understand the interaction between the components. For this reason, we
have used UV-Vis spectroscopy to measure the concentrations of the suspensions. According to the Beer-Lambert law, there is a linear relationship between the concentration and the absorbance of solutions at relatively low concentrations. Based on this linear relationship the suspensions’ concentrations are measured via the UV-Vis test. Therefore, first, the calibration plots are derived at the wavelength of maximum absorbance (230nm) and the linear equations for the relationship between absorbance and concentration are derived, Figure 3.13.

\[
\text{GO suspension: } A_{\text{GO}} = 37.83C_{\text{GO}} \\
\text{GOP suspension: } A_{\text{GOP}} = 53.03C_{\text{GOP}}
\]

![Figure 3.13 Calibration plots of absorbance at 230nm versus concentration of (a) GO, (b) GOP suspensions.](image)

**3.3.6.3: Analyzing the stability of GO and GOP suspensions**

Graphene sheets possessing a 2D structure and strong $\pi-\pi$ interactions tend to stack to each other and precipitate from the GO and GOP colloidal suspensions. Therefore, the concentration of the suspensions decreases with time, and more deposits will accumulate in the bottom of the container. The stability of suspensions containing the pure and
modified GO sheets was compared to see if the copolymer has any effect on the precipitation rate of the sheets.

To evaluate the stability of the GO and GOP suspensions, the UV-Vis measurements were carried out to record the absorbance of the suspensions at 230nm at different times, and the changes in concentration were calculated for each suspension, Figure 3.14. According to the Beer-Lambert law observing a decrease in the absorbance of solutions will indicate the precipitation of GO nanosheets and the low stability of the suspension. The more remarkable change in GO suspension concentration indicates its tendency to precipitation, while GO sheets modified with POGL are more stabilized. The higher stability of the GOP suspension implies that the POGL chains yield effective steric stabilization of the GO sheets by anchoring to their surface.

Also, the change in the concentration of pure GO suspension after 15 hours (the time given to the suspension to mix with PP fibers) is more than 10%, while this amount is only 2% for GOP suspension. These findings indicated that the presence of the copolymer nanoshell on the GO sheets prevents their aggregation and enhances dispersibility.

Figure 3.14 Change in concentration of the suspensions with time.
3.3.6.4: Optimizing the required amount of POGL for modifying GO

In practical applications removal of unattached POGL chains cannot be conducted, thus it is required to find the optimum amount of POGL to cover GO sheets. Because the excess amount of POGL will soften the final material, and also, a lesser amount of copolymer will result in a non-uniform covering and linking the copolymer chains between GO sheets and layer stacking. Therefore, investigating the state of GO dispersion is a helpful approach to identify the appropriate amount of the functionalizing agent. It has been reported that better distribution of the GO sheets in the suspension will give a higher absorbance recorded by UV-Vis. Based on this concept, the absorbance of different GOP suspensions of different ratios are measured to identify the best mixture with the highest ability to coat the GO sheets. Accordingly, we found that 1GO/2.5POGL is the lowest concentration of POGL that gives the best dispersion of the sheets.

3.4: Conclusions

The following conclusions can be drawn as a result of the study reported in Chapter 3:

- POEGMA-GMA-LMA copolymer was successfully synthesized through solution free-radical polymerization, and its molecular weight and chemical properties were characterized.

- Go sheets were functionalized with the copolymer in an aqueous environment.
• Modification of the GO sheets with POGL molecules was confirmed by the increase in the thickness of the GO sheets by AFM.

• Chemical and thermal analysis of the GOP sheets further supported the attachment of the copolymer to the GO sheets.

• Putting the observations from AFM and DSC tests together and considering the size of the copolymer coils, it could be concluded that the copolymer chains were flattened on the GO surface without any clustering.

• The linear relationship between the concentration and absorbance of GO and GOP suspensions was established based on the Beer-Lambert law.

• UV-Vis measurements indicated that GOP suspension is more stable than GO solution.

• The optimum GOP ratio was identified based on the relationship between GO exfoliation level and the absorbance intensity of the suspension.

3.5: References


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CHAPTER FOUR

FABRICATION AND CHARACTERIZATION OF
POLYPROPYLENE/ GRAPHENE OXIDE COMPOSITES

4.1: Introduction

This chapter is devoted to i) Introducing GO and GO/copolymer nanoplates to the PP fibers from water suspensions, ii) Melt processing the PP/GO and PP/GOP composites, iii) investigating the effect of GO and GO-copolymer on the morphological, rheological, thermal, and mechanical properties of the PP matrix.

To ease processing the PP/GO composites, the virgin and modified GO sheets are introduced to PP fibers from an aqueous environment before the melt processing. Then the fibers decorated with the nanoplates are dried, extruded, and pressed to obtain the test samples. The influence of the stiff GO sheets on the enhancement of thermal and mechanical properties of PP is expected. The primary purpose of this chapter is to embed GO sheets encapsulated with the POGL chains in the PP matrix. Upon the success of this approach, the incompatibility of hydrophilic GO and hydrophobic PP can be reduced to some extent. This nanolayer is also hypothesized to improve the GO dispersion in PP. Hence, the functional characteristics of GO nanosheets could be utilized while they are shielded inside the PP matrix by the copolymer nano-shell wrapping around them.
4.2: Experimental

4.2.1: Materials

PP fiber (Denier=1.5dpf, diameter=15\(\mu\)m, length=3mm) was supplied by Minifibers Inc.

4.2.2: Introducing GO sheets to PP fibers

PP short fibers were rinsed three times with DI water to remove the surfactants. The water evacuated after each rinse was tested via UV-Vis to assure the removal of all the processing additives from the fiber surface. The cleaned fibers were then mixed with aqueous graphene oxide and graphene oxide/copolymer suspensions and stirred for 15hrs to obtain PP/GO and PP/GOP mixtures, Figure 4.1. The mass of GO in the suspensions was 2wt.% of solid content, and the mass of the added PP fiber was 98%; thus, the resulting masterbatches would be PP/2%GO and PP/2%GOP.

![Figure 4.1 Attachment of GO nanoplates to the fibers](image)

4.2.3: Analyzing GO attachment to the PP fibers

The process of covering the PP fibers by the GO sheets is studied via UV-Vis analysis. The absorbance of the solutions was recorded using Ultraviolet-visible (UV-Vis) spectroscopy (UV3600; Shimadzu). After mixing the PP fibers with GO and GOP suspensions and
attaching the sheets to the fibers, the number of available GO sheets in the suspensions reduces, leading to lower concentrations of the suspensions. Based on the reduction of the absorbance peak’s intensity of the suspensions, the amount of GO attached to the PP fibers could be calculated. Then the experimental data were fitted on the Freundlich isotherm equation to understand better the GO adsorption process in the PP/GO and PP/GOP mixtures.

4.2.4: Morphological analysis of PP/GO fibers

PP fibers decorated with GO sheets were dried at room temperature and then placed in a desiccator to remove the moisture. Field emission scanning electron microscopy (FE-SEM) (Hitachi S-4800) was used to observe the PP/GO fibers' morphology.

4.2.5: Melt processing of PP/GO composites

The PP/GO and PP/GOP fibers were dried at room temperature and then placed in a vacuum oven to fully remove the adsorbed water. Then the dried fibers were extruded (CSI MAX mixing extruder, CSI custom scientific instruments inc.) twice at 190°C. The extrudates were hot-pressed (Carver hot press) at 190°C for 5 minutes under 3.8MPa pressure to produce the test specimens, Figure 4.2. Consequently, PP, PP/2%GO, and PP/2%GOP composites were fabricated. The samples were compression molded in the required sizes for the morphological, mechanical, and thermal tests.
4.2.6: Morphological analysis of PP/GO composites

Optical microscopy (Olympus LEXT OLS 4000 confocal laser microscope) was used to observe the morphology of the composites. Polymer composites were pressed to fabricate ~30μm thick films to conduct optical microscopy.

4.2.7: Thermal analysis of PP/GO composites

Thermal properties of the samples were analyzed by differential scanning calorimetry (DSC) (2920; TA Instruments) at a heating/cooling rate of 20 °C/min and a temperature range of -50 °C to 200 °C. Thermogravimetric analysis (TGA) (AutoTGA 2950HR V5.4A) was performed under nitrogen gas from room temperature to 600 °C at a ramp rate of 10 °C min⁻¹ to examine the thermal stability of the materials.

4.2.8: Rheological analysis of PP/GO composites

The materials' melt flow index (MFI) was studied using a XNR-400 melt flow indexer at 230°C and under 2.16Kg mass. MFI values were reported as the mass (g) of the material pushed out of the chamber in 10 minutes. Rheological behaviors were assessed using a rheometer (ARES rheometer, TA Instruments Inc.) at three different temperatures at parallel plate mode.
4.2.9: Mechanical analysis of PP/GO composites

Mechanical properties of the composites were analyzed in low and high deformation rates. Dynamic mechanical analysis (DMA) (Q800; TA Instruments) was done at a frequency of 5Hz and a temperature range of -50°C to 100°C and a heating rate of 3°C/min. Samples with a thickness of 1mm and a width of 5mm were clamped perpendicularly between two arms, while about 15mm of their length was under deformation. A tensile tester (5582; Instron) was used to measure the mechanical properties of the composites in three-point bending mode according to ASTM D790. The tested samples had a thickness of 1.5mm and width of 12.8mm, and the tested span length was 25.4mm. These samples were compressed at a deformation rate of 1mm/min until they broke or reached 10mm of deformation. The specimens that did not experience breakage would continue deformation without a change in their behavior; for this reason, we stopped them at 10mm of deformation to be able to compare results for different samples.

4.3: Results and discussions

4.3.1. Analyzing attachment of GO to the PP fibers

Graphene oxide was introduced to PP fiber through mixing GO and GOP suspensions with PP fibers in water. It was expected that the POGL molecules bonded to the GO sheets attach to the surface of PP fibers with their free hydrophobic parts. Knowing the concentration of the suspensions at each step of the modification process is a necessity to understand the adsorption mechanism.
To evaluate the amount of GO adsorbed onto the surface of PP fibers, we took portions of the suspensions out at specific time intervals and measured their absorbance at 230nm to calculate the correlated concentration after up-taking GO by the fibers.\(^1\) Consequently, the amount of adsorbed GO (mg GO/m\(^2\) fiber) could be determined based on the difference of the initial and the final concentrations.

Specific adsorbed GO = \(\frac{(C - C') \times V}{A_f}\)  \(\text{(4.1)}\)

where \(C\) and \(C'\) (mg/ml) are the initial and final concentrations of the suspensions, respectively; \(V\) (ml) is the total volume of the suspension, and \(A_f\) (m\(^2\)) is the total surface area of the fibers. It is observed that the amount of specific adsorbed GO is increasing by increasing the concentration of both suspensions; however, a higher adsorption is observed for the GOP suspension, which can be attributed to the higher affinity of the GOP sheets with the PP fibers, Figure 4.3.
Figure 4.3 Specific adsorbed GO at different concentrations of GO and GOP suspensions.

It should be pointed out that measuring the absorbance of pure POGL of various concentrations mixed with PP fibers showed no change in concentration, confirming no significant adsorption of POGL by the fibers. It can be hypothesized that in this situation, the POGL chains make coils, with their hydrophobic parts hidden inside, so they are not bond to the PP fibers. But in the presence of GO sheets, the chains open up and connect to GO through their hydrophilic parts, and then the free hydrophobic part will connect to PP as is shown in Figure 3.10.

The interaction between GO and PP fibers and the process of GO adsorption from water to the fibers could be understood by investigating the equilibrium adsorption isotherms. For this purpose, the amount of adsorbed GO onto the unit weight of the fibers was determined for suspensions of different original concentrations.
\[ q_e = \frac{(C_0 - C_e) \times V}{m} \]  \hspace{1cm} (4.2)

where \( q_e \) is the equilibrium amount of up-taken GO per unit weight of the dry PP fiber (mg GO/g PP fiber), \( C_0 \) and \( C_e \) (mg/ml) are the original and equilibrium concentrations of the GO suspension, respectively, \( V \) (ml) is the volume of the suspension, and \( m \) (g) is the mass of the dry fiber. Different isotherm equations were fitted on the experimental data to describe the adsorption of the solute (GO and GOP) onto the solid surface (PP fiber). The fitting results showed that the adsorption tendencies are well consistent with Freundlich isotherm.

\[ q_e = K_F C_e^{\frac{1}{n_F}} \]  \hspace{1cm} (4.3)

where \( K_F \) represents the Freundlich constant and \( 1/n_F \) describes the heterogeneity factor (adsorption intensity). This model can be applied to the adsorption of a multilayer in a heterogeneous surface, Figure 4.4. This finding has been previously reported for GO systems. Based on this empirical model, first, stronger binding sites are occupied, and by completion of the adsorption procedure, the adsorption energy decreases exponentially. Freundlich model describes heterogeneous adsorption and formation of multilayers with no saturation concentration.

The fitted equations showed that \( 1/n_F \) is less than 1 for the PP/GOP system, indicating the favorable adsorption. However, \( K_F \) is higher for the PP/GO system, meaning that this system has a higher adsorption capacity.

PP/GO system: \( q_e = 21.25C_e^{2.19} \)
PP/GOP system: $q_e = 2.4C_e^{0.91}$

Figure 4.4 Fitting the experimental data on Freundlich model.

It could be concluded that GO adsorption on the PP fibers does not reach a saturation level. This implies that GO-fiber interactions are dominant until the first layer of GO covers the fiber, and then GO-GO interactions result in the formation of the successive layers. The ability of GOP sheets to attach to the fibers proves their higher affinity to the fibers and the favorable adsorption of the PP/GOP system. On the other hand, after deposition of the first layers of the sheets, the unmodified GO sheets could develop multilayers. However, the modified sheets have more interlayer distances and are less prone to stacking, reducing their adsorption capacity on the fibers.

4.3.2: Morphological analysis of PP/GO fibers

After completing the adsorption process, the PP fibers are evacuated from the suspensions and dried. The fibers immersed in a 0.5mg/ml GO suspension were dried and put in a desiccator to remove the moisture completely by vacuum. Following, they were placed on a carbon tape and visualized with the scanning electron microscope (SEM) to see the
morphology of the GO sheets on the PP surface, Figure 4.5. The neat PP fiber has a smooth surface, comparing to that of the modified ones. The wrinkled 2D GO nanoplates could be seen enveloping the fiber. The concentration of the graphene oxide used for this microscopy is lower than the concentration of GO in the PP/GO composites; because a large amount of the sheets stacking on the fibers might not be clear to observe. These fibers wrapped by the GO sheets can be used to produce high-strength composites containing low amounts of graphene oxide.

Figure 4.5 SEM images of (a) pristine PP fiber, (b) PP fiber immersed in a 0.5mg/ml GO solution.

4.3.3: Morphological analysis of PP/GO composites

The resultant modified fibers were extruded and compression-molded by a hot press at elevated temperature and pressure\(^5\) to produce the test materials.

Morphology of the pure PP polymer and the composites was evaluated using optical microscopy, Figure 4.6. For this purpose, thin films with a thickness of ~30\(\mu\)m were prepared, and the observation was done through light transmission mode. PP spherulitic structures could be observed in the pure matrix.\(^6\) Addition of GO sheets hinders these crystal domains and reduces their size. GO sheets are well distributed and easily seen in
the composites, indicating that they have preserved their original sheet-like structure during the processing steps. Single-layer and multi-layers of the sheets could be observed, which confirmed the success of the composite processing method.

4.3.4: Thermal analysis of GO and PP/GO composites

Thermogravimetric analysis (TGA):

TGA was conducted to examine the thermal stability of the nanocomposites, Figure 4.7. It was found that GO boosts the thermal stability of PP and shifts both the onset and the maximum of degradation temperature of the PP/GO composite to higher temperatures.\(^7\) As reported before, GO sheets reduce the mobility of polymer chains resulting in a slower degradation rate.\(^5\) The thermoconductive GO nanoplates facilitate the heat conduction in the composites.\(^8\) Also, due to the gas barrier properties of the GO sheets, the diffusion of volatile materials through the composite will be delayed.\(^9\) These effects result in the elevation of the thermal stability of the composites.\(^10\) As expected, POGL molecules hide the GO sheets and diminish their thermal stabilizing effect; therefore, PP/GOP’s decomposition behavior is like that of the PP matrix.
Differential scanning calorimetry (DSC):

Glass transition temperature and the melting point of most polymers are affected by their structure because both the amorphous and crystalline regions are influenced by the cohesive energy and molecular packing factor. Therefore the temperatures at which the transitions occur will change upon a change in the polymer material structure.\textsuperscript{11}

The changes in crystallization behavior of the PP composites can be monitored by DSC as the samples were heated from -50 °C to 200 °C to eliminate their thermal history, followed by the cooling cycle to identify the crystallization peak. The second heating was done to detect the melting temperatures, Figure 4.8.
The effect of GO and GOP on the crystallization mechanisms of PP composites could be investigated based on Keith-Padden’s theory. This theory relates the radial growth rate (G) of spherulites to the nucleation and growth mechanisms\textsuperscript{12}:

\[
G = G_0 \exp \left(-\frac{\Delta E}{RT}\right) \times \exp \left(-\frac{\Delta F^*}{RT}\right)
\] (4.4)

where G is the radial growth rate, \(G_0\) is the growth rate of a perfect crystal, \(\Delta E\) is the free energy of activation for a chain crossing the barrier to the crystal, \(\Delta F^*\) is the free energy of formation of a surface nucleus, T is temperature, and R is the gas constant. The first part of the equation conveys the role of crystal growth, and the second part represents the influence of nucleation. \(\Delta E\) is correlated to the molecular rearrangement, and it does not change with temperature; therefore, crystal growth will be higher at elevated temperatures.
On the other hand, $\Delta F^*$ is inversely related to temperature, and it decreases as temperature increases.

The experimental observations are well according to Keith-Padden predictions. Low concentrations of GO nanoparticles can act as heterogeneous nucleation agents that initiate a large number of crystals\textsuperscript{13} and increase the crystallization rate. These crystals are smaller than the neat PP crystals grown from a small number of homogenous nuclei. But a higher percentage of graphene prevents crystallization growth and decreases the rate of crystallization. After the addition of graphene and bonding between graphene and the polypropylene chains, the movement and alignment of these chains will be restricted. Consequently, the crystalline percentage of the composites will be lower\textsuperscript{14}.

The results of DSC analyses are summarized in Table 4.1. The results indicate that the addition of GO to PP causes minor (3-5 °C) increase in crystallization and melting temperatures (Tc and Tm) of the material. Thus, the nanosheets act as additional heterogeneous nucleation sites\textsuperscript{15} that initiate formation of thicker lamellas constituting semi-crystalline spherulites\textsuperscript{16-17}. In contrast, PP/GO has lower degree of crystallinity (decrease of 4%) than pure PP. We associate this observation with ability of GO sheets to arrest physically growth of larger spherulites as indicated by optical microscopy images.

However, when the sheets are wrapped by the copolymer, the addition of GOP to PP causes smaller changes in Tc and Tm of the material compared to GO addition. Therefore, the POGL shell effectively screens the GO surface and does not cause additional heterogeneous nucleation. It is noticeable that PP/GOP has a significantly lower degree of
crystallinity than pure PP and PP/GO. As for the GO, we connect this finding to GOP sheets' ability to physically arrest growth of larger spherulites. These findings confirm the effect of POGL chains as a compatibilizing shell to decrease the interaction of the PP matrix and the surface of nanosheets.

Table 4.1 DSC results of PP composites.

<table>
<thead>
<tr>
<th>sample</th>
<th>Melting</th>
<th>Crystallization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tm</td>
<td>ΔHm (J/g)</td>
</tr>
<tr>
<td>PP</td>
<td>158</td>
<td>97</td>
</tr>
<tr>
<td>PP/GO</td>
<td>161</td>
<td>88</td>
</tr>
<tr>
<td>PP/GOP</td>
<td>160</td>
<td>71</td>
</tr>
</tbody>
</table>

4.3.5: Understanding the effect of GO/PP interphase on the composites’ properties

It has been proven that in polymer nanocomposites, the effective volume fraction of the reinforcing phase is higher than the nominal filler volume fraction. Indeed, the contribution of the interphase to the reinforcement should be considered. The amount of the influential interphase is a function of the filler surface chemistry, the polymer structure, the filler/polymer interactions, and the processing conditions.30

Therefore, we needed to understand what fraction of PP chains are affected by the GO sheets. These chains could be segmentally or entirely restricted in the vicinity of the sheets. It has been assumed that the distribution of the GO sheets in the matrix is uniform and ideal. We consider one GO sheet as a cube with a length and width of 2µm and a thickness of 1nm for these calculations. Therefore, the volume of one single GO sheet will be
0.004\mu m^3. The 2% weight fraction of GO used in the composites is converted to volume fraction, considering the density of GO and PP to be 1.8g/cm^3 and 0.92g/cm^3, respectively.

\[
f_v = \frac{f_w}{f_w + (1-f_w) \frac{\rho_f}{\rho_m}} = \frac{0.02}{0.02 + (1-0.02) \times \frac{1.8}{0.92}} = 0.01
\] 

(4.5)

The total number of GO sheets when 1vol.% is added to the composite could be calculated by dividing the total volume of the sheets by the volume of one sheet. It is known that the interphase layer thickness in a polymer/GO composite equals the end-to-end distance of the polymer chains. We calculated this parameter for the used polypropylene:

\[
\sqrt{r^2} = \sqrt{nc_{\infty}l} = \sqrt{\left[\frac{2\times282000}{42}\right] \times 5.5 \times 0.15nm} = 40.8nm
\] 

(4.6)

Where \( \sqrt{r^2} \) is the end-to-end distance of the polymer chains, \( n \) is the number of C-C bonds, \( c_{\infty} \) is the characteristic ratio of the polymer, and \( l \) is the length of a C-C bond. The calculated end-to-end distance for a PP chain with a molecular weight of 282000g/mol and the characteristic ratio of 5.5 will be \( \sim40.8nm \). Therefore, Interphase volume on one GO sheet=\( L^2 \times \) Interphase thickness \( \times 2 = 0.326\mu m^3 \). Consequently, the volume fraction of the interphase (the ratio of the affected chains over the volume of the matrix) will be obtained.

Volume fraction of the intherphase

\[
= \frac{\text{total volume of interphase}}{\text{volume of matrix=total volume - GO volume}}
\]

\[
= \frac{\text{Interphase volume on one GO sheet}\times\text{number of GO sheets}}{\text{total volume - volume of one GO sheet}\times\text{number of GO sheets}} = 83.7\%
\]
We built the plot that shows the interphase's volume percentage in PP/GO composites loaded with different amounts of filler, Figure 4.9.

![Graph showing the volume percentage of the interphase in PP/GO composites](image)

Figure 4.9 The volume percentage of the PP chains affected by GO at its different loadings.

It could be seen that by adding only 1% GO (by volume), about 84% of the matrix chains will be affected and confined in the vicinity of the GO sheets. The origin of the impact of low GO loadings on the mechanical properties of PP can be justified based on this plot. The 2D structure of GO makes it more influential comparing to other geometries of carbon fillers at a similar concentration.

### 4.3.6: Rheological analysis of PP/GO composites

As stated by Murayama, rheology deals with the deformation and flow of matter.\textsuperscript{11} Rheological behavior is a measure of the filler dispersion in the nanocomposites and also predicts the processability of the materials.\textsuperscript{18}
To have a primary understanding of the flow behavior of the samples, their melt flow index (MFI) was measured at 230°C under 2.16Kg of load, and the results are summarized in Table 4.2. GO sheets decreased the MFI of pure PP from 11.6 g/10min to 5.3g/10min. However, the modified GO sheets increased the MFI to 8.9 g/10min, which could be attributed to the shielding effect of the POGL chains. The viscosity of each material is calculated based on Equation (7.5) (which will be more explained in chapter 7).

Table 4.2 MFI and viscosity of PP composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MFI(230°C,2.16Kg/10min)</th>
<th>Viscosity (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>11.6</td>
<td>625</td>
</tr>
<tr>
<td>PP/GO</td>
<td>5.3</td>
<td>1368</td>
</tr>
<tr>
<td>PP/GOP</td>
<td>8.9</td>
<td>815</td>
</tr>
</tbody>
</table>

Rheological measurements were carried out in a shear rate range of 0.1 to 10 s\(^{-1}\) at three different temperatures, Figure 4.10.
All three samples including PP, PP/GO, and PP/GOP displayed a shear-thinning behavior as the viscosity decreased by increasing the shear rate. In essence, the liquid-like behavior of the composites at low shear rates changes to a solid-like behavior at higher shear rates. When the applied shear rate is low enough, the available time for the chains to re-orient will be more than their relaxation time. But as the applied shear rate exceeds the critical frequency, the given time for chain movements will be lower than their relaxation time, and consequently, the material shows a solid-like behavior, where the storage modulus is independent of shear rate, and it shows a plateau at high frequencies, Figure 4.11.
Figure 4.11 The schematic representation of the rheological response of polymer nanocomposites to shear rate. $\phi_c$ is the percolation threshold of the filler.\textsuperscript{19}

Moreover, since polymer chains have enough freedom to rotate at low shear rates, the viscosity of the composite material is mainly determined by the contribution of the filler network. For this reason, the structure of the 3D network of filler aggregates could be better understood at low frequencies. On the other hand, at high shear rates, the frozen polymer chains will be governing the system's viscosity, and the filler volume fraction is less influential on the rheological behavior of the system.

Pure polypropylene demonstrates a Newtonian behavior at low shear rates, and its viscosity is almost independent of the shear rate.\textsuperscript{20} As theorized by Einstein, adding a filler increases the viscosity of the composite material; as the PP/GO composite possessed a higher viscosity than the pure matrix. This also indicates the restricted movements of PP chains in the vicinity of GO sheets. The more prominent shear thinning behavior and lower viscosity of PP/GO at high shear rates are originated from the filler orientation. When GO sheets are covered with the POGL chains, they have a reduced impact on the viscosity, and it could be assumed that the nanoplates are somewhat shielded from the matrix. The
difference in viscosity is more prominent at lower temperatures, and as the temperature increases, the viscosity will be mostly dependent on the PP matrix. These results confirm the effect of GO and GOP on the PP matrix as identified by the MFI findings.

The power-law equation describes the relation between viscosity, $\eta$ (Pa.s), and shear rate, $\dot{\gamma}$ (s$^{-1}$):$^{22}$

$$\eta = K\dot{\gamma}^{\mu-1} \quad (4.7)$$

where $K$ is the consistency coefficient (Pa.s$^\mu$) and $\mu$ is the dimensionless flow behavior index. This equation is fitted on the experimental data, and the results are summarized in Table 4.3. The obtained $\mu$ for all samples is lower than one, indicating the non-Newtonian behavior, and this shear-thinning characteristic is more significant for the reinforced samples. The lower viscosity of PP/GOP composite compared to that of PP/GO facilitates its processing, an essential criterion in industrial application.

Table 4.3 Rheological parameter of PP composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>190 ℃</th>
<th>195 ℃</th>
<th>200 ℃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k$</td>
<td>$\mu$</td>
<td>$k$</td>
</tr>
<tr>
<td>PP</td>
<td>1289</td>
<td>0.85</td>
<td>892</td>
</tr>
<tr>
<td>PP/GO</td>
<td>2142</td>
<td>0.71</td>
<td>1711</td>
</tr>
<tr>
<td>PP/GOP</td>
<td>1583</td>
<td>0.76</td>
<td>1005</td>
</tr>
</tbody>
</table>
4.3.7. Dynamic Mechanical Analysis (DMA)

Storage modulus:

Dynamic Mechanical Analysis is the measurement of the response of a polymeric material to vibrational forces. It is employed to evaluate the interfacial interactions between the GO layers and the PP matrix at low deformations and investigate the effect of GO and GOP on the mechanical properties of the matrix.

Storage modulus is a measure of the stiffness of the material\textsuperscript{15}, Figure 4.12. At low temperatures (below $T_g$ of PP), composites containing unmodified and modified GO nanoplates have higher storage modulus because of the stiff GO sheets. The storage modulus of PP at the glassy region increases 10% after incorporating GO nanosheets. However, for the modified sheets, the relatively soft copolymer covering shields the nanoplates from the matrix and reduces their stiffening effect. Consequently, the storage modulus of PP/GOP at -40°C is only 5% higher than that of PP. As the temperature increases to above the glass transition of PP, the storage modulus decreases for all the samples, but this reduction is somewhat more significant for the PP/GOP composite containing low $T_g$ POGL chains. The storage modulus of PP/GO at room temperature is 1975MPa, which is 7% higher than PP (1840MPa), while the modulus of PP/GOP decreases to 1730MPa, 7% lower than the pure matrix, due to the softening effect of the POGL chains. Further temperature increment to the rubbery plateau region lowers the modulus of PP to 656MPa. At this condition, the modulus of PP/GO is 20% higher than PP, which can be associated with the high stiffness and stability of GO at high
temperatures. Interestingly, the PP/GOP has the same modulus as PP, which confirms the copolymer nano shell's shielding effect.

![Storage Modulus vs Temperature Graph](image)

Figure 4.12 Storage modulus of PP, PP/GO, and PP/GOP as a function of temperature.

The crystalline structure of the materials is also influential on their mechanical properties. According to Nielsen\textsuperscript{23}, a higher crystallinity leads to a higher storage modulus:

\[
\log_{10} G = 6.763 + 4.77W_c
\]  

(4.8)

where \( G \) is the storage modulus of the semicrystalline polymer and \( W_c \) is the degree of crystallinity. Based on this equation, the PP/GOP composite will possess a lower storage modulus due to its lower crystallinity than PP/GO. On the other hand, PP/GO has a lower degree of crystallinity than pure PP; still, the stiff GO sheets increase this composite's storage modulus, which was expected according to the rule of mixture for composites.
Overall, it is shown that the storage modulus of PP/GOP is more similar to PP than PP/GO. Consequently, it could be stated that the copolymer enveloping is shielding GO from PP and the thermo-mechanical properties of PP are not significantly influenced by the modified GO sheets.

**Loss modulus:**

The loss moduli of the materials were determined as a function of temperature, Figure 4.13, and the results are summarized in Table 4.4. The peak temperature and peak intensity are the coordinates of the plot's maximum. Peak area and Full Width at Half Maximum (FWHM) are obtained by integrating the peak.

<table>
<thead>
<tr>
<th>sample</th>
<th>peak temperature (°C)</th>
<th>peak area</th>
<th>peak intensity (MPa)</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>11.1</td>
<td>2264.7</td>
<td>153.2</td>
<td>23.7</td>
</tr>
<tr>
<td>PP/GO</td>
<td>8.1</td>
<td>2770.8</td>
<td>182</td>
<td>24.2</td>
</tr>
<tr>
<td>PP/GOP</td>
<td>10</td>
<td>2152.5</td>
<td>170.8</td>
<td>23.7</td>
</tr>
</tbody>
</table>

Loss modulus of PP/GO and PP/GOP at room temperature are 19% and 11% higher than PP. The loss modulus peaks of PP/GO and PP/GOP composites are broader than the pure PP. A broad damping peak shows the existence of microheterogeneity due to the different segmental environments. In essence, some of the PP chains are segmentally or entirely restrained by the GO nanoplates, while the rest of the chains are free to move; therefore, there would be different loss timescales across the sample, which lead to a broad loss peak.
We associate the higher peak area of PP/GO with the broader distribution of mobilities of the PP chains in the vicinity of the nanoplates. The chains in direct contact with the GO surface have reduced mobility. At the same time, chains in contact with those chains are less entangled and therefore have higher mobility. The chains in the vicinity of the modified sheets are not interacting with the GO surface and have mobility close to the bulk PP, resulting in less energy damping\textsuperscript{24} and lower loss modulus peak area. The addition of virgin GO to PP reduces its Tg, which could be justified by the reduced density for PP chains contacting the chains in contact with the GO surface. So more free volume will be provided for these low-density chains and facilitates their mobility.

![Figure 4.13 Loss modulus of PP, PP/GO, and PP/GOP as a function of temperature.](image)

**Tan delta:**

Glass transition results from the initiation of micro-Brownian motion of the amorphous chains. The origin of los tangent $\delta$ is the internal friction, and it is defined as the ratio of dissipated energy to the maximum potential energy stored per cycle.\textsuperscript{11} The glass transition
temperature associated with the peak temperature of \( \tan \delta \) is slightly higher than that of loss modulus. Loss tangent angle plots of the samples are analyzed, Figure 4.14, and the results are summarized in Table 4.5. Based on these findings, the damping factor of the composites is increased as the GO and GOP sheets are added to PP. The tan delta peak intensity at \( T_g \) for PP/GO and PP/GOP is 8\% and 14\% higher than PP, respectively. This confirms that there are more energy dissipation options for the PP chains in interaction with GO sheets. The larger peak area of PP/GOP indicates a higher interphase volume between PP and modified GO due to the better dispersion of the nanosheets inside the matrix. Crystallization shifts tan delta peak to higher temperatures by inhibiting the molecular motions in the amorphous parts, which could be the reason for the higher \( T_g \) of PP compared to that of PP/GO. Moreover, in the PP composite containing virgin GO nanoplates, PP chains in the vicinity of the sheets are confined by the weak Van der Waals interactions with the GO surface and possess a higher density; while the chains close to these confined chains are less entangled and have a lower density, and consequently have a higher degree of mobility. This fact results in the lower glass transition temperature of the PP/GO composite. This stiffening effect of GO sheets on their nearby chains has been seen before, as the viscosity of PP/GO is significantly higher than PP and PP/GOP materials. In PP/GOP composite, PP chains less interact with GO surface, and the stiffening effect would be observed to a lower extent.
Table 4.5 Results of analyzing tanδ peak of PP, PP/GO, and PP/GOP.

<table>
<thead>
<tr>
<th>sample</th>
<th>Tg</th>
<th>tan delta intensity</th>
<th>crystallinity%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>13.1</td>
<td>0.0630</td>
<td>47</td>
</tr>
<tr>
<td>PP/GO</td>
<td>12.1</td>
<td>0.0679</td>
<td>43</td>
</tr>
<tr>
<td>PP/GOP</td>
<td>14.1</td>
<td>0.0720</td>
<td>35</td>
</tr>
</tbody>
</table>

Figure 4.14 Tanδ of PP, PP/GO, and PP/GOP as a function of temperature.

The ultimate objective of this research was to add functionality to the thermoplastic matrix without deteriorating its properties. The DMA results proved that the presence of GO decorated with the copolymer does not decrease the substantial mechanical properties of
PP. In essence, PP has become a functional material while its mechanical properties are preserved.

4.3.8: Tensile test of PP composites

The tensile test was done in compression mode (three-point bending flexural test) to evaluate the mechanical performances of samples at large deformations, Figure 4.15. The flexural modulus was computed based on the slope of stress-strain curves at the linear part. Flexural strength and strain are calculated based on the peak point of the stress-strain curves, and the toughness is the area under these curves.

We expected an increase in the moduli of the materials since the elastic modulus of GO is reported to be ~ 0.25 TPa (2-4 orders of magnitude higher than the modulus for engineering polymers).\textsuperscript{25-27} The flexural modulus of PP/GO increases by about 25% compared to pure PP, while this increment is only 5% for PP/GOP composite. We note a significant difference in mechanical properties between PP/GOP and PP/GO materials. Namely, the addition of GOP to the PP matrix does not significantly influence its mechanical properties in terms of flexural modulus, strength, and strain. We connect this finding to the ability of POGL, enveloping the nanosheets, to effectively shield the GO surface from interaction with PP macromolecules.

The flexural strength just slightly decreases for PP/GO (9%) and PP/GOP (4%) compared to PP. The mechanical interlocking between the polypropylene chains and the wrinkled surface of GO reduces the mobility of these chains. Yun et al. have attributed the reduction
in tensile strength and strain to maximum to the inhibited molecular rearrangement and orientation in the tensile axis direction in the presence of graphene oxide sheets.\textsuperscript{16}

Flexural strain at maximum and toughness of the materials decreased to a much higher degree, but the decrease of PP/GOP toughness is considerably lower than that for PP/GO. While the addition of GO causes the strain to maximum and toughness of PP to decrease 37\% and 75\%, respectively, this reduction is 7\% and 43\% after incorporation of the modified sheets. The results indicate that the polymer chains' segmental mobility and molecular rearrangement of the PP chains, and mechanical deformation in the stretching direction\textsuperscript{28} are restricted due to the interaction of the PP chains with GO sheets. The decrease in the mobility of the macromolecules at their dry-contact points with GO’s surface leads to higher modulus and lower toughness/deformation limit. These conclusions have been reported for high-density polyethylene/maleic anhydride polyethylene (HDPE/MAPE) containing GO, where the presence of GO decreased the ductility but improved the modulus of the composites.\textsuperscript{28} The negative influence of GO on ductility is compensated to a good extent after modifying the GO sheets with the compatibilizing POGL chains. It is speculated that POGL chains decrease the interaction between the GO surface and the matrix, and consequently, the PP/GOP composite can be stretched to a greater extent before failure; since there are intermolecular interactions between the PP chains and the POGL molecules grafted on the basal planes of GO sheets. Also, a decrease in the degree of crystallinity of the PP matrix can contribute to the increased ductility of PP/GOP compared to PP/GO material.\textsuperscript{5}
4.3.9: Theoretical prediction of mechanical properties of the composites

The experimental results were compared with the theoretical predictions to obtain a better insight into the reinforcement mechanisms of the composites. For this purpose, we first needed to evaluate the level of filler orientation in the matrix since it has a high impact on the mechanical properties. According to the optical microscopy images, the nanoplates are oriented in the x-y direction. We attributed this orientation to the effect of extrusion and compression molding processes, Figure 4.16. The orientation of graphene nanosheets in a polymeric matrix under shear forces has been reported previously. Consequently, it could
be implied that the force is applied in the transverse direction related to the graphene oxide sheets’ orientation during the three-point bend test.

![Figure 4.16 Effect of a) extrusion, and b) pressing on the GO orientation in the composites.](image)

Rule of mixtures (Equation 4.9) and inverse rule of mixtures (Equation 4.10) predict the upper bound and the lower bound of the modulus of a composite system which are correlated to the moduli of a unidirectional material in its longitudinal and transverse directions, respectively. Halpin–Tsai model (Equations 4.11 and 4.12) predicts the modulus of a unidirectional composite material while it involves the filler geometry. Finally, the Takayanagi model (Equation 4.13) estimates the modulus of a composite containing a discontinuous rubber filler in a continuous plastic matrix.

\[
E_c = E_m \varphi_m + E_f \varphi_f \quad (4.9)
\]

\[
E_c = \left( \frac{\varphi_m}{E_m} + \frac{\varphi_f}{E_f} \right)^{-1} \quad (4.10)
\]

\[
\frac{E_c}{E_m} = \frac{1 + \xi \eta \varphi_f}{1 - \eta \varphi_f} \quad (4.11)
\]
\[
\eta = \frac{(\frac{E_f}{E_m})^{-1}}{(\frac{E_f}{E_m})+\xi}
\]

\[
E_c = \left(\frac{\phi}{\lambda E_f + (1-\lambda) E_m} + \frac{1-\phi}{E_m}\right)^{-1}
\]

where \(E_c\) is the modulus of the composite, \(E_m\) and \(E_f\) are the moduli of the matrix and the filler, respectively, and \(\phi_m\) and \(\phi_f\) are the volume fractions of the matrix and the filler, respectively. In the Halpin-Tsai equation \(\xi\) is the shape factor where \(\xi = 2(1/t)\) in the longitudinal direction and \(\xi = 2(w/t)\) in the transverse direction, having \(l=\)filler length, \(w=\)filler width, and \(t=\)filler thickness. In case of GO nanoplates length and width of the sheets are assumed to be equal to 2\(\mu m\) and the thickness is about 1nm. Therefore, the shape factor equals 4000 in both directions. In the Takayangi equation, \(\phi\) and \(\lambda\) are the filler volume fractions in the longitudinal and transverse direction, which are equal in case of GO embedded composites.

To calculate the flexural modulus of the modified sheets, we have considered them as a composite material where POGL is the matrix and GO is the filler. Based on the AFM images of GOP sheets in Figure 3.5, the thickness of GO and POGL layers are 1nm and 3nm, respectively. Thus, it could be assumed that the volume fraction of GO is 25% and that of POGL is 75%. Then the modulus of this 75%POGL/25%GO composite is predicted using Equations 4.9, 4.10, 4.11, and 4.13, Table 4.6.
Table 4.6 Prediction of the flexural modulus of GOP sheets based on different theoretical models.

<table>
<thead>
<tr>
<th>Material</th>
<th>Flexural modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>1112</td>
</tr>
<tr>
<td>GO</td>
<td>33000</td>
</tr>
<tr>
<td>POGL</td>
<td>10</td>
</tr>
<tr>
<td>GOP, eq. 4.9</td>
<td>8258</td>
</tr>
<tr>
<td>GOP, eq. 4.10</td>
<td>13</td>
</tr>
<tr>
<td>GOP, eq. 4.11</td>
<td>11</td>
</tr>
<tr>
<td>GOP, eq. 4.13</td>
<td>13</td>
</tr>
</tbody>
</table>

Afterwards, the flexural modulus of PP/GO and PP/GOP composites are predicted, and the results based on different theories are summarized in Table 4.7.

Table 4.7 Comparing the experimentally obtained moduli for PP/GO and PP/GOP with the theoretical calculations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>rule of mixtures</th>
<th>inverse rule of mixtures</th>
<th>Halpin-Tsai</th>
<th>Takayanagi</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>1113±45</td>
<td>-</td>
<td>-</td>
<td>--</td>
<td>-</td>
</tr>
<tr>
<td>PP/GO</td>
<td>1410±102</td>
<td>1750</td>
<td>1134</td>
<td>1737</td>
<td>1120</td>
</tr>
<tr>
<td>PP/GOP (E\textsubscript{GOP} from eq. 4.9)</td>
<td>1167±96</td>
<td>1255</td>
<td>1132</td>
<td>1255</td>
<td>1115</td>
</tr>
<tr>
<td>PP/GOP (E\textsubscript{GOP} from eq. 4.10)</td>
<td>1167±96</td>
<td>1090</td>
<td>420</td>
<td>1090</td>
<td>1112</td>
</tr>
<tr>
<td>PP/GOP (E\textsubscript{GOP} from eq. 4.11)</td>
<td>1167±96</td>
<td>1090</td>
<td>377</td>
<td>1090</td>
<td>1112</td>
</tr>
<tr>
<td>PP/GOP (E\textsubscript{GOP} from eq. 4.13)</td>
<td>1167±96</td>
<td>1090</td>
<td>420</td>
<td>1090</td>
<td>1112</td>
</tr>
</tbody>
</table>

According to the calculations, the experimentally measured modulus of the PP/GO composite is well between the upper and lower bounds. The theoretical predictions for PP/GOP composite are closer to the experimental result. However, using the rule of mixing for estimating the modulus of GOP is unrealistic because the copolymer covering
diminishes the strengthening effect of the GO sheets dramatically, and the overall modulus of the encapsulated sheets is more dominated by the soft copolymer nanoshell. The other three models predict the modulus of GO/POGL very similar to that of POGL. The rule of mixture, Halpin-Tsai, and the Takayanagi models resulted in a modulus of about 1.1GPa for PP/GOP, when the $E_{GOP}$ was calculated based on the inverse rule of mixture, Halpin-Tsai, and the Takayanagi models. On the other hand, the inverse rule of mixture gives very low numbers for modulus of PP/GOP which are far from reality. Therefore, it could be inferred that the modulus of the GO/POGL composite is closer to its lower band, while the modulus of the PP/GOP composite is above its higher band. This finding confirms the efficient load transfer and continuity in the PP/GOP composite.

4.4: Conclusions

The following conclusions can be drawn as a result of the study reported in Chapter 4:

- GO sheets were introduced to PP fibers dispersed in water. Fitting the experimental data on Freundlich isotherm confirmed the formation of GO multilayers on the fibers’ surface.
- PP fibers covered with GO sheets were extruded and pressed to obtain PP/GO composites.
- The morphology of pressed pure PP and PP composites films was analyzed via optical microscopy. The uniform 2-D dispersion of the nanoplates in the composites and the PP spherulites intruded by GO and GO/POGL sheets could be clearly observed.
• PP/GO composites were more thermally stable than pure PP, which was due to the gas barrier properties of GO sheets. Modification of these sheets with the copolymer diminished the effect of GO.

• According to the DSC results, GO sheets increased the nucleation rate by acting as nucleation surfaces but decreased the growth rate due to the chain confinement in the vicinity of the sheets. The PP/GOP interlocking decreased the overall crystal percentage.

• The viscosity and shear thinning behavior of PP increased by the addition of GO sheets. However, GOP nanoplates did not change the viscosity of PP dramatically and were supposed to be shielded from the matrix.

• Composites containing unmodified and modified GO had higher storage modulus because of the stiff GO sheets. As the temperature increased, the storage modulus decreased for all the samples, but this reduction was slightly more significant for the PP/GOP composite containing low T<sub>g</sub> POGL chains.

• The larger tanδ peak area of PP/GOP indicates a higher interphase volume between PP and GOP sheets due to the better dispersion of the nanosheets inside the matrix.

• The tensile test showed the positive impact of stiff GO nanoplates on the flexural modulus of the PP/GO composites. Modifying GO with the copolymer improved the toughness and ductility of the composites.
Based on the PP/GO interphase thickness calculations, it was discerned that about 84% of PP chains are influenced by adding the 0.01 volume fraction of GO, and this could be the reason for the dramatic effect of GO on the properties of PP.

4.5: References


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CHAPTER FIVE

3D PRINTING OF PP/GO COMPOSITES

5.1: Introduction

This chapter is devoted to i) processing PP/GO masterbatches based on PP pellets, ii) 3D printing the processed extrudates, and iii) examining the mechanical properties of the obtained materials.

Our purpose in this chapter is to explore if the PP/GO composites are printable and if the presence of GO will impact the characteristics of the printed materials. The polypropylene used in this part of the research is PP pellet with MFI of 1.3 g/10 min, 2.16kg. This MFI has been converted to molecular weight, giving 510,000g/mol for the PP pellets.\(^1\) The molecular weight of the PP fiber was about 280,000 g/mol calculated based on its MFI which is 12 g/10min, 2.16kg. Like the previous sample preparation experiments, GO sheets are introduced to PP powder from an aqueous environment before the melt processing. Then the PP material decorated with the nanoplates is dried and extruded to obtain filaments with a diameter of 1.75 mm. Then the filaments are 3D printed to obtain samples of different sizes for the mechanical characterization. The influence of GO and GO/copolymer sheets on PP's mechanical properties are investigated. The properties of the 3D printed specimens based on PP pellets are compared with the compression-molded pieces. Due to the limited supply of PP fiber, we could not 3D-print PP fibers to compare them with 3D-printed PP pellets.
5.2: Experimental

5.2.1: Materials

PP pellet (MFI=1.3g/10min, 230°C, 2.16Kg) was supplied by Braskem America, Inc.

5.2.2: Fabricating PPp/GO masterbatches

To distinguish PP pellets and PP fibers, we refer to them as PPp for PP pellet and PPf for PP fiber for nomenclature of the fabricated composites. Before mixing with GO, the PP pellet was powdered using a cryogenic tissue grinder (BioSpec products, CTGIII). According to the optical microscopy images, the average diameter of PP powder particles is 150µm, which gives a specific surface area of about 220 cm²/g. While the specific surface area of PP short fibers with a diameter of 15µm and length of 3mm, is about 2900 cm²/g. This means that the surface available for GO adsorption is much lower in the case of PP pellets.

First, PP powder was mixed with a suspension of GO sheets in water during the wet processing step to obtain PPp/2wt.%GO and PPp/2wt.%GOP to prepare masterbatches. In the melt processing step, the dried at room temperature polymer/GO masterbatch was extruded twice using a Noztek pro pellet and powder filament extruder at 230°C to prepare the filaments with a diameter of 1.75 mm. This diameter was required based on the geometrical specifications of the 3D printer. Pure PP pellets were also extruded at the same conditions to be able to compare the unfilled and composite samples with a similar thermal history.
5.2.3: 3D printing of PPp/GO composites

Finally, at the printing step, the pure PP and composite filaments were 3D printed using a big builder dual feed (V2.2XL020H, Builder 3D) 3D printer at 230°C to obtain 6.5×2×35mm³ rectangular samples for DMA testing. A thin polypropylene film was attached to the printing bed using double-sided tape, so the printed structures would stick to the PP film and not be wrapped. Consequently, PPp, PPp /GO, and PPp /GOP samples were fabricated. Table 5.1 provides the key abbreviations for the samples containing GO.

Table 5.1 List of the fabricated samples and their compositions.

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPp</td>
<td>100%PP pellet</td>
</tr>
<tr>
<td>PPp/GO</td>
<td>98%PP pellet + 2%GO</td>
</tr>
<tr>
<td>PPp/GOP</td>
<td>98%PP pellet + 2%GOP</td>
</tr>
</tbody>
</table>

5.2.4: Morphological analysis of PPp/GO composites

Optical microscopy (Olympus LEXT OLS 4000 confocal laser microscope) was used to observe the morphology of the PP pellet composites. Polymer composites were pressed to fabricate ~30μm thick films to conduct optical microscopy.

5.2.5: Mechanical analysis of PPp/GO composites

Mechanical properties of the composites were analyzed in low deformations. Dynamic mechanical analysis (DMA) (Q800; TA Instruments) was done at a frequency of 5Hz and
a temperature range of -50°C to 100°C and a heating rate of 3°C/min. Samples were clamped perpendicularly between two arms, while about 15mm of their length was under deformation.

5.3: Results and discussions

5.3.1: Morphological analysis of PPp/GO composites

PP/GO composites based on PP pellets were extruded and compression-molded by a hot press at elevated temperature and pressure\(^2\) to produce the test materials. Morphology of the pure PP pellets and the composites was evaluated using optical microscopy, Figure 5.1. For this purpose, thin films of the samples with a thickness of \(30\mu m\) were prepared, and the observation was done through light transmission mode. PP spherulitic structures could be observed in the pure matrix.\(^3\) Addition of GO sheets hinders these crystal domains and reduces their size. GO sheets are well distributed and easily seen in the composites, indicating that they have preserved their original sheet-like structure during the processing steps. Single-layer and multi-layers of the sheets could be observed, which confirms the success of the composite processing method. Optical microscopy images of PP fiber composites are shown in Figure 4.6.

Figure 5.1 Optical microscopy images of (a) PPp, (b) PPp/GO, (c) PPp/GOP.
5.3.2. Dynamic mechanical analysis of the pressed PPp/GO composites

We needed to investigate the mechanical properties of the pressed composites based on PP pellets prior to evaluating the 3D printed structures. Dynamic mechanical analysis is employed to assess the interfacial interactions between the GO layers and the PP matrix at low deformations and investigate the effect of GO and GOP on the mechanical properties of the matrix, Figure 5.2. At low temperatures, composites containing pristine GO have a slightly lower storage modulus. Encapsulating the nanoplates with the soft copolymer shell reduces the storage modulus of the PP matrix more significantly. The lower modulus of the composites can be correlated to the dry contact between the nanofiller and the host matrix. As the temperature increases up to room temperature, the storage modulus decreases for all the samples, the differences decrease, and the three materials show close storage moduli.

The dynamic mechanical analysis of PPf composites have been presented in Figures 4.11, 12, and 13. The storage modulus of the PP pellet at low temperatures is about 1000MPa higher than that of PP fiber, which can be due to the higher molecular weight of the PP pellet. However, the presence of GO in PPf composites enhanced the storage modulus, while PPp/GO composites are weaker than the host matrix.

Comparing the loss modulus plots of the PPp and PPf materials, it could be seen that the PPp/GOP composite has the lowest peak area, which could be ascribed to the stronger interaction between the modified GO and the PPp matrix that result in less mobility of the confined high molecular weight chains and less energy damping. Overall, the damping of
PPp/GO composites is lower than the unfilled material, while in the case of PPf/GO composites, the addition of GO elevates the mechanical energy dissipation.

We suggested that the GO nanoplates cannot disperse finely in the high molecular weight PPp material, and their large agglomerates reduce the storage modulus and damping of the filled materials. This hypothesis needs thorough investigation by conducting further mechanical and microscopical characterizations.

Figure 5.2 Dynamic mechanical analysis of pressed PPp composites.
5.3.3. Dynamic Mechanical Analysis of 3D-printed PPp/GO composites

Before 3D printing, the extruded filaments were placed in a vacuum oven to remove all the remaining moisture and prevent the introduction of voids in the final structures. However, the high temperatures of extrusion and 3D printing cause evaporation of the moisture trapped in the GO sheets, which results in the generation of voids on the surface of printed parts, resulting in surface roughness and brittleness of the final materials. On the other hand, the empty spaces between the printed layers result in a lower density of the final structure; therefore, two pressed and printed samples of the same dimensions will not have equal weights. All these factors conclude in lower mechanical properties of the 3D printed samples compared to those of the pressed ones.

The 3D printed PP pellet samples have been analyzed through the DMA test, and the negative impact of 3D printing on the mechanical properties of the materials can be observed, Figure 5.3. As has been discussed before, the weak interface between the printed layers causes the reduction of mechanical strength. This effect is more dramatic for neat PP because as one layer of PP is printed, it cools down quickly, and the successive layer will not adhere to it firmly. However, the presence of thermally conductive GO increases the melting and interdiffusion of layers; consequently, the storage modulus will be slightly higher.
Figure 5.3 Dynamic mechanical analysis of 3D printed PPp composites.

Due to the limited supply of PP fibers, we could not fabricate 3D-printed parts out of these fibers and compare the mechanical properties of the printed PP pellets and PP fibers.
5.3.4. Comparing mechanical properties of pressed and 3D-printed PPp/GO composites

Comparing mechanical properties of pressed and 3D-printed PPp/GO composites shows the much lower strength of printed specimens as expected.

3D printing of semicrystalline polymers like PP is challenging because of the thermal shrinkage of the printed structure after it cools down to room temperature. It has been shown that embedding metal particles can prevent the distortion of the printed parts. Based on this finding, we conclude that the presence of GO increases the durability and consequently the mechanical properties of the printed parts.

To obtain a 3D printed composite with desired characteristics, uniform distribution of nanoparticles in the matrix polymers is required. Surface treatment and functionalization of the nanofillers are usually done to realize a homogenous dispersion and good interfacial bonding between nanoparticles and polymers.

One of the main drawbacks of FDM printing is the limitation of using feed materials in the form of filaments. Filler dispersion would be significantly limited in the small cross-section of the filaments. Also, there would be a higher possibility of creating voids in the filaments and the final printed structure. This factor can be one of the main reasons of the dramatically lower mechanical properties of the printed PPp/GO composites compared to those of the pressed ones. Nonetheless, to reduce the adverse effect of poor GO dispersion, a second extrusion process has been conducted to enhance the distribution of fillers.
Figure 5.4 Comparing mechanical properties of pressed and 3D-printed PPp/GO composites.

5.4. Conclusions

- Mechanical properties of the pressed PP pellet composites containing GO and GOP are lower than pure PP.
• The storage modulus of pressed PP pellet at low temperatures is about 1000MPa higher than that of PP fiber.

• The weak interface between the printed PPp layers causes the reduction of mechanical strength.

• Presence of thermally conductive GO increases the melting and interdiffusion of printed layers; consequently, the storage modulus will be slightly higher than neat PP.

• Comparing mechanical properties of pressed and 3D-printed PPp/GO composites shows the much lower strength of printed materials as expected.

5.5. References


CHAPTER SIX
MICROWAVE TREATMENT OF POLYPROPYLENE/GRAPHENE OXIDE COMPOSITES

6.1: Introduction

This chapter is devoted to i) understanding the effect of microwave radiation on polypropylene and polypropylene/graphene oxide composite, ii) examining the impact of encapsulating GO with the copolymer nanoshell on the microwave absorption of PP/GOP, iii) analyzing the mechanical properties of the composites before and after heating with microwave, iv) assembling and dissembling pressed and 3D-printed parts via microwave heating.

Based on previous chapters' explained results, GO sheets are incorporated into the PP matrix, while this polymer's thermal and mechanical properties are almost intact. The presence of GO inside the matrix could add new characteristics to the polymer, e.g., thermal conductivity, electrical conductivity, and electromagnetic waves absorption. The main goal of this chapter is to exploit the microwave absorption ability of GO sheets embedded polymer composites and utilize this feature to weld pressed and printed polymeric parts.

The initial microwave experiments are conducted based on PP fiber samples. After confirming the microwave absorption of the composites, we started using PP pellets to fabricate the composites since we had planned to 3D print them, which needs a larger amount of material, and our supply of PP fibers was limited. So, the mechanical testing of
the samples before and after microwave were conducted for the pellet-based samples. However, during the welding experiments, we realized that the high molecular weight PP pellet-based composites would not diffuse well as heated with the low-power microwave oven we have. Therefore, we switched back to the lower viscosity PP fiber composites that showed good diffusion and welding results.

6.2: Experimental

6.2.1: Materials

The materials used for this part of the experiments were based on both PP fibers and PP pellets. To distinguish PP pellets and PP fibers, we refer to them as PPp for PP pellet and PPf for PP fiber for nomenclature of the fabricated composites. The materials, including PP, PP/GO, and PP/GOP, were used in different parts of the experiments. As mentioned in previous chapters, PP fibers and pellets have MFI of 12 and 1.3 (g/10min, 2.16kg), respectively. This difference in MFI causes different behaviors and results, which will be explained in the context of this chapter.

6.2.2. Microwave treatment of the samples

The microwave oven used for heating the materials was a laboratory microwave (BP-095; microwave research and application Inc.) with a power of 1000W operating at the frequency of 2.45GHz. During the microwave treatment experiments, the test specimens were placed right at the center of the oven cavity to ensure that they were located at the maximum standing wave amplitude. A box made of polypropylene foam was placed in the microwave cavity as an isolating chamber to reduce the heat loss of the samples through
conduction in the oven. Two optical temperature sensors were used to record the temperature of the sample and the ambient temperature inside the cavity online. A hole was made in the upper wall of the microwave oven by the manufacturer to enter the thermometers in the cavity. A FOTEMP1-H (OEM fiber optic signal conditioner, Micronor sensors) connected to a TS3 fiber optic thermometer was recording the ambient temperature to ensure that the cavity is not getting too hot, and the temperature increment of the sample is because of its inside heating and not due to the hot environment. A FOTEMP1-OEM-MNT (OEM 1-channel fiber optic signal conditioner PCB module, Micronor sensors) attached to a TS3 fiber optic thermometer was monitoring the temperature of the samples. We ensured that there was good contact between the probe and the sample and, if possible (in case of the pieces where no mechanical testing was conducted afterward), a hole was made in the sample to insert the probe in it to obtain a more accurate temperature recording. The measured temperature range by this TS3 fiber optic thermometer probe is -200°C to +300°C. The schematic representation of the microwave radiation experiment is shown in Figure 6.1.
6.2.3: Thermal analysis of composites before and after microwaving

TGA measurements were conducted to investigate the impact of microwave radiation on the thermal properties of the composites. Thermogravimetric analysis (AutoTGA 2950HR V5.4A) was performed under nitrogen gas from room temperature to 600 °C at a ramp rate of 10 °C min⁻¹ to examine the thermal stability of the materials.

6.2.4: Mechanical analysis of composites before and after microwaving

Mechanical properties of the composites before and after microwaving were analyzed in low and high deformation rates. Dynamic mechanical analysis (Q800; TA Instruments) was done at a frequency of 5Hz and a temperature range of -50°C to 100°C and a heating
rate of 3°C/min. Samples were clamped perpendicularly between two arms, while about 15mm of their length was under deformation. A tensile tester (5582; Instron) was used to measure the mechanical properties of the composites in three-point bending mode according to ASTM D790. These specimens were compressed at a 1mm/min deformation rate until they broke or reached 10mm of deformation.

6.3: Results and discussions

6.3.1. Analyzing the effect of GO on microwave absorption of PPf/GO composites

Firstly, the effect of a low amount of GO on the microwave absorption of PPf was examined, Figure 6.2. Two identical 1cm³ cubes of PPf and PPf/2%GO based on PP fibers were heated up in the microwave, and the temperature increment was recorded for the two samples. As expected, PP was almost transparent to the microwave radiation, and the temperature change was negligible. But, for the sample containing GO, since the GO sheets perform as microwave absorbers, the overall temperature of the sample increased dramatically. It is known that microwave heating is the heat generation due to the interactions between the material and the microwaves¹ and is a function of the strength of the electric field, frequency, and dielectric loss properties of the material. Dielectric properties of filled composites is a function of the type of the filler, the concentration and morphology of the filler, and the sample preparation method. Therefore, at a constant microwave treatment situation, the higher dielectric loss of the GO sheets results in a higher temperature. While Galindo et al. had reported that PP-graphene samples were not heated up inside the microwave, even with a 10%loading of the filler², the PPf/GO samples
fabricated in this research were melted quickly. We associate this phenomenon with the better distribution of GO in our case.

GO sheets add a significant amount of loss to the composite material due to their high dielectric loss. Also, the massive volume of polymer/GO interface increases the amount of dielectric loss. As the microwave loss of the material increases, the penetration depth of the microwave decreases; therefore, the whole sample cannot be heated up efficiently. On the other hand, the low thermal conductivity of the polymer matrix prevents heat conduction through the specimen, and the accumulated heat will generate hot spots. Therefore we have used samples with small thicknesses to obtain a relatively uniform temperature distribution across the sample.¹

Figure 6.2 Change in temperature of PPf and PPf/GO versus time of exposure to microwave radiation.
Through investigating the thermal degradation behavior of the PPf/GO sample that had been exposed to microwave radiation beyond its melting point, it was inferred that the high temperature experienced by the sample had caused degradation, where the decomposition onset temperature lowered dramatically, Figure 6.3. Therefore, microwave heating could be a method to degrade the thermoplastic polymers reinforced with microwave absorbing fillers. In a similar research, thermal degradation of poly(vinyl alcohol)/graphene composites after prolonged microwave radiation exposure has been reported.\(^3\)

![Figure 6.3 TGA plots of PPf/GO composite before and after exposure to microwave radiation.](image)

We realized that the temperature of the samples could be controlled by manipulating the power of the microwave. This experiment aimed to heat up the sample to a specific temperature in a periodic manner, Figure 6.4. This finding is helpful when a material is required to experience a temperature increment periodically for a particular application.
6.3.2. Impact of GO nanoplates modification on their microwave absorption behavior in PPf composites

To realize the effect of the compatibilizing POGL chains on the microwave absorption of the composites, two identical DMA samples (30×5×1mm$^3$) of PPf/GO and PPf/GOP based on PP fibers were exposed to microwave radiation, and their temperature was recorded with time, Figure 6.5. The heating rate of PPf/GOP is much higher than that of PPf/GO, which can be associated with the better distribution of the modified GO sheets in the matrix. As a result, the heating points are uniformly distributed throughout the sample, and there will not be hot spots$^2$. Consequently, a uniform increase in temperature will occur, and the overall temperature will be higher than the PPf/GO composite. The stronger electromagnetic waves absorption of polymer composites due to a more uniform filler distribution has been reported before.$^4$ Furthermore, a more extensive interface between
the polymer and the filler will lead to a stronger interfacial polarization and more significant microwave dissipation.\textsuperscript{5}

Based on the finding of this part of the experiments, PPf/GOP was selected as a better microwave absorber material, and it was used for the rest of the experiments.

Figure 6.5 Microwave heating of PPf composites containing unmodified and modified GO.

A reason for the lower temperature of these specimens compared to similar samples in Figure 6.2 can be cooling down the samples’ surface and heat transfer through convection. The temperature of small DMA samples does not go up too much and cools down quickly in the microwave oven due to their larger surface to volume ratio. In comparison, bigger pieces of samples or a bundle of small samples reach higher temperatures. To address this issue, we have made a hole in the samples to be able to measure their temperature in depth. However, it was impossible to make a hole for those samples that needed to be
mechanically tested. So, we just ensured that there was good contact between the probe and the sample surface.

It has been reported that at a constant power of the microwave, there is a saturation temperature at which longer radiation time will not result in higher temperatures. In this situation, higher temperatures will be achievable by increasing the instrument's power. Based on this finding, we suggest that the low power of our microwave oven limits the highest temperature obtained for these samples. However, these results represented here can be used as an initiative for future experiments and investigations.

6.3.3. Modeling the heat transfer through PP/GO and PP/GOP composites

The heat transfer in solids module of COMSOL Multiphysics® (version 5.6) was used to model experimental heating of PP/GO and PP/GOP samples in the microwave, as shown in Figure 6.5. Both samples were considered as homogenous cubes with an internal heating source. In essence, the microwave absorbing GO nanoplates that heat the composite materials were considered as the heat sources.

The model sample is a 1cm$^3$ cube placed on an isolating surface (resembling the Teflon plate under the test specimen). The surrounding air cools down the sample through heat convection with $h=100$W/m$^2$.K. The microwave oven's nominal power is 1000W that is the incident radiation. The power received by the two cubes is changed until the experimental heating profiles are generated. Introducing a power rate of 1.1W results in a core temperature of about 42°C after 30s, similar to heating the PP/GO sample. The
required power rate to reach the temperature of PP/GOP (110°C) after 30s is 5.3W, Figure 6.6. These findings confirm that the modified graphene sheets are more powerful sources.

![Graph showing temperature distribution](image1)

It could be concluded that PP/GO and PP/GOP composites having identical filler volume fractions of ~1% absorb different amounts of microwave radiations. The finer dispersion of the modified sheets in the PP matrix could be the reason for the higher heating efficiency.
of PP/GOP; because a greater number of point heat sources provide more amount of heat in total.

If we consider the nominal power of the microwave oven as the input energy $I_0=1000\text{W}$ and assume the received power by the PP/GO and PP/GOP samples equal to $I_{PP/GO}=1.1\text{W}$ and $I_{PP/GOP}=5.3\text{W}$, respectively, we could calculate the ratio of absorbance of the two composite materials:

$$\frac{A_{PP/GOP}}{A_{PP/GO}} = \frac{-\left(\log \frac{I}{I_0}\right)_{PP/GOP}}{-\left(\log \frac{I}{I_0}\right)_{PP/GO}} = \frac{\log I_{PP/GO} - \log I_0}{\log I_{PP/GOP} - \log I_0} = \frac{\log 5.3 - \log 1000}{\log 1.1 - \log 1000} = 1.738$$

Also, $I_0$ was changed in the range of $100\text{W}$ to $10^5\text{W}$, and the ratio is still $\sim 1.74$, so we could say that even if the amount of the incident power is not equal to the nominal power of the microwave, the microwave absorption of the PP/GOP composite is 1.74 times higher than PP/GO.

6.3.4: Mechanical analysis of pressed PPp composites before and after microwaving

In the next part of the experiments, extruded and pressed PP pellet-based samples were microwaved up to $150^\circ\text{C}$ before they started melting. We wanted to evaluate the effect of microwave heating on the internal diffusion of polymer chains. In other words, it is known that when the total temperature of the sample is around $150^\circ\text{C}$, the temperature of the polymer chains in the vicinity of the nanoplates could be higher, which can result in melting and interdiffusion of those chains. The right amount of interdiffusion can lead to higher mechanical properties while applying an excessive amount of heat can reduce the mechanical properties of the specimens by melting and deforming them.
According to the DSC results, no significant change was observed in the samples before and after the microwave. This implies that no dramatic rearrangement of the polypropylene chains has happened after microwave heating. Also, based on the constant melting temperature of the samples before and after radiation, it could be inferred that this amount of heat is not enough to degrade the polymer chains and reduce their molecular weight.

The storage modulus of a PPp/GOP sample exposed to microwave radiation (up to 150°C) was measured to evaluate the effect of the radiation and heating on its mechanical properties, Figure 6.7. This sample was first tested with DMA in a temperature range of -50°C to 50°C, so it could not be damaged during the test. Then it was heated up in the microwave for three minutes and tested again from -50°C to 100°C. It was observed that microwave radiation not only did not decrease its storage modulus but also had a minor positive effect on the modulus at low temperatures. Therefore, it is verified that exposure to microwave radiation does not have a destructive influence on the mechanical properties of the composites before they reach their melting temperature.
Figure 6.7 Storage modulus of PPp/GOP composite before and after microwave heating.

3Point bending test was also conducted for all three samples before and after microwaving to confirm the non-detrimental influence of microwaving on the mechanical properties of the composites, Figure 6.8 The elastic modulus, tensile strength, and tensile strain values were almost the same for the non-treated and treated samples.
Figure 6.8 3Point bending test of PPp composites before and after microwave radiation.

6.3.5: Mechanical analysis of 3D printed PPp composites before and after microwaving

It was hypothesized that microwave radiation would increase the mechanical properties of 3D printed samples by enhancing the adhesion of the printed layers. We believed that an optimum amount of heat could be applied to the printed parts to experience local melting and interdiffusion in the vicinity of GO nanosheets. In that case, the empty spaces between
the layers could be filled up, leading to a greater mechanical load-bearing and higher elastic modulus, Figure 6.9.

We printed PP pellet composites and measured their mechanical properties via DMA before and after microwave radiation to examine this hypothesis, Figure 6.10.

Based on the obtained results, it could be seen that the PPp sample is almost intact after microwaving. However, the storage modulus of PPp/GO and PPp/GOP decreases after microwaving. Despite the attempt to keep the temperature of the samples below their melting temperature, it seemed that some internal melting and deformation had happened to the composites, which led to their slight deformation and weaker mechanical behavior.
6.3.6: Using the microwave absorber PPp composite to weld pressed polymeric parts

There are other applications for these microwave absorbing materials. They have been exploited for shielding electromagnetic waves to protect electronic devices from electromagnetic interferences. Moreover, fracture healing can occur in a microwave absorber composite material. The heat produced in the vicinity of the microwave absorber filler can cause the melting of the polymer chains. If these chains are well above their glass transition temperature, they can diffuse into each other and heal the crack.

These materials can also be used for welding polymeric structures. For this reason, after examining the mechanical characteristics of the microwaved composites, we placed a pressed 1.5mm thick PPp/GOP piece between two PPp plates with a thickness of 1.5mm and microwaved them for 5 min until the composite material melted slightly. After applying
a little amount of pressure, the pieces were attached to each other. We needed to conduct a 3point bending test to evaluate the assembly's welding strength by observing the part's delamination behavior under compression. Therefore, the excess part of the bottom PPp plate was cut off, Figure 6.11.

The assembled part delaminated under compression testing, which infers the weak adhesion of the layers. Further attempts to melt down a whole PPp/GOP plate were not successful, and we could not attach the pure and composite parts to each other under microwave radiation. We concluded that this could be due to the high molecular weight and viscosity of the PP pellets, which would not be able to diffuse efficiently to bind two pure PPp parts. Consequently, we decided to use low viscosity polypropylene fiber to enhance the diffusion and adhesion of the melted composite to the pure structures.
6.3.7: Using the PP fiber composite to weld pressed polymeric parts

The PPf/GOP based on PP fibers is a microwave absorber composite that can be applied to weld different polymeric parts under microwave radiation. Efficient welding will lead to obtaining pieces with mechanical properties close to those of the bulk materials. To examine the welding efficiency of this material, it was placed between two pieces of pure PPf, and the whole assembly was treated with microwave radiation under slight pressure for 3 minutes. The outcome was a sandwich of PPf/GOP between two pure PPf plates. This piece was bent through a 3-point bending test, and the bending continued until the assembly broke, Figure 6.12. This test was done for more samples, and each time the sandwich broke from the area under tension, but it did not delaminate, Figure 6.12, inset. This observation confirmed that the welding is strong enough, and the assembly will perform as a uniform material under tension. For the sake of comparison with the welded parts, the bending test was carried out for a free sandwich of the three plates while they were not attached to each other.
In a similar study, Wu et al.\textsuperscript{8} have used carbon nanotube/PP composite powders for welding two PP plates with the aid of microwave radiation. They showed that a longer microwave radiation time results in more binder material melting and greater bonding strength of the
welded part. The positive effect of radiation time on the strength of the joints is reported in other researches.\textsuperscript{9} Wu et al.\textsuperscript{8} also observed that all the fractures happened between the interface of PP plates and the binding composite layer. However, in our experiments, none of the welded samples were delaminated from the interfaces, which approves the superiority and efficiency of this binding method. It is worth mentioning that they had used 4\% of CNT, while only 2\% of GOP is used in our research.

6.3.8: Using the PPf composite to weld 3D printed polymeric parts

After confirming the ability of PP fiber composites reinforced with graphene oxide, we used them for further applications.

Smoothing the external surface of printed parts via melting the top layer is also enforceable using a microwave absorber coating material. Most importantly, this nanocomposite can be used for assembling and dissembling polymeric parts, especially 3D printed parts, by heating the microwave absorber part. Zhang et al.\textsuperscript{10} embedded CNT into acrylonitrile butadiene styrene to enhance the interlayer adhesion of the additive manufactured parts. This welding method does not require bulk heating, which could cause the deformation of the molded or printed components. Moreover, they reported higher mechanical and electrical properties of the samples exposed to microwave.\textsuperscript{10}

We planned to attach pure PPf structures to each other which is not possible through conventional heating. For this purpose, we printed pure PPf pieces with a few layers of the microwave absorbing composite on them while the composite performs as a binder under microwave exposure, Figure 6.13.
We printed two pieces as follows: i) 25 layers of PPf/GOP was printed first, and then PPf was printed on the bottom side of the piece, and ii) 25 layers of PPf was printed first, and then PPf/GOP was printed on the top side of the piece, subsequently. The thickness of the layers was 0.2mm. Part 1 was placed on part 2, so their black parts were facing each other. After microwaving for 3 minutes, the composite materials were melted and diffused into each other, so the two pieces were firmly welded. This simple experiment approves the efficiency of the fabricated composite to weld pure polymeric parts, which cannot be heated up due to their low thermal conductivity. These polymers would just need a few layers of this composite printed on their top layer to let them attach under microwave radiation. This technique is clean and fast, and easy to control.

Moreover, the welded parts can be simply separated by exposure to microwave radiation. The same amount of heat and microwave power would be required to melt the black layers and detach them, Figure 6.14. Based on the rough surface of the separated parts, it could be concluded that the strength and efficiency of this welding method are pretty high and can be used for industrial applications.
6.4. Conclusions

- Adding 2wt.% of graphene oxide to PP changed it from a transparent to a microwave absorbing material. The temperature of this composite under microwave exposure increased quickly in a few minutes.

- This composite could be degraded by applying microwave radiation for a prolonged time.

- The heating rate of PPf/GOP is much higher than that of PPf/GO, which can be associated with the better distribution of the modified GO sheets in the matrix.

- It is verified that exposure to microwave radiation does not have a destructive influence on the mechanical properties of the composites before they reach their melting temperature.
• We could not attach the pure and composite PP pellet-based parts to each other under microwave radiation which can be correlated to the high molecular weight and viscosity of the PP pellets that would not diffuse efficiently to bind two pure PP parts.

• Using the PP fiber composite to weld pressed polymeric parts showed that the welding is strong enough, and the assembly will perform as a uniform material under tension and will not delaminate.

• The PP fiber composite was successfully used to weld, and un-weld 3D printed polymeric parts in a controllable and straightforward way.

6.5. References


CHAPTER SEVEN
POLYSTYRENE/POLYPROPYLENE/GRAPHENE OXIDE COMPOSITE BLENDS

7.1: Introduction

This chapter is devoted to i) preparation and characterization of polystyrene/graphene oxide composites, ii) processing polystyrene/polypropylene blends reinforced with GO and GOP in different compounding orders, and iii) characterization of the blends and investigating the morphology and the impact of virgin and modified graphene oxides on PS/PP blends.

We use the graphene oxide modified with copolymer as a compatibilizer in immiscible polystyrene (PS)/polypropylene (PP) blends. The copolymer containing hydrophobic and hydrophilic side chains is expected to attach to the GO sheets and push them to the blend interface. The PS/PP/GO blend composites are fabricated through a combination of solution mixing and melt processing methods. In the materials' processing stage, GO is either premixed with PS or with PP. We examine the influence of GO modification and the mixing order on the morphological and mechanical properties of the blends.

7.2: Experimental
7.2.1: Materials

PP fibers (Denier=1.5dpf, diameter=15μm, length=3mm) and PS pellets (Mw~280,000,) were supplied by Minifibers Inc. and Sigma Aldrich Inc, respectively. PS was powdered using a cryogenic tissue grinder (BioSpec products, CTGIII) before mixing with GO.

7.2.2: Fabricating PS/PP blends

80PS/20PP/0.4GO weight parts blends were prepared in three steps. In the wet processing step, PS powder and PP fibers were mixed with GO and GOP sheets suspensions in water to obtain PS/0.5wt.%GO, PS/0.5wt.%GOP, PP/2wt.%GO, and PP/2wt.%GOP masterbatches. The dried at room temperature polymer/GO masterbatches were extruded (CSI MAX mixing extruder, CSI Inc.) during the first melt processing step. PP/GO and PS/GO mixtures were extruded twice at 190°C and 200°C, respectively.

Pure PP and PS were also melt processed at the same conditions to avoid the influence of processing history on the properties of the blends. Finally, the PS and PP-based extrudates were mixed and extruded to obtain the ultimate blends. Two different mixing orders were employed to examine the influence of GO localization on the morphology and final properties of the blends. In PS-GO/PP, GO was first premixed with PS, while in PS/PP-GO, the premixed PP-GO masterbatches were extruded with pure PS.

The resultant materials were hot-pressed (Carver hydraulic press) at 200°C for 5 minutes under 3.8MPa pressure to produce the test specimens. Consequently, PP, PP/GO, PP/GOP,
PS, PS/GO, PS/GOP, PS/PP, PS/PP-GO, PS/PP-GOP, PS-GO/PP, and PS-GOP/PP samples were fabricated. Table 7.1 provides the key abbreviations for the samples.

**7.2.3: Morphological analysis of the blends**

Optical microscopy (Olympus LEXT OLS 4000 confocal laser microscope) was used to observe the composites' morphology. Polymer composites were pressed to fabricate ~30μm thick films to conduct optical microscopy.

Table 7.1 List of the fabricated samples and their compositions.

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>100%PP</td>
</tr>
<tr>
<td>PP/GO</td>
<td>98%PP+2%GO</td>
</tr>
<tr>
<td>PP/GOP</td>
<td>98%PP+2%GOP</td>
</tr>
<tr>
<td>PS</td>
<td>100%PS</td>
</tr>
<tr>
<td>PS/GO</td>
<td>99.5%PS+0.5%GO</td>
</tr>
<tr>
<td>PS/GOP</td>
<td>99.5%PS+0.5%GOP</td>
</tr>
<tr>
<td>PS/PP</td>
<td>80%PS+20%PP</td>
</tr>
<tr>
<td>PS/PP-GO</td>
<td>80%PS+20%[PP/GO]</td>
</tr>
<tr>
<td>PS/PP-GOP</td>
<td>80%PS+20%[PP/GOP]</td>
</tr>
<tr>
<td>PS-GO/PP</td>
<td>80%[PS/GO]+20%PP</td>
</tr>
<tr>
<td>PS-GOP/PP</td>
<td>80%[PS/GOP]+20%PP</td>
</tr>
</tbody>
</table>
7.2.4: Rheological analysis of the blends

The composite blends’ melt flow index (MFI) was studied using an XNR-400 melt flow indexer at 230°C and under 2.16Kg mass. MFI values were reported as the mass of the material pushed out of the chamber in 10 minutes.

7.2.5: Thermal analysis of the blends

Differential scanning calorimetry (DSC) (Model 2920; TA Instruments) was carried out at a heating/cooling rate of 20 °C/min and a temperature range of -50°C to 200°C. Thermogravimetric analysis (TGA) (AutoTGA 2950HR V5.4A) was performed under nitrogen gas from room temperature to 600 °C at a ramp rate of 10 °C/min.

7.2.6: Mechanical analysis of the blends

Mechanical properties of the materials were analyzed in low and high deformation rates. Dynamic mechanical analysis (DMA) (Q800; TA Instruments) was done at a frequency of 5Hz and a temperature range of -50°C to 100°C and a heating rate of 3°C/min. Samples with a thickness of 1mm and a width of 5mm were clamped perpendicularly between two arms, while about 15mm of their length was under deformation. A tensile tester (5582; Instron) was used to measure the mechanical properties of the samples in three-point bending mode according to ASTM D790. The tested samples had a thickness of 1.5mm and width of 12.8mm, and the tested span length was 25.4mm. These samples were compressed at a 1mm/min deformation rate until they broke or reached 10mm of deformation. The specimens that did not experience breakage would continue deformation without a change in their behavior; for this reason, we stopped them at 10mm of deformation to be able to compare results for different samples.
7.3. Polystyrene/graphene oxide composites

7.3.1: Morphological analysis of PS/GO composites

Figure 7.1 shows the optical microscopy images of PS/GO composites. In the composite materials, the distribution of exfoliated GO sheets is observable at a micrometer scale. GO sheets can be observed throughout the whole sample. Since the concentration of GO in the PS composites is lower than that of the PP composites, the GO and GOP sheets are lesser packed, and separated sheets can be observed in the amorphous PS matrix.

Figure 7.1 Optical microscopy images of PS, PS/GO, and PS/GOP.
7.3.2: Thermal analysis of PS/GO composites

Differential Scanning Calorimetry measurements of the samples are given in Figure 7.2. Samples were first heated from -50 °C to 200 °C to remove their thermal history. The DSC measurements demonstrate that the addition of GO and GOP (at 0.5wt.%) to PS does not alter its glass transition temperature. Thus, the mobility of PS chains in the material is not restricted by the virgin and modified GO nanosheets.

![Figure 7.2 Differential Scanning Calorimetry of PS, PS/GO, and PS/GOP.](image)

7.3.3. Mechanical analysis of PS/GO composites

**Dynamic Mechanical Analysis (DMA):**

Dynamic mechanical analysis was employed to evaluate the interfacial adhesion of the components at low deformations, Figure 7.3. The low amount of GO does not dramatically affect PS composites' behavior, but still, a higher modulus at lower temperatures is seen for the composites. At the beginning of the measurements, the storage moduli of PS/GO and PS/GOP are about 1% and 3% higher than PS, respectively. As the temperature
increases, the soft copolymer causes a reduction in the modulus. A similar trend is seen for loss modulus. The intensity of the loss factor of PS decreases after the addition of GO, but the peak position is not shifted. It is hypothesized that the degree of freedom of the chains is reduced in the PS/GO composites.

Figure 7.3 Dynamic mechanical analysis of PS, PS/GO, and PS/GOP.

Tensile test:
The tensile test was done in compression mode (three-point bending flexural test) to evaluate the mechanical behavior of the samples at large deformations. The results of this test for PS/GO composites are presented in Figure 7.4. The addition of GO and GOP to PS did not change its flexural modulus at room temperature, similar to the storage moduli of PS and its PS/GO and PS/GOP composites, where no significant difference was observable at room temperature.

However, the incorporation of GO in PS decreased its flexural strain and stress to maximum and toughness dramatically. The flexural strength decreased for PS/GO compared to the virgin polymer by 26%. Flexural strain at maximum and toughness of this composite decreased to a much higher degree as they decreased by 33% and 55%, respectively. This decrease has been reported previously for PP composites reinforced with GO.\(^1\) The results have indicated that the polymer chains’ segmental mobility is restricted due to their interaction with GO sheets. The decrease in the mobility of the macromolecules leads to higher modulus and lower toughness/deformation limit.

The copolymer nanoshell shields the GO plates from the PS matrix, eliminates the dry contacts between PS and the nanosheets, and consequently reduces the negative influence of GO on the ductility of PS. Therefore, the tensile strength, strain to maximum, and toughness of PS/GOP are 17%, 24%, and 37% lower than neat PS, which are substantially higher than those of PS/GO composite.
7.4. Using GO and GOP to compatibilize PS/PP blends

The majority (~65%) of the thermoplastic polymer materials in use and ending up in landfills are polyolefins with about an additional 5-8% of PS-based materials. These materials are recycled to a very low degree. Presently, the additional cost of recycling, associated with the sorting of plastic waste components, is one of the main barriers to the economic profitability of the recycled plastics industry. The potential solution is the mechanical recycling of mixed plastic waste. However, the positive mixing enthalpy
usually results in the formation of immiscible blends having separated phases with a low level of interfacial adhesion, decreasing the stress transfer through the interface.\textsuperscript{7-9} The low interfacial adhesion reduces the mechanical properties of the recycled mixed materials. Those phase-separated blends typically require compatibilization. Effective compatibilization of an immiscible blend results in (i) a decrease of the interfacial tension causing stabilization of the dispersed phase against coalescence (which leads to a reduction in the dispersed phase size) and (ii) enhancement of adhesion between the phases in contact.\textsuperscript{4, 6, 9}

The compatibilization can be accomplished either through chemical or physical methods by adding small amounts of functional components. Many compatibilizers are macromolecular species with a blocky structure (e.g., block or graft copolymers), where one constitutive block is miscible with one blend component and a second block is miscible with the other blend component.\textsuperscript{6} These macromolecules can be pre-made or generated in-situ during a reactive blending process.\textsuperscript{10} Also, a range of intermolecular interactions induced via the addition of functionalized (macro)molecular species can be used to increase compatibility between polymer blend components.\textsuperscript{4, 11} Recently, compatibilization strategies using nanoparticles and nanoplatelets have been explored to improve the mechanical properties of immiscible polymer blends.\textsuperscript{4, 12-15} In this case, efficient compatibilization requires localization of nanomaterials at the matrix/minor phase interface, which is driven by their shape, size, chemical composition, and surface coating. Significant efforts have been put in the employment of carbonaceous materials in this compatibilization methodology since they mostly contain the same elemental composition.
as the polymers do, have a lower density, and can reinforce the blends in addition to the compatibilizing effect. To this end, graphene oxide having a large π-conjugated system is compatible with certain polymers.\textsuperscript{15-16} It has been demonstrated that the affinity of GO to non-polar polymers, such as polyolefins, can be increased via surface modification of the nanomaterial.\textsuperscript{1,17-18}

To this end, in this chapter, we worked on the compatibilization of PS/PP blends with virgin GO and GO modified with copolymer layer (GOP) to improve the blends' mechanical properties. This blend was selected since polystyrene and polypropylene are commodity polymers extensively used in various applications, which are recycled to a very low degree. These two polymers are thermodynamically immiscible and have relatively low interfacial adhesion at the phase boundary. To obtain GOP, the surface of GO sheets was modified with the amphiphilic bottlebrush copolymer from water.\textsuperscript{19} The introduction of GO into the blend was also conducted from water, where PS or PP was suspended in water dispersion of GO and dried prior to melt-processing in an extruder. Thus, we envisioned that the addition of the compatibilizing nanomaterial could be conducted during the mechanical recycling washing stage in a real-world situation. The effect of GO and modified GO on the morphology and properties of PS/PP blends are studied. Moreover, since the mixing sequence is an important fabrication parameter determining the final properties of the blends, the influence of mixing order on GO sheets' preferred localization is examined by employing two different mixing sequences. The mixing order significantly affects the level of nanofiller distribution, dispersivity, and localization in the multiphase polymer system.\textsuperscript{20-21}
7.4.1. Thermodynamics of compatibilization using GO and GOP

For GO to serve as a compatibilizer for PS/PP blend, the material has to populate the phase boundary between PS and PP. It is known that polar GO sheets have a low affinity to non-polar PP, but they have a higher level of interaction with PS chains through the $\pi-\pi$ interactions. Thus, GO sheets will tend to concentrate in the PS phase. To corroborate this suggestion, we employed thermodynamic relationships to estimate the prevailing localization of the sheets in the PS/PP blend. To this end, we calculated surface energies and their (polar and dispersive) components for all the materials and in-contact pairs and determined the interfacial energies in the system\textsuperscript{7,23-25}, Tables 7.4 and 7.5.

The surface energies of PP and PS were obtained from a database.\textsuperscript{26} The surface energies of PLMA and POEGMA chains of POGL were approximated based on the surface energies of polyethylene (PE) and polyethylene glycol (PEG), respectively.\textsuperscript{26}

To calculate GO and GOP's surface energy, we used contact angle measurement method. GO and GOP were coated on a silicon wafer, and hexane and water were used to make the droplets on the test surfaces. The contact angles were obtained at room temperature, and the results were used to calculate the surface energy of the solid substrate by the Owens-Wendt method, Equation 7.1.\textsuperscript{27}

\begin{align*}
\gamma_{11}(1 + \cos \theta_1) &= 2\sqrt{\gamma_S^d \gamma_{11}^d} + 2\sqrt{\gamma_S^p \gamma_{11}^p} \\
\gamma_{12}(1 + \cos \theta_2) &= 2\sqrt{\gamma_S^d \gamma_{12}^d} + 2\sqrt{\gamma_S^p \gamma_{12}^p} \\
\gamma_S &= \gamma_S^d + \gamma_S^p
\end{align*}

(7.1)
where $\gamma_s$ and $\gamma_l$ are the surface tensions of the solid and liquid, respectively. The subscripts $d$ and $p$ correspond to dispersion and polar components of the surface tension, respectively. Surface free energy ($\gamma_s$) and its polar ($\gamma_s^p$) and dispersion ($\gamma_s^d$) components of the GO and GOP solid surfaces were determined using two sets of contact angle measurements of water and hexadecane. The $\gamma_l^p$ and $\gamma_l^d$ components of liquids taken from literature$^{28}$ were used in the calculations, Table 7.2. Analysis of water and hexadecane contact angles was done using a KRUSS DSA10 drop shape analyzer 20s after droplet deposition on the grafted copolymer surface.

Table 7.2 Water and hexadecane contact angles for GO and GOP.

<table>
<thead>
<tr>
<th></th>
<th>$\gamma_l^d$ (mN/m)</th>
<th>$\gamma_l^p$ (mN/m)</th>
<th>$\gamma_l$</th>
<th>GO</th>
<th>GOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecane (1)</td>
<td>26.35</td>
<td>0</td>
<td>26.35</td>
<td>0°</td>
<td>0°</td>
</tr>
<tr>
<td>Water (2)</td>
<td>21.8</td>
<td>51</td>
<td>72.8</td>
<td>0°</td>
<td>(51 ± 2)°</td>
</tr>
<tr>
<td>Surface Energy (mN/m)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>73.1</td>
<td>50.8</td>
</tr>
</tbody>
</table>

For calculating the surface energy of POGL, we did not use the results of contact angle measurement because this block copolymer can show different behaviors in this experiment. Depending on the substrate that the copolymer is coated on, it can expose its hydrophobic or hydrophilic sidechains to the test liquid and result in different contact angles. Therefore, we used the rule of the mixture to obtain the surface energy of POGL. In this regard, we have assumed that the surface energy of this copolymer is mainly determined by its POEGMA and PLMA side chains. The surface energies of these two materials were approximated by those of PEG and PE, respectively.$^{26}$ Ignoring GMA parts...
of the POGL chains, 92.78% of their weight would be POEGMA, and 7.22% would be PLMA, Table 7.3.

Table 7.3 Surface energy of POGL based on its POEGMA and PLMA side chains.

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight percent (%)</th>
<th>Surface energy (mN/m)</th>
<th>$\gamma_d$ (mN/m)</th>
<th>$\gamma_p$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POEGMA</td>
<td>92.78</td>
<td>42.9 (PEG)</td>
<td>30.9</td>
<td>12</td>
</tr>
<tr>
<td>PLMA</td>
<td>7.22</td>
<td>35.7 (PE)</td>
<td>35.7</td>
<td>0</td>
</tr>
<tr>
<td>POGL</td>
<td>100%</td>
<td>42.4</td>
<td>31.3</td>
<td>11.1</td>
</tr>
</tbody>
</table>

Table 7.4 Surface energies of the used materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\gamma$ (mN/m)</th>
<th>$\gamma_d$ (mN/m)</th>
<th>$\gamma_p$ (mN/m)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>73.1</td>
<td>26.4</td>
<td>46.8</td>
<td>Contact angle measurements, Owens-Wendt method\textsuperscript{27}</td>
</tr>
<tr>
<td>GOP</td>
<td>50.8</td>
<td>26.4</td>
<td>24.5</td>
<td>Contact angle measurements, Owens-Wendt method\textsuperscript{27}</td>
</tr>
<tr>
<td>PLMA</td>
<td>35.7</td>
<td>35.7</td>
<td>0</td>
<td>Considering surface energy of polyethylene (PE) equal to that of PLMA\textsuperscript{26}</td>
</tr>
<tr>
<td>POEGMA</td>
<td>42.9</td>
<td>30.9</td>
<td>12</td>
<td>Considering surface energy of polyethylene glycol (PEG) equal to that of POEGMA\textsuperscript{26}</td>
</tr>
<tr>
<td>POGL</td>
<td>42.4</td>
<td>31.3</td>
<td>11.1</td>
<td>Using rule of mixture based on the surface energies and the weight fractions of PLMA and POEGMA in POGL.</td>
</tr>
<tr>
<td>PP</td>
<td>30.1</td>
<td>30.1</td>
<td>0</td>
<td>\textsuperscript{26}</td>
</tr>
<tr>
<td>PS</td>
<td>40.6</td>
<td>34.5</td>
<td>6.1</td>
<td>\textsuperscript{26}</td>
</tr>
</tbody>
</table>

After obtaining the surface energies of all components, the surface energies of materials pairs were calculated based on equation 7.2\textsuperscript{27} and are presented in Table 7.5.

\[
\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p}
\]  
(7.2)
Table 7.5 Surface energy of materials pairs.

<table>
<thead>
<tr>
<th>Materials pair</th>
<th>( \gamma_1 )</th>
<th>( \gamma_2 )</th>
<th>( \gamma_p )</th>
<th>( \gamma_1 )</th>
<th>( \gamma_2 )</th>
<th>( \gamma_{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/GO</td>
<td>30.1</td>
<td>26.35</td>
<td>0</td>
<td>46.76</td>
<td>30.1</td>
<td>73.11</td>
</tr>
<tr>
<td>PP/GOP</td>
<td>30.1</td>
<td>26.35</td>
<td>0</td>
<td>24.48</td>
<td>30.1</td>
<td>24.73</td>
</tr>
<tr>
<td>PP/POGL</td>
<td>30.1</td>
<td>31.25</td>
<td>0</td>
<td>11.13</td>
<td>30.1</td>
<td>11.16</td>
</tr>
<tr>
<td>PS/GO</td>
<td>34.5</td>
<td>26.35</td>
<td>6.1</td>
<td>46.76</td>
<td>40.6</td>
<td>32.37</td>
</tr>
<tr>
<td>PS/GOP</td>
<td>34.5</td>
<td>26.35</td>
<td>6.1</td>
<td>24.48</td>
<td>40.6</td>
<td>12.14</td>
</tr>
<tr>
<td>PS/POGL</td>
<td>34.5</td>
<td>31.25</td>
<td>6.1</td>
<td>11.13</td>
<td>40.6</td>
<td>1.63</td>
</tr>
<tr>
<td>PP/PS</td>
<td>30.1</td>
<td>34.5</td>
<td>0</td>
<td>6.1</td>
<td>30.1</td>
<td>6.40</td>
</tr>
<tr>
<td>PP/PLMA</td>
<td>30.1</td>
<td>35.7</td>
<td>0</td>
<td>0</td>
<td>30.1</td>
<td>0.48</td>
</tr>
<tr>
<td>PS/PLMA</td>
<td>34.5</td>
<td>35.7</td>
<td>6.1</td>
<td>0</td>
<td>40.6</td>
<td>6.12</td>
</tr>
<tr>
<td>PS/POEGMA</td>
<td>34.5</td>
<td>30.9</td>
<td>6.1</td>
<td>12</td>
<td>40.6</td>
<td>2.12</td>
</tr>
<tr>
<td>PP/POEGMA</td>
<td>30.1</td>
<td>30.9</td>
<td>0</td>
<td>12</td>
<td>30.1</td>
<td>12.01</td>
</tr>
</tbody>
</table>

Next, the spreading and wetting coefficients were calculated to forecast the equilibrium morphology of the PS/PP-GO and PS-GO/PP blends. Table 7.6 includes the spreading and wetting coefficients for the mixtures. The spreading coefficient elucidates the likelihood of a matrix/inclusion interface to be covered with an additive in a three-component system:

\[
\lambda_{31} = \gamma_{12} - \gamma_{32} - \gamma_{13}
\]  

(7.3)

where \( \lambda_{31} \) is the spreading coefficient for an additive to cover the PP/PS boundary, and \( \gamma_{12}, \gamma_{32}, \) and \( \gamma_{13} \) are the interfacial energies for PP/PS, additive/PS, and additive/PP interfaces, respectively. Component 3 (additive) is predicted to localize at the PP/PS boundary if \( \lambda_{31} \) is positive.
Furthermore, the wetting coefficient, $\omega_a$, has been calculated for anticipating different situations of the systems according to the following equation:\textsuperscript{30}

$$\omega_a = \frac{\gamma_{32} - \gamma_{31}}{\gamma_{12}}$$

(7.4)

The wetting coefficient detects the location of the GO sheets in the equilibrated PS/PP blends. If $\omega_a > 1$, component 3 will be located in phase 1 (PP), if $\omega_a < -1$, component 3 will be located in phase 2 (PS), and when $-1 < \omega_a < 1$, component 3 will go to the interface of phases 1 and 2.
Table 7.6 Spreading coefficient and wetting coefficient of the blends.

<table>
<thead>
<tr>
<th>Material</th>
<th>Role</th>
<th>Material</th>
<th>( \gamma_{21} )</th>
<th>( \gamma_{23} )</th>
<th>( \lambda_{31} )</th>
<th>( \omega_{a} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/GO/PP</td>
<td>phase 1</td>
<td>PP</td>
<td>6.4</td>
<td>32.4</td>
<td>47.0</td>
<td>-73.0</td>
</tr>
<tr>
<td></td>
<td>phase 2</td>
<td>PS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>covering 3</td>
<td>GO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS/GOP/PP</td>
<td>phase 1</td>
<td>PP</td>
<td>6.4</td>
<td>12.1</td>
<td>24.7</td>
<td>-30.5</td>
</tr>
<tr>
<td></td>
<td>phase 2</td>
<td>PS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>covering 3</td>
<td>GOP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS/POGL/PP</td>
<td>phase 1</td>
<td>PP</td>
<td>6.4</td>
<td>1.6</td>
<td>11.2</td>
<td>-6.4</td>
</tr>
<tr>
<td></td>
<td>phase 2</td>
<td>PS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>covering 3</td>
<td>POGL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS/POEGMA/PP</td>
<td>(Both sides of GO covered with POEGMA)</td>
<td>phase 1</td>
<td>PP</td>
<td>6.4</td>
<td>2.1</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>phase 2</td>
<td>PS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Covering 3</td>
<td>POEGMA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS/PLMA/PP</td>
<td>(Both sides of GO covered with PLMA)</td>
<td>phase 1</td>
<td>PP</td>
<td>6.4</td>
<td>6.1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>phase 2</td>
<td>PS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Covering 3</td>
<td>PLMA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS/POEGMA-PLMA/PP</td>
<td>(One side of GO covered with POEGMA and toward PS. One side of GO covered with PLMA and toward PP)</td>
<td>phase 1</td>
<td>PP</td>
<td>6.4</td>
<td>2.1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>phase 2</td>
<td>PS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Covering 3</td>
<td>POEGMA</td>
<td>for PS and PLMA</td>
<td></td>
<td></td>
<td>0.26</td>
</tr>
</tbody>
</table>
Based on the thermodynamic calculations, if the GO sheets are added to PS/PP blend, they will not spread over the PP/PS interface and prefer to be situated in the PS phase. Decreasing the surface energy of GO can result in nanosheet localization at the PP/PS interface. In this regard, we modified the GO sheets with the POGL copolymer to improve the compatibilizing ability of GO in the PS/PP blends. The polar OEGMA monomer ensures the water solubility of the molecule. GMA is insoluble in water and can react with the functional groups of GO through its epoxy groups. LMA is a non-polar monomer used to balance the copolymer's polar/non-polar characteristic. We expected this copolymer to form covalent bonding with the GO sheets to coat the surface of the nanosheets.

POGL is an example of molecular bottlebrushes, a special case of graft copolymers (also referred to as cylindrical polymer brushes or molecular brushes), which are linear macromolecules with relatively long side chains anchored to the backbone at high grafting densities. Since POGL has two types of side chains PEG and PE (polyethylene glycol of OEGMA and polyethylene/lauryl of LMA), depending on the environment, the macromolecule can adopt different conformations. For instance, if PE side chains have a higher affinity to the surrounding, they are extended, while PEG chains are collapsed. In this scenario, the PE side chains dominate POGL interaction with a polymer material. The opposite situation is realized in the environment with a higher affinity to OEGMA chains. Thermodynamic calculations show that, indeed, modification of GO with POGL macromolecules can alter the preferred localization of GO in the blend, Table 7.6. Four main scenarios can be realized, Figure 7.5. Presume the surface of GO sheets is covered
with POGL macromolecules without preferred conformation for the side chains (PEG and PE chains are extended or collapsed simultaneously). In that case, the GOP sheets will prefer the PS phase. If PEG side chains are extended over the collapsed PE chains, the GOP will localize in the PS phase. The GO sheets covered with POGL will be more tending to the PP phase if PE side chains extend and shield the PEG chains. Finally, the PE chains on the one side of GO sheets can face the PP phase while the PEG chains on another side are extended toward the PS phase. Spreading coefficient and wetting coefficient calculations imply that the last situation will provide the greatest thermodynamic prospect for the GO sheets to go to the PS/PP interface and cover the dispersed domains inside the matrix.
Figure 7.5, a) All the PEG molecules are pointing out of the GO sheets, b) All the LMA molecules are aligned toward both of PS and PP phases, and c) The LMA chains face the PP phase, and the PEG chains are opened toward the PS phase.

7.4.2. Melt flow behavior of the blends

Along with interfacial tension, the viscosity of polymer blend components is a critical parameter that influences the phase dispersion and the localization of fillers. To this end, we measured melt viscosities of the involved materials and their mixtures using a capillary rheometer, and the data is presented in Table 7.7.

This method is an inexpensive approach to investigate the rheology of polymer melts. According to Shenoy et al., the melt flow index of a polymer is related to its viscosity through the following equation:

\[ MFI = 4.98 \times 10^4 \rho L/\eta \]  

(7.5)

where MFI is the melt flow index of the material, \( \eta \) is the viscosity, \( \rho \) is the density, and \( L \) is the nozzle length. Therefore, based on the relationship between viscosity and MFI, and
knowing that L=0.16m (cylinder length) for the used melt flow indexer, we could calculate the viscosity of the materials. The blend materials' density was estimated based on the rule of mixture. The low amount of GO is not influential on the density of the materials, so it is not considered in the density calculations of the blends.

Table 7.7 MFI and viscosity of PS, PP, and PS/PP materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>MFI (g/10min, 230°C, 2.16Kg)</th>
<th>Density(g/cm^3)</th>
<th>Viscosity (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>11.6</td>
<td>0.91</td>
<td>625</td>
</tr>
<tr>
<td>PP/GO</td>
<td>5.3</td>
<td>0.91</td>
<td>1368</td>
</tr>
<tr>
<td>PP/GOP</td>
<td>8.9</td>
<td>0.91</td>
<td>815</td>
</tr>
<tr>
<td>PS/PP</td>
<td>12.1</td>
<td>0.998</td>
<td>657</td>
</tr>
<tr>
<td>PS/PP-GO</td>
<td>6.6</td>
<td>0.998</td>
<td>1205</td>
</tr>
<tr>
<td>PS/PP-GOP</td>
<td>5.9</td>
<td>0.998</td>
<td>1348</td>
</tr>
<tr>
<td>PS-GO/PP</td>
<td>7.8</td>
<td>0.998</td>
<td>1019</td>
</tr>
<tr>
<td>PS-GOP/PP</td>
<td>5.4</td>
<td>0.998</td>
<td>1473</td>
</tr>
<tr>
<td>PS/PP-P</td>
<td>6.6</td>
<td>0.998</td>
<td>1205</td>
</tr>
<tr>
<td>PS</td>
<td>2</td>
<td>1.02</td>
<td>4064</td>
</tr>
<tr>
<td>PS/GO</td>
<td>1.3</td>
<td>1.02</td>
<td>6252</td>
</tr>
<tr>
<td>PS/GOP</td>
<td>1.4</td>
<td>1.02</td>
<td>5805</td>
</tr>
</tbody>
</table>

For the materials considered here, the viscosity of phases and blends is significantly increased by GO sheets' presence, Table 7.7. It is expected since the addition of (nano)filler is generally shown to increase the viscosity of polymer melts via the polymer/surface interactions leading to the interphase formation in the vicinity of the filler.\textsuperscript{1,22,38-43} Higher filler's surface area and level of interaction cause a greater increase in the melt viscosity.
At relatively low filler content, the influence of nanofiller on the viscosity can be fitted to Einstein type equation:\(^\text{41, 43}\)

\[
\eta_r = 1 + [\eta] \phi + k([\eta] \phi)^2
\]  

(7.6)

where the relative viscosity, \(\eta_r\) is the ratio between viscosities of filled and neat polymer material, \(\phi\) is filler content, \([\eta]\) and \(k\) are apparent intrinsic viscosity and interaction constant, respectively. Stronger interaction between nanofiller and polymer is quantified by increasing \([\eta]\) and \(k\). Our data shows that GO and GOP interact differently with the polymers constituting the blends, where the highest relative viscosity of 2.2 is observed when GO is mixed with PP (\(\eta_r = \eta_{PP/GO} / \eta_{PP} = 2.2\)). Hence, GO interacts with PP macromolecules to a higher extent than with PS chains. This trend is not observed for GOP, where the level of interfacial interaction for both polymers is practically the same. We associate this observation with the shielding of the GO surface by the anchored POGL shell. It is necessary to point out that GO and GOP are interacting with PS to virtually the same extent.

The overall viscosity of an immiscible polymer blend depends on the viscosity of its components, phase morphology, and interfacial interactions, and can be approximated via log-additive rule:\(^\text{6, 44-45}\)

\[
\log (\eta) = \Sigma \phi_i \log(\eta_i)
\]  

(7.7)

where \(\phi_i\) and \(\eta_i\) are volume fraction and viscosity of component \(i\), respectively. The blends are characterized in four major categories: additive blends following Equation. 7.7, blends with positive or negative deviation from the log-additivity, and blends that exhibit both positive and negative deviations (typically when their phase structure changes). The
positive deviation is observed for the blends with strong interfacial interaction, while the opposite effect is observed when interactions are weak. We calculated viscosities for the blends using the log-additive rule, considering the volume fraction of the PS and PP phase 78% and 22%, respectively, Table 7.8. For all blends prepared, there is a negative deviation from the rule. The highest deviation is for the neat PS/PP blend. In fact, the PS/PP viscosity is only slightly higher than the viscosity of the low viscosity component, PP. This behavior was previously reported for PS/PP blends, where PS had a significantly higher viscosity than PP. Adding GO and GOP enhanced the blend viscosity significantly, which indicates the interfacial activity of the GO additives. GOP brings viscosity somewhat closer to the additive rule and, therefore, the sheets modified with POGL bottlebrush have the higher interfacial activity.

Table 7.8 Predicting viscosity of the blends based on Equation. 7.7.

<table>
<thead>
<tr>
<th>Material</th>
<th>Viscosity (Pa.s)</th>
<th>Predicted Viscosity (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/PP</td>
<td>657</td>
<td>2692</td>
</tr>
<tr>
<td>PS/PP-GO</td>
<td>1205</td>
<td>3198</td>
</tr>
<tr>
<td>PS/PP-GOP</td>
<td>1348</td>
<td>2854</td>
</tr>
<tr>
<td>PS-GO/PP</td>
<td>1019</td>
<td>3767</td>
</tr>
<tr>
<td>PS-GOP/PP</td>
<td>1473</td>
<td>3555</td>
</tr>
</tbody>
</table>

7.4.3. Morphology of PS/PP blends

Figure 7.6 shows the optical microscopy images of PS/PP, PS/PP-GO, PS/PP-GOP, PS-GO/PP, and PS-GOP/PP blends.
Figure 7.6 Optical microscopy images of a) PS/PP, b) PS/PP-GO, c) PS/PP-GOP, d) PS-GO/PP, and d) PS-GOP/PP blends.
As expected, the immiscibility of PS and PP results in phase separation, where one phase is continuous, and another phase is dispersed. The optical images show that the GOP nanosheets appear larger and less folded than unmodified GO. This observation confirms that the GOP has significantly lower interfacial tension with PP and PS than the unmodified GO.

Even though PP is a minority phase in these blends, it is not obvious that PP constitutes the dispersed phase. Here, the ratio between the melt viscosities of the blended polymers is an important factor to consider. Namely, in polymer/polymer mixture at a certain concentration of phase inversion, the dispersed phase becomes the matrix and vice versa.\textsuperscript{44-45} A number of models have been developed to approximate the phase inversion composition. These models have been applied to different polymer blend systems without leading to a universal rule since phase morphology found in polymer blends significantly depends on mixing time and conditions, interfacial modifiers, and the type of blenders/extruders used.\textsuperscript{47} In general, in the vicinity of phase inversion concentration, phase co-continuity can be observed as the volume fraction ($\varphi$) of minority low viscosity polymer is near the percolation threshold ($\varphi \approx 0.16$).\textsuperscript{44} The middle range of concentrations, at which phase co-continuity is found, can be roughly estimated, for instance, by Paul and Barlow empirical equation:\textsuperscript{48}

\begin{equation}
\varphi_{2\text{inv}} = \frac{1}{1 + \eta_1/\eta_2}
\end{equation}

where $\varphi_{2\text{inv}}$ is the volume fraction of blend's component 2 at the middle of the co-continuity region and $\eta_1$ and $\eta_2$ are the melt viscosities of components 1 and 2, respectively. We determined $\varphi_{2\text{inv}}$ for the polymer blends studied here, and the results are summarized in
Table 7.9. For all blends, but PS/PP-GO, $\phi_{2\text{inv}}$ is significantly lower than 0.22 (volume fraction of PP), indicating that PP should be the matrix and the highly viscous PS should form the dispersed phase.

Table 7.9 The calculated phase inversion points of PS/PP blends from Equation 7.8 based on PP volume fraction.

<table>
<thead>
<tr>
<th>Material</th>
<th>Inversion point ($\phi_{2\text{inv}}$) based on volume fraction of PP phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/PP</td>
<td>0.13</td>
</tr>
<tr>
<td>PS/PP-GO</td>
<td>0.25</td>
</tr>
<tr>
<td>PS/PP-GOP</td>
<td>0.17</td>
</tr>
<tr>
<td>PS-GO/PP</td>
<td>0.09</td>
</tr>
<tr>
<td>PS-GOP/PP</td>
<td>0.10</td>
</tr>
</tbody>
</table>

To investigate the morphology of the blends further, we conducted a solvent test. Specifically, we immersed the blend samples into toluene, a selective solvent for the PS phase. All tested samples were not disintegrated after the solvent extraction, indicating that the PP phase is continuous, Figure 7.7
The result suggests that in the case of PS/PP-GO, where calculated $\phi_{2\text{inv}}$ equals 0.26, a GO migration to the PS phase occurred. It appeared that the relocation raised the viscosity of the PS phase and reduced the viscosity of the PP phase, causing $\phi_{2\text{inv}}$ to be less than 0.22. In fact, the localization of GO in the PS dispersed phase can be observed in the optical microscopy images of the blends (Figure 7.6). Our thermodynamic estimations predicted this redistribution. The images of the PP phase that remained after the solvent extraction experiments provide additional information on the GO distribution. It is apparent that a significant number of GO sheets are still present in the PP phase. Since thermodynamic equilibrium cannot be reached during a short time of mixing in the extruder. Also, as indicated by the viscosity measurements, PP macromolecules actively interact with the GO surface, and adsorption of the macromolecules on the nanosheets can delay/prevent their
transfer into the PS phase. For the PS-GO/PP blend, significant migration of GO into PP was not observed (as predicted by the wetting coefficient). We also found that GOP migration from PP to PS (for PS/PP-GOP) and from PS to PP (for PS-GOP /PP) is more pronounced than the migration for the blends containing unmodified GO sheets. We associate this phenomenon with the ability of POGL chains to reorient and express their alkyl side chains in PP and their PEG side chains in PS.

**Measuring the inclusions’ size in the blends based on optical microscopy**

The dispersed PS phase's size is measured for 100 inclusions in each sample, and the size distributions are summarized in Figure 7.8 and Table 7.10.
Figure 7.8 Distribution of the PS inclusions’ size in the PS/PP blends obtained from optical microscopy images.

Table 7.10 Average PS inclusions’ size in the PS/PP blends obtained from optical microscopy images.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average inclusions’ diameter (µm) based on optical microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/PP</td>
<td>6.4</td>
</tr>
<tr>
<td>PS/PP-GO</td>
<td>4.3</td>
</tr>
<tr>
<td>PS/PP-GOP</td>
<td>5.4</td>
</tr>
<tr>
<td>PS-GO/PP</td>
<td>5.7</td>
</tr>
<tr>
<td>PS-GOP/PP</td>
<td>3.9</td>
</tr>
</tbody>
</table>
After comparing PS/PP blend and PS/PP/GO blends, it can be concluded that the size of these domains somewhat decreases in the presence of GO sheets. For polymer blend with dispersed morphology, the size of the dispersed phase is a function of the components content, their viscosity, and interfacial tension:\(^49\)

\[
d = \frac{4\gamma \left( \frac{\eta_d}{\eta_m} \right)^{0.84}}{G\eta_m} \text{ for } p > 1
\]

\[
d = \frac{4\gamma \left( \frac{\eta_d}{\eta_m} \right)^{(-0.84)}}{G\eta_m} \text{ for } p < 1
\]

(7.9)

where \(\gamma\) is interfacial tension, \(d\) is the number average particle diameter, \(G\) is the shear rate, \(\eta_m\) is the melt viscosity of the matrix, \(\eta_d\) is the melt viscosity of the dispersed phase, and \(p\) \((\eta_d/\eta_m)\) is the viscosity ratio. In our case \(p > 1\), thus with a decrease of \(\eta_d/\eta_m\), the size of the dispersed phase has to decrease if interfacial tension does not change. The data for \(\eta_d/\eta_m\) calculated based on the measured viscosities are presented in Table 7.11.

Table 7.11 The viscosity ratio of the dispersed (PS) phase to the matrix (PP) phase in PS/PP blends.

<table>
<thead>
<tr>
<th>Material</th>
<th>(\eta_d/\eta_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/PP</td>
<td>6.5</td>
</tr>
<tr>
<td>PS/PP-GO</td>
<td>3.0</td>
</tr>
<tr>
<td>PS/PP-GOP</td>
<td>5.0</td>
</tr>
<tr>
<td>PS-GO/PP</td>
<td>10.0</td>
</tr>
<tr>
<td>PS-GO/PP</td>
<td>9.3</td>
</tr>
</tbody>
</table>

The spreading/wetting coefficients (Table 7.6) predict that GO does not have a thermodynamic tendency to occupy the blend's interface. Therefore, it can be suggested initially that for PS/PP, PS-GO/PP, and PS/PP-GO, interfacial tension is close.
Accordingly, the smallest size for PS inclusions is observed for the PS/PP-GO blend having the smallest predicted value of $\eta_d / \eta_m$. The size of PS droplets in the PS-GO/PP blend has to be the largest because of the highest $\eta_d / \eta_m$ value. Nevertheless, the size of the inclusions in this case is somewhat smaller than that for the PS/PP material. Thus, as already indicated by the values of the blend viscosity, GO has certain interfacial activity in the blends. The formation of a transition zone at the PS/PP interface by GO sheets to decrease the thermodynamically unfavorable contacts can be in accordance with the "slim-fast mechanism" theory. The theory predicts that nanosheets have a specific ability to cover significant parts of the interface to effectively protect two opposing blend polymers from each other. It also can be suggested that, in the course of the melt mixing, selected GO sheets can adsorb PS chains on one side and PP chains on another side and attain the ability to decrease the interfacial tension in the system. GO has a nonhomogeneous surface where about half of the GO surface contains different types of C-O linkages, and the other half are C-C bonds. Thus, many non-oxidized areas on the GO surface have a higher affinity to PP macromolecules. Moreover, it has been found that a larger GO lateral size concludes in lower oxidation degrees. This implies that some large GO sheets might be non-polar enough to go to the PS/PP interface.

For investigating the blends containing modified nanosheets, Figure 7.8 and Table 7.10 show the size of the PS phase in PS-GOP/PP (~ 3.9 µm) and PS/PP-GOP (~ 5.4 µm) blends. As in the case of the blends containing virgin GO, the size of the PS domains does not correlate directly with the $\eta_d / \eta_m$ ratio (Table 7.11). Thus, according to Equation. 7.9, interfacial tension at PS/PP interface decreases significantly by the presence of GOP.
compared to PS/PP blends. The lowest interfacial tension value is for the PS-GOP/PP blend, where the nanosheets covered with POGL are premixed with the PS phase. Thus, as predicted by thermodynamical calculations, POGL material absorbed on GO nanosheets can rearrange at the interface, presenting a significant number of alkyl chains to the PP phase and PEG moieties to PS. Thus, during a limited time of the melt mixing, the rearrangement is the most efficient when GOP is premixed with PS. We associate this observation with (a) highly thermodynamically unfavorable PP/PEG contact ($\gamma = 12$ mN/m) in comparison to less unfavorable PS/alkyl contact ($\gamma = 6$ mN/m) and (b) highly thermodynamically favorable PP/alkyl contact ($\gamma = 0.4$ mN/m) in comparison to less favorable PS/PEG contact ($\gamma = 2.1$ mN/m), Table 7.5. Thus, it appears that the rearrangement for GOP located in the PS phase (presenting mainly the PEG moieties at the surface) is more efficient than that for the nanosheets situated in the PP phase (exhibiting mostly alkyl sub-chains to the boundary).

### 7.4.4. Differential Scanning Calorimetry of PS/PP blends

Figure 7.9 and Table 7.12 display DCS results for PS/PP, PS-GO/PP, PS-GOP/PP, PS/PP-GO, and PS/PP-GOP blends. Samples were first heated from -50 °C to 200 °C to remove their thermal history. There is no significant change in $T_g$ of PS and $T_c/T_m$ of PP for the blends compared to pure PS and PP, respectively. However, the distribution of the lamella thicknesses is wider, as indicated by broadening the melting peaks in the blends. The degree of crystallinity of PP in the PS/PP blend is $\sim 7\%$ higher than the one observed for pure PP, indicating that surface of PS droplets can serve as additional heterogeneous
nucleation sites. However, the addition of GO considerably reduced the degree of crystallinity of the PP phase. The crystallinity of PP-GO is about 4% less than pure PP, while this reduction of crystallinity from PS/PP to PS/PP/GO is about 10%. Thus, in the blend, GO sheets interfere with the spherulite growth.

The degree of crystallinity of PP in the PS-GOP/PP and PS/PP-GOP blend is lower than the one observed for the pure PP/PS blend. The decrease is higher for PS/PP-GOP (~20% decrease) than PS-GOP/PP (14% decrease). Based on the reduction of the degree of crystallinity of PP in the PS-GOP/PP and PS/PP-GOP blend, as for virgin GO-containing materials, the GOP nanosheets impede the spherulite growth. The effect on the degree of crystallinity is more pronounced when GOP is preblended with PP prior to the blend formation.

It is well established that the crystallization behavior of a crystallizable polymer in a polymer blend depends on the phase morphology of the material. To this end, Omonov et al. studied the crystallization of polypropylene in PS/PP blend as a function of the blend morphology.\textsuperscript{47} It was found that if PP is a continuous phase, the nucleation is heterogeneous, and Tc is close to the one observed for the pure PP. If PP forms a dispersed phase, the droplet volume limits the nucleation mode. The material demonstrates comparable crystallization peaks connected to heterogeneous nucleation and homogeneous nucleation at a much lower temperature (~ 76 °C in their study). In our case, we observed predominantly heterogeneous nucleation (Figure 7.9) since the major crystallization peak is close to the Tc of pure PP. We did observe a small peak of homogeneous nucleation at ~50°C. This result shows that some small amounts of PP can be located in PS droplets. For
GOP-containing materials, the extent of homogeneous nucleation is even lower than that for other PS/PP blends discussed in this work. Hence there is no significant amount of PP material inside PS droplets.

![Graph showing DSC measurements for PS/PP blends.]

Figure 7.9 Differential Scanning Calorimetry of PS/PP blends.

Table 7.12 Thermal properties of PP, PS, and PS/PP composites obtained from DSC measurements.

<table>
<thead>
<tr>
<th>sample</th>
<th>Tg of PS phase</th>
<th>melting of PP phase (second heating)</th>
<th>crystallinity of PP phase (cooling)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Tm</td>
<td>ΔHm (J/g)</td>
</tr>
<tr>
<td>PP</td>
<td>-</td>
<td>158</td>
<td>97</td>
</tr>
<tr>
<td>PP/GO</td>
<td>-</td>
<td>161</td>
<td>88</td>
</tr>
<tr>
<td>PP/GOP</td>
<td>-</td>
<td>160</td>
<td>71</td>
</tr>
<tr>
<td>PS/PP</td>
<td>103</td>
<td>155</td>
<td>21</td>
</tr>
<tr>
<td>PS/PP-GO</td>
<td>105</td>
<td>156</td>
<td>17</td>
</tr>
<tr>
<td>PS/PP-GOP</td>
<td>104</td>
<td>155</td>
<td>13</td>
</tr>
<tr>
<td>PS-GO/PP</td>
<td>103</td>
<td>156</td>
<td>17</td>
</tr>
<tr>
<td>PS-GOP/PP</td>
<td>103</td>
<td>157</td>
<td>16</td>
</tr>
<tr>
<td>PS</td>
<td>104</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PS/GO</td>
<td>104</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PS/GOP</td>
<td>103</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
7.4.5. Mechanical properties of PS/PP bends

To evaluate the mechanical properties of the materials studied here, we conducted a three-point bending flexural test, and the results obtained for the blends are summarized in Figure 7.10. Due to the thermodynamic immiscibility of PS and PP, PS/PP blends are expected to demonstrate negative deviation from an ideal mixing (additive) rule in terms of mechanical properties since the PS/PP blends interface acts as a mechanical defect.\textsuperscript{6-7, 9, 15} We report the influence of GO addition on mechanical properties in terms of comparing the mechanical behavior of PS/PP/GO with that of the uncompatibilized PS/PP blend.

The addition of GO to the PS/PP blend somewhat improves the values of flexural strength and strain. Adding GO to the PS phase prior to the blend formation increases the strength and strain by 9% and 16% compared to PS/PP material, respectively. Obviously, the same pattern is observed for the toughness, where PS-GO/PP blend toughness is 25% higher than the toughness of the PS/PP blend. The addition of GOP to the PS/PP blend definitely improves the strength and strain demonstrated by the blend. The highest flexural strength and strain among PS/PP, PS/PP/GO, and PS/PP/GOP materials are shown by PS-GOP/PP. Thus, the pre-blending of GOP with PS increases the strength and strain by 25% and 26% compared to PS/PP material, respectively. The toughness of PS-GOP/PP is 48% higher than the toughness of PS/PP material.

Our findings confirm the positive effect of GO on the affinity between PP and PS phases. Mechanical testing, along with the (above-mentioned) viscosity results, indicates significant localization of GO at the interface, which has a compatibilizing effect on the
PS/PP blend. The localization is more efficient when GO is premixed to the PS phase. In contrast to the observed results, the thermodynamical calculations showed that pristine GO would locate inside the PS phase. However, our calculations employ the notion of uniformity of GO surface. In reality, about half of the GO surface contains different types of C-O linkages, and the other half are C-C bonds, confirming that there is a notable amount of non-oxidized areas on GO that can be tending to the PP phase.

It is obvious that pre-localization of GOP in the PP phase does not offer the same level of improvement. As we compare all blends studied here in terms of mechanical properties in all categories, PS-GOP/PP material demonstrate the best mechanical characteristics (except for its flexural modulus).
After adding the virgin and with POGL modified GO sheets to PS/PP blend, we examined the impact of POGL addition on the mechanical properties of the blends, Figure 7.11. Specifically, 80PS/20PP/POGL weight parts blends were fabricated. The amount of POGL added was the same as was used to prepare PS/PP/GOP blends. The preceding experiment established that POGL is immiscible with PP and PS, Figure 7.12. We found that the order of POGL addition to the blend has a vital impact on the mechanical properties. When the bottlebrush is added to the PS phase prior to the blend fabrication, the presence of POGL
significantly decreases flexural modulus (~16%) and increases flexural strain (~21%) compared to the unmodified PS/PP blend. The POGL incorporation does not change the flexural strength. In the case of the bottlebrush premixing with the PP phase, the mechanical behavior of the PS/PP blend is entirely different. The modulus does not change, while the strength and strain significantly increase. Namely, the strength and strain increase by ~16% and ~43%. The obtained results indicated that POGL is capable of modifying PS/PP interface and, to a certain extent, compatibilize the blend. The localization of POGL at the interface was also corroborated by the decrease of the average size of PS inclusions in the presence of POGL from ~6.4 to ~5 micrometers, Table 7.13 and Figure 7.13. Interestingly, the size of the PS droplets is not dependent on the order of the bottlebrush addition.

The strong dependence of the mechanical properties on the premixing order indicates that the molecular bottlebrush adopts different interfacial conformations depending on the order. We associate this phenomenon with the dissimilarity in macromolecules’ initial conformation in the PS and PP materials prior to the blend fabrication. Based on the thermodynamical affinity signified by the interfacial tension (Table 7.5), the alkyl sub-chains of the LMA monomeric units are exposed at the POGL/PP interface in the PP phase. In the PS phase, PEG sub-chains occupy the POGL/PS interface. When PS is mixed with PP, the lowest energy conformation for POGL at the interface is when the alkyl sub-chains are exposed to the PP phase, while the PEG sub-chains protrude into the PS phase. We suggest that the reorientation of POGL during rapid (non-equilibrium) melt mixing is more efficient from the PP phase. Indeed, given that LMA is a minority component, PEG sub-
chains of OEGMA (majority component) can promptly reach the PS phase during the mixing. While in the PS phase, where POGL/PS interface is occupied with the PEG sub-chains, it is more changing for the alkyl sub-chains to reach the PP/PS interface.

![Bar chart showing mechanical properties of PS/PP, PS/PP-POGL, and PS-POGL/PP blends.](image)

Figure 7.11 Mechanical properties of PS/PP, PS/PP-POGL, and PS-POGL/PP blends.
Figure 7.12 Optical microscopy images of a) PS/PP-POGL, and b)PS-POGL/PP at 100x magnification.

Figure 7.13 Size of PS inclusions in PS/PP, PS/PP-POGL, and PS-POGL/PP blends.
Table 7.13 Average PS inclusions' size in the PS/PP and PS/PP/POGL blends obtained from optical microscopy images.

<table>
<thead>
<tr>
<th>sample</th>
<th>Average inclusions’ diameter (m) based on optical microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/PP</td>
<td>6.4</td>
</tr>
<tr>
<td>PS/PP-POGL</td>
<td>5.0</td>
</tr>
<tr>
<td>PS-POGL/PP</td>
<td>5.0</td>
</tr>
</tbody>
</table>

7.6. Conclusions

- The PS/PP/GO blend composites were fabricated through a combination of solution mixing and melt processing methods. In the materials' processing stage, GO was either premixed with PS or with PP.
- Adding 0.5wt.%GO to PS reduces its ductility. The copolymer nano shell shields the GO plates from the PS matrix, resulting in higher ductility of PS/GOP than PS/GO.
- If the GO sheets are added to PS/PP blend, they will not spread over the PP/PS interface and prefer to be situated in the PS phase.
- Thermodynamic calculations show that modification of GO with POGL macromolecules can alter the preferred localization of GO and make them populate the PP/PS interface.
- Adding GO and GOP enhanced the blend viscosity significantly, which indicates the interfacial activity of the GO additives. GOP brings viscosity somewhat closer
to the additive rule and, therefore, the sheets modified with POGL bottlebrush have the higher interfacial activity with the host matrices.

- PP and PS phases are immiscible, and the low viscosity PP phase constructs the continuous phase despite its lower concentration.

- Adding GO to the blend somewhat improved the flexural strength and strain to the maximum compared to PS/PP. The addition of GOP has a higher positive effect. Comparing all the blends studied here, PS-GOP/PP material demonstrate the best mechanical characteristics (except for its flexural modulus).

- POGL is capable of modifying PS/PP interface and, to a certain extent, compatibilize the blend. The localization of POGL at the PS/PP interface was corroborated by the decrease of the average size of PS inclusions in the presence of POGL.

7.7. References


CHAPTER 8: CONCLUSIONS

This chapter is devoted to the concluding body of work presented in this dissertation. The study of graphene oxide-thermoplastic nanocomposites resulted in a number of observations about these materials. The following major conclusions can be drawn:

- GO sheets can be modified with copolymer molecules to boost the dispersion and adhesion of the filler in the matrix.
- Pristine and modified GO nanoplates can be introduced to PP fibers from a water environment.
- Polymer/GO composites could be fabricated through a combination of solution mixing and melt mixing processes.
- GO and GOP sheets did not reduce the thermal and mechanical properties of the composites.
- The weak interface between the 3D printed PP layers causes the reduction of mechanical strength.
- PP-GO composites could absorb microwave, and GOP sheets are better microwave absorbers than neat GO sheets.
- Microwave heat-able composites can be degraded for recycling.
- Polymeric parts can be welded using microwave-absorbing polymer composites.
- GO and GOP can act as a compatibilizer and elevate the mechanical properties of the PS/PP blends.
• Modification of GO with POGL macromolecules can alter the preferred localization of GO and make them populate the PP/PS interface.
MAJOR ACCOMPLISHMENTS

In the course of this study, it was:

✓ Developed methodology for fabrication and characterization of polypropylene materials containing graphene oxide sheets modified with bottlebrush copolymers.

✓ Uncovered structure-property relationships in the polypropylene materials containing graphene oxide sheets modified with bottlebrush copolymers.

✓ Proposed and realized strategy for obtaining polymer/graphene oxide nanocomposites with added functionality without deteriorating properties of polypropylene matrix.

✓ Demonstrated employment of the functional nanocomposites as microwave absorbing materials to weld and un-weld polymeric parts.

✓ Developed strategy for compatibilization of immiscible polystyrene/polypropylene blends using modified graphene oxide sheets.
FUTURE WORKS

The following future work is proposed:

- Investigating the microwave-materials interactions and measuring the electromagnetic wave transmission of samples in different frequencies.
- Applying the developed nanocomposite fabrication method for fabricating functional composites using other than polypropylene thermoplastic matrices.
- Exploiting nanomaterials of different geometries (e.g. carbon particles, carbon nanotubes, and short carbon fiber) to obtain functional composites.
APPENDIX

TEXTILE FUNCTIONALIZING USING NANOCELLULOSIC FIBERS

Introduction

We developed a fabric modification technique in collaboration with the laboratory of Professor S. Minko at the University of Georgia, using cellulose nanofibrils (CNF). This green, inexpensive, and facile method introduces functional agents to the surface of fabrics using nanocellulose fibrils. In essence, CNF are composed of cellulose fibers in an amorphous nanostructured form. The large number of oxygen and hydroxyl groups of CNF and its high surface area provide an excellent floor for new functional groups' attachment. Using this property of CNF, we have used them as a carrier to dye different kinds of fabrics.

\[ \text{Chemical structure of cellulose.} \]

From a practical point of view, our process has been designed to be readily scalable and transferable between different fabrics and to consist of a small number of technological steps. We target a fabrication method where chemical processes and fabric modification are
separated in space and time; thus, the conditions for the chemical reactions are no longer restrained by the substrate and chemical proficiency of the operator.

Figure A.2 Scheme of using CNF to introduce functional agents to the fabrics

In this method, the aqueous mixture of the dye and CNF is prepared first, then applied to the fabrics through conventional dying techniques. We first examined the efficiency of this method to dye cotton fabric and have done extensive investigations to understand the effect of CNF, dye, and copolymers on its stiffness and color. Then, four more fabrics, including cotton, non-woven polypropylene, spun polypropylene, polyester, and nylon, were treated with this method. Finally, non-woven polypropylene has been selected to investigate the effect of CNF on the properties of the fabric.
Part1: Cotton fabric

Experimental

Materials:

The following solutions were used as the functionalizing agents:

Cellulose: 9wt.% CNF, 108662

Blue cellulose: 2wt.% CNF+ Everzol Blue BRF 150%: R34738517

Yellow cellulose: 2wt.% CNF+ Everzol Yellow 3RS H/C: R3436621

Red cellulose: 2wt.% CNF+ Everzol Red 3 BS H/C: R3329503

The colored cellulose samples were prepared at Professor S. Minko’s laboratory.

The fabrics used for this part of the research included:

Fabric 1 - 100% Cotton woven,

400M, item No: 1403002

Approximate weight: 3.21 ounces/yard²

Fabric 2- 100% Cotton knit interlock

Bleached, 24 cut interlock from 40/1 yarn

Fabric 3- 100% Cotton woven

Bleached and mercerized

3x1 twill 110 X 53 and ends X Pics
Fabric cleaning:

Fabrics were cut and immersed in chloroform, methanol, and acetone for 10 minutes on an orbital shaker. Then, they were dried with nitrogen stream.

Immersing fabrics in solution:

For all samples, the immersion time of fabric in solution was 15 hours on the orbital shaker with a rate of 3 rpm.

Drying fabrics:

Fabrics were removed from the solutions. The excess solution was removed from the fabrics by three times passing through the squeegee machine (rate: 2 rpm, pressure: 30 bar). After that, the fabrics were dried at 60°C for 15 min and 120°C for 60 min in an air convection oven. Dried samples were exposed to standard ambient conditions for one overnight. The thermal dye fixation step is necessary to accelerate and stabilize the diffusion of the dye into the fabric matrix.

![Thermal Curing Graph](image)

Figure A.3 Thermal curing of the treated fabrics.
**Stiffness test:**

For stiffness measurements, each sample was cut into three 20.5 cm×2.5 cm pieces, and for each piece, measurements were done four times using a Shirley Stiffness Tester. The test was done according to ASTM D1388-96 test method (cantilever option).

![Stiffness Test](image)

Figure A.4 Measuring stiffness of the fabrics.

**Colorfastness test:**

The test was done according to AATCC TM61-1996: The machine's temperature was adjusted at 40°C. Detergent (0.37 wt. %Detergent WOB, 1993 +200 ml water) and 10 steel balls were added to the canister. After 2 min of preheating the canisters, 5cm×10cm fabrics were added to the canisters, and holders rotated at a rate of 40 rpm for 45 min. Then, the samples were rinsed three times in DI water at 40 for 1 min. Pad rollers pushed the excess water, and fabrics were dried in an air oven at 70 for 15 min. Each period of this test approximates five typical hand or home launderings.
Results and discussion:

i) Colorless samples

Pure CNF:

In order to measure the effect of CNF on the stiffness of the fabrics, all three types of fabrics were soaked in different concentrations (0.125wt.%, 0.25wt.%, 0.5wt.%, 1wt.%) of nano fibrillated cellulose (CNF), and the stiffness test was done. Three pieces of each sample were tested. The reported numbers are an average of 12 measurements.

The stiffness of the original fabric 1 was 2.85 cm, while for the dried fabric 1, it was 5.75 cm. So, we could see that the procedure will increase the stiffness.

Table A.1 Effect of CNF concentration on stiffness of fabrics.

<table>
<thead>
<tr>
<th>CNF Concentration (wt. %)</th>
<th>Stiffness of fabric 1 (cm)</th>
<th>Stiffness of fabric2 (cm)</th>
<th>Stiffness of fabric3 (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.75</td>
<td>4.48</td>
<td>5.71</td>
</tr>
<tr>
<td>0.125</td>
<td>5.99</td>
<td>5.67</td>
<td>5.87</td>
</tr>
<tr>
<td>0.25</td>
<td>6.08</td>
<td>7.40</td>
<td>8.15</td>
</tr>
<tr>
<td>0.5</td>
<td>6.95</td>
<td>8.25</td>
<td>6.46</td>
</tr>
<tr>
<td>1</td>
<td>6.74</td>
<td>5.13</td>
<td>7.69</td>
</tr>
</tbody>
</table>
Figure A.5 Effect of CNF concentration on stiffness of fabrics.
It is observed that the stiffness is increased after the addition of CNF, but the trend is not the same for all samples.

**CNF modified with polymer:**

Results showed that the stiffness of fabrics increases after the addition of CNF, which can be attributed to the addition of the high-modulus nano cellulose fibers to fabrics and increased friction between interwoven fibers. To address this challenge, we have used molecular bottlebrush reactive copolymer additives such as poly(Oligo Ethylene Glycol methyl ether Methacrylate- Glycidyl Methacrylate- Lauryl Methacrylate) (P1) and poly(Oligo Ethylene Glycol methyl ether Methacrylate- Glycidyl Methacrylate) (P2). If these bottle brush copolymers could decrease the friction between CNF and the fabric, the stiffness of the CNF-dye treated fabric would decrease.

We examined two methods of using polymers to color the fabrics: Method 1) the dye and CNF were mixed and applied. Then, fabrics were immersed in 1wt. % polymer solution (immersion method). Method 2) The dye and CNF and 1wt. % polymer solution were mixed and applied to the fabrics (mixing method).
As the first step, one piece of each fabric was soaked in 1wt. % solution of POEGMA-GMA-LMA for 15 hours. The stiffness test was done after drying. Measurements showed that the amounts of CNF up-take by the fabric for 0.25 wt.% and 1wt.% solutions are about 0.5 % and 2 %, respectively, and for the 1wt. % solution of polymer, the up-take amount is about 2nwt.%.
Figure A.7 Effect of immersion of fabrics in polymer 1 on stiffness.
It can be seen that the stiffness of all fabrics is decreased after immersion in polymer 1.

Table A.2 Change in stiffness of fabrics after immersion in polymer 1.

<table>
<thead>
<tr>
<th>CNF concentration (wt. %)</th>
<th>fabric 1</th>
<th>fabric2</th>
<th>fabric3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.90</td>
<td>0.68</td>
<td>0.55</td>
</tr>
<tr>
<td>0.125</td>
<td>1.13</td>
<td>1.05</td>
<td>0.63</td>
</tr>
<tr>
<td>0.25</td>
<td>0.85</td>
<td>1.63</td>
<td>1.88</td>
</tr>
<tr>
<td>0.5</td>
<td>2.00</td>
<td>1.55</td>
<td>1.25</td>
</tr>
<tr>
<td>1</td>
<td>1.40</td>
<td>0.85</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Therefore, the experiments were narrowed down to two concentrations (0.25wt. % and 1wt. %) for fabric 1. The concentration of polymers was kept 1wt. %.

Four methods of using polymers, including immersion of treated fabrics in polymer 1, immersion of treated fabrics in polymer 2, immersion of non-treated fabrics in a mixture of CNF+ polymer 1, and immersion of non-treated fabrics in a mixture of CNF+ polymer 2 were used for one piece of each sample.
Table A.3 Effect of using polymer on stiffness of fabric 1.

<table>
<thead>
<tr>
<th>CNF wt. %</th>
<th>Fabric 1+CNF</th>
<th>Fabric 1+CNF, soaked in polymer 1</th>
<th>Fabric 1 + (CNF mixed with polymer 1)</th>
<th>Fabric 1+CNF, soaked in polymer 2</th>
<th>Fabric 1+(CNF mixed with polymer 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>5.8</td>
<td>4.95</td>
<td>4.22</td>
<td>4.83</td>
<td>4.41</td>
</tr>
<tr>
<td>1</td>
<td>6.55</td>
<td>5.15</td>
<td>5.37</td>
<td>5.25</td>
<td>6.41</td>
</tr>
</tbody>
</table>

It can be seen that polymers reduce the stiffness of fabrics. For 0.25 wt.%, mixing CNF and polymers shows a higher improvement, and both polymers show the same amount of reduction in stiffness. While for 1 wt.% sample, immersion in polymers has a better effect, and polymer 1 has higher efficiency.
Figure A.8 the effect of using polymer on stiffness of fabric 1.

ii) Colored samples

Pure red CNF:

In the next step, dyed CNF was used to see how CNF works for colored samples. Fabric 1 was soaked in red-dyed CNF solution, and the results were compared with fabric 1 soaked in pure CNF solution.
**Stiffness:**

It is observed that there is no significant change in stiffness by using the red CNF.

Table A.4 comparing the stiffness of fabric 1 modified by CNF and red CNF.

<table>
<thead>
<tr>
<th>Concentration (wt. %)</th>
<th>Stiffness of fabric with pure nanocellulose (cm)</th>
<th>Stiffness of fabric with red dyed nanocellulose (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.75</td>
<td>5.75</td>
</tr>
<tr>
<td>0.125</td>
<td>5.99</td>
<td>5.32</td>
</tr>
<tr>
<td>0.25</td>
<td>6.08</td>
<td>5.92</td>
</tr>
<tr>
<td>0.5</td>
<td>6.95</td>
<td>7.05</td>
</tr>
<tr>
<td>1</td>
<td>6.74</td>
<td>6.62</td>
</tr>
</tbody>
</table>

Figure A.9 Comparing the stiffness of fabric modified by CNF and red CNF.
-Color measurements:

In order to see the effect of the concentration of red CNF on the color of fabrics, color spectrometry measurements were done for each concentration. The numbers reported for each concentration are an average of 30 numbers.

Table A.5 Change in color of samples with concentration of red CNF.

<table>
<thead>
<tr>
<th>red CNF concentration (wt.%)</th>
<th>L*: white</th>
<th>a*(+a*: red, -a*: green)</th>
<th>b*(+b*: yellow, -b*: blue)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>47.59±0.40</td>
<td>48.36±0.71</td>
<td>-10.53±0.27</td>
</tr>
<tr>
<td>0.25</td>
<td>39.87±0.36</td>
<td>51.91±0.62</td>
<td>-4.88±0.51</td>
</tr>
<tr>
<td>0.5</td>
<td>34.50±0.26</td>
<td>50.46±0.63</td>
<td>2.22±0.51</td>
</tr>
<tr>
<td>1</td>
<td>30.39±0.41</td>
<td>46.58±0.54</td>
<td>8.03±0.51</td>
</tr>
</tbody>
</table>

Figure A.10 Change in color of samples with concentration of red CNF.
It is observed that the color is almost homogenous for each concentration, and there is no considerable difference across the sample.

The whiteness decreases as the concentration increases, and the hue goes from blue to yellow. The amount of redness decreases after a slight increase.

Figure A.12 shows that the absorbance of fabric with higher concentrations is more than that of lower concentrations. Therefore, a darker color is observed.
Table A.6 The visible spectrum: wavelengths and colors

<table>
<thead>
<tr>
<th>color</th>
<th>wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Violet</td>
<td>380–450 nm</td>
</tr>
<tr>
<td>Blue</td>
<td>450–495 nm</td>
</tr>
<tr>
<td>Green</td>
<td>495–570 nm</td>
</tr>
<tr>
<td>Yellow</td>
<td>570–590 nm</td>
</tr>
<tr>
<td>Orange</td>
<td>590–620 nm</td>
</tr>
<tr>
<td>Red</td>
<td>620–750 nm</td>
</tr>
</tbody>
</table>
Figure A.12 Change in a) absorbance and b) reflectance of fabric 1 with concentration of red CNF.
- **Colorfastness:**

To investigate dye fixation and color retention, the colorfastness test was done. Colorfastness to laundering test was done for fabrics with four different concentrations of red-dyed cellulose to see how the color changes after washing the fabrics. Then, color spectrometry measurements were done for washed samples. The numbers reported for each concentration are an average of 10 numbers.

Table A.7 color of washed samples with concentration of red CNF.

<table>
<thead>
<tr>
<th>concentration</th>
<th>L*: white</th>
<th>a*(+a*: red, -a*: green)</th>
<th>b*(+b*: yellow, -b*: blue)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>55.92±0.27</td>
<td>40.35±0.74</td>
<td>-11.87±0.08</td>
</tr>
<tr>
<td>0.25</td>
<td>47.22±0.27</td>
<td>50.92±0.86</td>
<td>-8.64±0.30</td>
</tr>
<tr>
<td>0.5</td>
<td>41.33±0.27</td>
<td>54.31±0.63</td>
<td>-2.56±0.91</td>
</tr>
<tr>
<td>1</td>
<td>37.60±0.31</td>
<td>54.81±0.37</td>
<td>3.20±0.55</td>
</tr>
</tbody>
</table>
Figure A.13 Change in color of washed samples with concentration of red CNF (w stands for washed fabrics).
Figure A.14 comparing Color of fabric 1 with different concentrations of red CNF, a) 0.125wt. %, b) 0.25wt. %, c) 0.5wt. %, d) 1wt. %. First row: before washing, second row: after washing.
Figure A.15 Change in a) absorbance and b) reflectance of washed fabric 1 with concentration of red CNF.
The results show that after washing, the whiteness of samples is increased. Also, the absorbance area is decreased, meaning that washed fabrics show lighter colors.

![Graph showing the effect of washing on the area under the absorbance peak.](image)

**Figure A.16** Effect of washing of fabrics on the area under the absorbance peak.

**Red CNF modified with polymer**

**-Stiffness:**

As mentioned before for colorless samples, two types of polymers were used to improve the fabrics' stiffness and color stability properties. The methods of using polymers for red CNF were the same as the methods used for neat CNF.

First, one piece of fabric 1 was soaked in 1 wt.% solution of POEGMA-GMA-LMA for 15 hours. The stiffness test was done after drying.
Figure A.17 Effect of soaking fabric 1 in polymer 1 on its stiffness.

It can be seen that the stiffness of samples is decreased after using the polymer solution.

Then, two concentrations (0.25wt. % and 1wt. %) of red CNF were selected. The concentration of polymers was kept 1wt. %. Again, our methods of using polymers, including immersion of treated fabrics in polymer 1, immersion of treated fabrics in polymer 2, immersion of non-treated fabrics in mixture of CNF+ polymer 1, and immersion of non-treated fabrics in mixture of CNF+ polymer 2, were used for one piece of each sample.
Table A.8 Effect of using polymer on stiffness of fabric 1 modified with red CNF.

<table>
<thead>
<tr>
<th>Red CNF wt. %</th>
<th>fabric 1 + red CNF</th>
<th>fabric 1 + red CNF, soaked in polymer 1</th>
<th>fabric 1+(red CNF mixed with polymer 1)</th>
<th>fabric 1+red CNF, soaked in polymer 2</th>
<th>Fabric2+(red CNF mixed with polymer 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>5.975</td>
<td>5.075</td>
<td>4.017</td>
<td>4.775</td>
<td>4.283</td>
</tr>
<tr>
<td>1</td>
<td>6.9</td>
<td>5.6</td>
<td>4.258</td>
<td>4.9</td>
<td>4.433</td>
</tr>
</tbody>
</table>

Figure A.18 Effect of using polymer on stiffness of fabric 1 modified with red CNF.
The results showed that polymers reduce stiffness. Polymer 2 has a better effect than polymer 1, and mixing red CNF with polymer shows a higher reduction in the stiffness of the fabrics.

-Color measurements:

To investigate the color stability of fabrics after using the polymers, i-color measurements were done for the following samples.

1- Four pieces of fabric 1 were soaked in four different concentrations of red CNF.

2- Four pieces of fabric 1 were soaked in four different concentrations of red CNF, and then samples were washed (colorfastness test).

3- Four pieces of fabric 1 were soaked in four different concentrations of red CNF, and then samples were soaked in polymer 1 (1wt. % PEGMA-GMA-LMA). After that, they were washed (colorfastness test).
Figure A.19 Comparing whiteness of washed fabric 1 before and after immersion in polymer 1.

Obviously, the color of samples soaked in the polymer mixture is lower than previous samples because they would lose some amount of their color during the following processes.

Four methods of using polymer were investigated, and the color of samples after washing was compared.
Table A.9 Effect of using polymers on colorfastness of fabrics.

<table>
<thead>
<tr>
<th>concentration wt. %</th>
<th>color</th>
<th>red fabric</th>
<th>red fabric - washed</th>
<th>red fabric soaked in polymer 1</th>
<th>red fabric soaked in polymer 1 - washed</th>
<th>red fabric mixed with polymer 1</th>
<th>red fabric mixed with polymer 1 - washed</th>
<th>red fabric soaked in polymer 2</th>
<th>red fabric mixed with polymer 2</th>
<th>red fabric mixed with polymer 2 - washed</th>
<th>red fabric mixed with polymer 2 - washed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>L*</td>
<td>39.87</td>
<td>47.22</td>
<td>46.23</td>
<td>48.74</td>
<td>51.77</td>
<td>61.83</td>
<td>46.24</td>
<td>47.98</td>
<td>50.91</td>
<td>60.62</td>
</tr>
<tr>
<td></td>
<td>a*</td>
<td>51.91</td>
<td>50.92</td>
<td>50.56</td>
<td>49.94</td>
<td>41.42</td>
<td>32.63</td>
<td>49.80</td>
<td>50.37</td>
<td>42.35</td>
<td>33.48</td>
</tr>
<tr>
<td>1</td>
<td>L*</td>
<td>30.39</td>
<td>37.60</td>
<td>36.48</td>
<td>38.28</td>
<td>35.99</td>
<td>43.93</td>
<td>36.29</td>
<td>37.97</td>
<td>34.59</td>
<td>43.10</td>
</tr>
<tr>
<td></td>
<td>a*</td>
<td>46.58</td>
<td>54.81</td>
<td>53.74</td>
<td>55.50</td>
<td>50.92</td>
<td>53.53</td>
<td>53.74</td>
<td>54.71</td>
<td>50.39</td>
<td>54.04</td>
</tr>
<tr>
<td></td>
<td>b*</td>
<td>8.03F</td>
<td>3.20</td>
<td>2.82</td>
<td>2.26</td>
<td>-0.67</td>
<td>-5.61</td>
<td>2.92</td>
<td>2.51</td>
<td>1.04</td>
<td>-4.88</td>
</tr>
</tbody>
</table>
Based on the numbers for the whiteness of samples, it is observed that soaking has a better effect than mixing. But no significant difference can be seen between the two types of polymers.
Further washing:

To reach a stable color of the fabrics, the colored fabrics were washed for the second and third time, which each time of colorfastness test resembles five times of domestic laundring. The lightness of the fabrics was compared.

Table A.10 Color of samples after each wash.

<table>
<thead>
<tr>
<th>CNF concentration (wt. %)</th>
<th>sample</th>
<th>lightness L* - 1th wash</th>
<th>lightness L* - 2nd wash</th>
<th>lightness L* - 3rd wash</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>non treated red fabric</td>
<td>39.87</td>
<td>47.22</td>
<td>48.49</td>
</tr>
<tr>
<td></td>
<td>soaked in polymer 1</td>
<td>46.23</td>
<td>48.74</td>
<td>49.00</td>
</tr>
<tr>
<td></td>
<td>soaked in polymer 2</td>
<td>46.24</td>
<td>47.98</td>
<td>48.62</td>
</tr>
<tr>
<td></td>
<td>mixed with polymer 1</td>
<td>51.77</td>
<td>61.83</td>
<td>63.24</td>
</tr>
<tr>
<td></td>
<td>mixed with polymer 2</td>
<td>50.91</td>
<td>60.62</td>
<td>62.13</td>
</tr>
<tr>
<td>1</td>
<td>non treated red fabric</td>
<td>30.39</td>
<td>37.60</td>
<td>37.98</td>
</tr>
<tr>
<td></td>
<td>soaked in polymer 1</td>
<td>36.48</td>
<td>38.28</td>
<td>38.58</td>
</tr>
<tr>
<td></td>
<td>soaked in polymer 2</td>
<td>36.29</td>
<td>37.97</td>
<td>38.55</td>
</tr>
<tr>
<td></td>
<td>mixed with polymer 1</td>
<td>35.99</td>
<td>43.93</td>
<td>44.84</td>
</tr>
<tr>
<td></td>
<td>mixed with polymer 2</td>
<td>34.59</td>
<td>43.10</td>
<td>44.45</td>
</tr>
</tbody>
</table>
Since samples modified with 1wt. % red CNF are more sensitive to washes; the corresponding numbers are presented in the following graph.

Figure A.21 Color of 1wt. %CNF samples after each wash.

It can be concluded that both copolymers positively affect the color stability of the modified fabrics, and the change of whiteness of fabrics colored with dyed-CNCF is more than that of fabrics colored with dyed-CNCF and then immersed in the polymer solution.

To better understand the effect of washing on color loss, subsequent centrifuges were done for the red-dyed solution. Red dyed CNF was centrifuged 13 times (time: 10 min, rate:
10,000 rpm). The solution was pipetted out each time, and the deposition was mixed with DI water and dispersed again. The color of each solution was pictured, then the gray value of these colors was measured using Image-J software, and the mean gray value versus the number of solutions was plotted.

![Graph showing mean gray value of centrifuged solutions of red CNF.](image)

**Figure A.22** Mean gray value of centrifuged solutions of red CNF.

It is observed that, after 8 times of centrifuging, the color of the solution almost remains constant, which is about two times of the colorfastness test. This finding can confirm the result of the second and third wash of fabrics.

Altogether, it can be said that immersing prepared fabrics (modified with CNF) in polymer solutions is better than mixing polymer and CNF. Also, it was observed that stiffness is decreased using the polymers. So, based on all gained results, we may conclude that it is
better to mix the dye and CNF and apply the solution to the fabrics. Then, immerse fabrics in a polymer solution. For this purpose, we selected polymer 1, OEGMA-GMA-LMA.

**iii) Using more dyed CNF solutions**

Three pieces of fabrics were cut and immersed in three different 1wt.% solutions of CNF +dye, including red, blue, and yellow dyes. After 15 hr, samples were dried, and i-color measurement and stiffens test were done. Then, the fabrics were immersed in a 1wt.% solution of OEGMA-GMA-LMA in water for 15 hours and were dried and tested again.

To remove unattached dyes, fabrics were immersed in DI water for 1 hour, then dried at T=70°C for 15min. Then i-color measurement was done for the samples.

Table A.11 Effect of using polymer on the stiffness of samples.

<table>
<thead>
<tr>
<th>color</th>
<th>condition</th>
<th>stiffness</th>
</tr>
</thead>
<tbody>
<tr>
<td>red</td>
<td>original</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>immersed in polymer</td>
<td>5.6</td>
</tr>
<tr>
<td>yellow</td>
<td>original</td>
<td>5.325</td>
</tr>
<tr>
<td></td>
<td>immersed in polymer</td>
<td>5.325</td>
</tr>
<tr>
<td>blue</td>
<td>original</td>
<td>4.825</td>
</tr>
<tr>
<td></td>
<td>immersed in polymer</td>
<td>4.525</td>
</tr>
</tbody>
</table>
Figure A.23 Effect of using polymer on the stiffness of samples.

Table A.12 Effect of using polymer and washing on color of samples.

<table>
<thead>
<tr>
<th>color</th>
<th>condition</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>red</td>
<td>original</td>
<td>31.46 ± 0.36</td>
<td>46.98 ± 0.51</td>
<td>6.66 ± 0.44</td>
</tr>
<tr>
<td></td>
<td>immersed in polymer</td>
<td>37.59 ± 0.37</td>
<td>53.76 ± 0.63</td>
<td>1.70 ±0.56</td>
</tr>
<tr>
<td></td>
<td>washed</td>
<td>38.82 ± 0.33</td>
<td>54.93 ± 0.73</td>
<td>1.86 ± 0.61</td>
</tr>
<tr>
<td>yellow</td>
<td>original</td>
<td>59.59 ± 0.78</td>
<td>32.28 ± 1.92</td>
<td>64.46 ± 0.99</td>
</tr>
<tr>
<td></td>
<td>immersed in polymer</td>
<td>64.13± 0.83</td>
<td>25.50 ± 1.75</td>
<td>66.35 ± 1.25</td>
</tr>
<tr>
<td></td>
<td>washed</td>
<td>64.70±0.79</td>
<td>24.61 ± 1.61</td>
<td>66.41 ±1.10</td>
</tr>
<tr>
<td>blue</td>
<td>original</td>
<td>31.69 ± 0.51</td>
<td>1.07 ± 0.32</td>
<td>-29.12 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>immersed in polymer</td>
<td>42.11± 1.40</td>
<td>-2.50± 0.58</td>
<td>-29.04 ± 0.57</td>
</tr>
<tr>
<td></td>
<td>washed</td>
<td>43.30 ± 1.45</td>
<td>-2.764 ± 0.52</td>
<td>-28.55± 0.57</td>
</tr>
</tbody>
</table>
It can be concluded that after immersion in polymer, the amount of color reduction through a typical washing is not significant.

**Conclusions:**

- The stiffness of fabrics is increased after the addition of CNF, but the trend is not the same for all samples.
- OEGMA-GMA-LMA and OEGMA-GMA polymers reduce the stiffness of fabrics. Immersion of CNF-treated fabrics in polymer solutions (immersion method) has a
better effect than immersion of non-treated fabrics in CNF+polymer solutions (mixing method). Polymer 1 has a higher impact than polymer 2.

- There is no significant change in stiffness by using the red CNF.
- The fabric's color is almost homogenous for each concentration of red CNF, and there is no vast difference across the sample.
- The amount of whiteness decreases as the concentration of red CNF increases.
- After washing the fabrics, the whiteness of the samples is increased.
- OEGMA-GMA-LMA and OEGMA-GMA polymers positively affect the color stability of fabrics. Immersion has a higher effect than mixing, but no significant difference can be seen between the two types of polymers.
- After 8 times of centrifuging, the color of the red CNF solution almost remains constant, which is about two times of the colorfastness test.
- It may be concluded that it is better to mix the dye and CNF and apply the solution to the fabrics. Then, immerse the fabrics in a polymer solution. For this purpose, we selected polymer 1, OEGMA-GMA-LMA.
Part 2: Applying the technique to dye fabrics from synthetic fibers

Introduction

In the next step, knowing that this dying technique works for cotton, we first examined the efficiency of the method mentioned above to dye four types of fabrics, including non-woven polypropylene, spun polypropylene, polyester, and nylon. Then, non-woven polypropylene has been selected to investigate the effect of CNF on the properties of the fabric.

Experiments

Non-woven polypropylene, spun polypropylene, polyester, and nylon fabrics were dyed using the dyed CNF in which the nanofibers were performing as the dye carriers. Like the previous experiments, fabrics were immersed in different concentrations of aqueous CNF solutions for 15 hours, pressed using a squeegee machine three times under a pressure of 30 bars to push out the excess solution, and then dried at 60°C for 15 minutes and 120°C for 60 minutes.

Results and discussions

- Color measurement:

The color measurements before and after washing the dyed fabrics indicated that only nylon could be efficiently colored by CNF. The poor dyeability and the low color stability of non-woven polypropylene spun polypropylene and polyester were attributed to their hydrophobicity.
The color of fabrics dyed with different concentrations of dyed-CNF was measured. As measurements confirm, different concentrations of CNF-dye do not significantly affect the color of the fabric except for nylon. It can be concluded that CNF-dye is not adsorbed by fabrics very well, which can be attributed to either thickness of fabrics or their hydrophobicity.
To investigate the stability of color on the fabric’s colorfastness test was done. It was observed that all fabrics but nylon lose their color and retain the whiteness of the pure fabric.
-Stiffness test:

The fabrics' stiffness was measured to see if the addition of CNF influences this feature of the fabrics. Based on these results, the stiffness of neat fabrics is higher than those of the CNF-modified ones. Particularly, when the dye is embedded in CNF, the stiffness is more significantly lower. However, for nylon, the fabric's stiffness treated with CNF is slightly higher than the pure fabric, which was expected due to the higher CNF-dye uptake of this
fabric. Therefore, it is concluded that using CNF to dye these four fabrics does not make the fabrics stiffer, which is unlike what has been previously reported for cotton fabric.

![Graph](image)

Figure A.28 Effect of CNF and dyed-CNFe on the stiffness of fabrics.

**Non-woven polypropylene (NPP)**

Among the four fabrics mentioned earlier, non-woven polypropylene (NPP) was selected for more investigations. It was hypothesized that NPP-CNFe fabrics could be processed to fabricate bulk pieces of these composites. The amphiphilic P2 copolymer was used to improve the interfacial adhesion between the polar CNF and non-polar NPP fabric. This copolymer contains a hydrophilic part (OEGMA) to attach to the surface of CNF and a hydrophobic part (LMA) to form bonding with the fabric. However, this copolymer might reduce the mechanical properties of the NPP-CNFe composites due to its low glass transition temperature. Consequently, we had four NPP samples as following: 1) N-PP: Non-woven
PP fabric in water, 2) N-PP-1CNF: Non-woven PP fabric in 1% CNF solution, 3) NPP-1CNF-0.1P2: Non-woven PP fabric in 1% CNF-0.1% P2 solution 4) N-PP-1CNF-1P2: Non-woven PP fabric in 1% CNF-1% P2 solution. All the fabric samples were immersed in the solutions for 15 hours and then dried at 60°C for 15 minutes and 120°C for 1 hour.

Optical microscopy images of the dried fabrics show the attachment of the nanocellulose fibrils on the fabric's surface.

Figure A.29 Optical microscopy images of the dried fabrics, a) NPP, b) NPP-1CNF, c) NPP-1CNF-0.1P2, d) NPP-1CNF-1P2.
-NPP-CNF bulk composites:

In the next phase of the experiments, the fabrics were chopped and compression-molded at 170°C-180°C under a pressure of 3.8 MPa to fabricate the bulk composites.

In the first step of materials characterization, we conducted differential scanning calorimetry (DSC) to evaluate the effect of CNF and P2 on the melting and crystallization behavior of NPP composites. Based on the DSC results, the addition of CNF increases the melting point of NPP from 158°C to 159°C, while the copolymer decreases this temperature to 157°C. It can be concluded that the nanofibers restrict the movement of PP chains, while the P2 copolymer facilitates these movements.

![Figure A.30 DSC measurements for NPP, NPP-1CNF and NPP-1CNF-1P2.](image_url)
Thermogravimetric analysis (TGA) was done to realize the decomposition behavior of the materials. As expected, CNF and P2 reduce the initial decomposition temperature of NPP. Taking an in-depth look at the derivative weight peak, we could see the larger peak area of NPP-1CNF-1P2 than that of NPP-1CNF, which confirms that more CNF is attached to NPP in the presence of P2 copolymer. Furthermore, the higher derivative weight peak temperature of NPP-1CNF-1P2 indicates the stronger attachment of CNF-P2 to NPP chains.

According to the TGA results, the P2 copolymer enhances the attachment of CNF to the NPP fabric. We used this finding to examine the coloring of NPP fabric using CNF-dye-P2 agents. We hypothesized that the attachment to NPP would be elevated when CNF-dye is modified with P2. Therefore, the fabric was colored using a mixture of 1%(CNF-dye)-1%P2 through the previously mentioned dying technique. One part of the dyed fabrics was compression-molded to evaluate the color stability during the pressing step. Comparing the color values presented in Figure A.32 shows that NPP-1% CNF-1P2 is darker and redder.
than the NPP-1CNF sample in both fabrics and pressed states. This means that the CNF-dye-P2 has higher efficiency to color NPP fabric compared to that of CNF-dye since P2 facilitates the attachment of dyed nanofibrils to the fabric.

\[ \Delta E_{ab}^* = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2} \]

Figure A.32 Color values of fabrics and bulk composites of NPP dyed with NPP-1CNF-dye and NPP-1CNF-dye-P2.

The final step was to investigate the mechanical properties of modified NPP fabric. Mechanical characterizations were conducted by running dynamic mechanical analysis (DMA) and tensile testing in compression mode.

DMA test was done at a frequency of 5Hz and a heating rate of 3°C/min. As expected, the stiff cellulose fibrils increase the storage modulus of the composites. However, the addition of soft copolymer chains reduces the modulus. Furthermore, based on the loss modulus and \(\tan\delta\), the damping ability of NPP-CNf is lower than that of pristine NPP, while the addition of 1%P2 could improve the loss factor to a high degree.
A tensile tester was used to measure the mechanical properties in bending mode according to ASTM D790. For the three-point bending test, samples with a size of 5cm*1.2cm*0.15cm were deformed at a 1mm/min compression rate. The samples' flexural modulus and flexural strength, and strain were calculated based on this test. It is observed that CNF improves the flexural modulus of NPP, especially when it is modified with 1%P2. The positive effect of P2 could be attributed to the improved interfacial adhesion between NPP and modified CNF. On the other hand, the flexural strength and strain are slightly lower for the NPP-CNFT composites, which is expected due to the composites' brittleness. Nevertheless, the addition
of 0.1%P2 could compensate for the negative effect of CNF on the flexural strain to some degree.

Figure A.34 Mechanical properties of bulk NPP composites obtained by pressing the fabrics
We also examined the effect of extrusion on the mechanical properties of the composite. In general, extrusion of the compounds is done to improve the filler distribution and the reinforced materials' final properties. Nevertheless, we saw that when the fabrics are pressed and extruded to prepare the test specimens, all the mechanical parameters are decreased by CNF and P2. This negative effect of the extrusion step on the mechanical properties can be attributed to the thermal degradation of NPP under the high temperatures of extrusion. As had been indicated by TGA, CNF and P2 decrease the thermal resistivity of NPP composites.
Figure A.35 Mechanical properties of bulk NPP composites obtained by extrusion and pressing the fabrics

Conclusions:

- Among non-woven polypropylene, spun polypropylene, polyester, and nylon fabrics, only nylon could be efficiently colored by the CNF-dye solution.
- Using CNF-dye to color the four fabrics did not make the fabrics stiffer.
- Optical microscopy images confirmed the attachment of CNF to the NPP fabric.
• Based on the DSC results, CNF increased the melting point of NPP, while P2 decreased this temperature.

• Based on TGA results, modifying CNF with PP caused enhanced attachment of CNF to NPP.

• CNF-dye-P2 had a higher efficiency to color NPP fabric compared to that of CNF-dye.

• CNF positively affected the composites' storage modulus, but it decreased the loss factor. P2 copolymer elevated the loss of the NPP-CNFP2 composites.

• CNF had a positive effect on the composites' storage modulus, but it decreased the loss factor. P2 copolymer elevated the loss of the NPP-CNFP2 composites.

• CNF improved the composites' elastic modulus based on mechanical characterization but reduced the tensile strain and strength. The addition of P2 could increase the deformability of the composites.

• The extrusion step to the composite processing procedure caused thermal degradation and deteriorated the mechanical properties.