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Optimizing EPDM/LLDPE Blends with Graphene Oxide: A Route to High-Performance Rubber Composites

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Rubber composites are gaining attention for tailor made application oriented films and coating. This study investigates the mechanical properties and morphology of EPDM/LLDPE/GO films and composites. The compositions were varied, and the resulting tensile strength, elongation at break, modulus and tear strength were measured. The results indicates that the addition of GO generally enhances the mechanical properties of the EPDM/LLDPE blend, with the optimal GO content varying depending on the specific property. For instance, the highest tensile strength and maximum elongation at break was observed at a certain GO concentration. The properties of EPDM/LLDPE/GO can be tailored by adjusting the composition to suite specific application requirements.

Keywords; EPDM. LLDPE. Graphene oxide. Solution – Intercalation. .FTIR. Mechanical Properties. Morphology

INTRODUCTION

Combining several polymers to produce a sophisticated material with unique physical properties is known as a polymer mix. As a straightforward and affordable method of creating polymeric materials with industrial applications in mind, polymer mixing has grown in popularity. The qualities of the blends can be adjusted to suit the intended uses by carefully choosing the constituent polymers. The practical importance of polymer blends has drawn a lot of scientific interest [1]. Many research has been published on the importance of ethylenepropylene diene terpolymer (EPDM) and linear low-density polyethylene (LLDPE) blends in the commercial sector [2, 3, 4, 5, 6]. The excellent weather resistance, flexibility, and lowtemperature resistance of EPDM, combined with the strength and processability of LLDPE, make these blends ideal for automotive sealing applications. Graphene oxide is a carbon-based nanomaterial with a high surface area and oxygen functional groups. GO has many applications in electronics, photonics and biomedicine. Furthermore, the combination of EPDM's excellent UV and weather resistance with LLDPE's toughness and flexibility and GO's high surface area provides a durable and long-lasting roofing solution. Additionally, EPDM's excellent electrical insulation properties, combined with LLDPE's mechanical properties and GO's high surface area make the composite suitable for electrical insulation applications.

The aim of the study is to be focused on analysing the mechanical properties of EPDM/LLDPE/GO films, specifically examining tensile strength, tensile strain, and modulus. This type of analysis is relevant in the context of material science and polymer engineering, where understanding the mechanical behaviour of films is crucial for various applications, including packaging. The study likely aims to determine how the composition of the film affects these properties, which can inform the design and optimization of materials for specific uses.

2. EXPERIMENTAL

2.1.MATERIALS

Ethylene propylene diene monomer was purchased from Dupont-Dow chemical company. LLDPE was purchased from ONGC Petro Additions Limited (O-Pal), sez-1, DAHEJ-392130, Gujarat, India. Toluene and Di cumyl peroxide were supplied by CDH, New Delhi. Double distilled water was used throughout the study.

2.2. PREPARATION OF EPDM/LLDPE BLEND AND GO COMPOSITES

The EPDM/LLDPE blends were prepared using a solution intercalation method. Firstly, EPDM and LLDPE granules (15 phr) and required amount of Graphene Oxide (0.5, 1, 3, 5 phr) were introduced into a three – necked flask(500ml). These particles were then dissolved in toluene under continuous stirring at 60^0C for a duration of 5 hours, to enhance crosslinking, 3phr of Di cumyl peroxide was added to the mixture just 4-5 minutes before completion of heating. Subsequently, the refluxed mixture was immediately transferred to a flat glass mould with dimensions of 100mm(length)x 100 mm(width) x 0.55 mm(thickness) and allowed to cool at room temperature, after a 24-hour period, the thin films of the blend were obtained by dipping the mould into water, after extracting the solvent. The resulting sheets were cut into various sizes for testing purposes.

3.CHARACTERIZATION

Tensile tests were performed according to ASTM D882 using an Instron UTM 3345 with a 500 N load cell. Samples were fixed between pneumatic grips with a gauge length of 50 mm and tested at a crosshead speed of 100 mm/min until failure. The tests were conducted at room temperature (25^0C) and 55% relative humidity. Samples with a dimension of 100mm×10mm with an average thickness of 0.3mm were used. The results were the average of eight measurements.

The Fourier transform infrared (FTIR) spectra were recorded on SHIMDAZU IRTracer-100 FTIR Spectrophotometer(Attenuated total reflectance (ATR)) in a humidity free atmosphere in the range of 400-4500 cm-1 in the science instrumentation centre at SFR College for women , Sivakasi.

The surface was coated with gold examined under a scanning electron microscope (CARL-ZEISS, Model EVO-50).

RESULT & DISCUSSION

FTIR ANALYSIS

Infrared spectroscopy is an important technique to evaluate possible changes in the chemical structures of the polymers such as neat EPDM and EPDM / LLDPE blends and also evaluate the chemical interactions between the components of the film.

In particular the EPDM spectrum exhibit the characteristic bands of saturated C-H Bonds: C-H symmetric and asymmetric stretching (2916 cm-1 and 2800 cm-1), C-H scissoring of CH3 group (1442 cm-1) C-H symmetric bending (1303 cm-1) and –(CH2-CH2-) backbone (732 cm-1) [15]. Thus, the FTIR spectrum of the pure EPDM shows the C H stretching vibration at 2962 cm-1, CH2 rocking vibration at 1442 cm-1, –CH3 symmetric bending vibration at 1365 cm due to the presence of propylene groups and the C–C stretching vibration at 2800 cm-1[16].

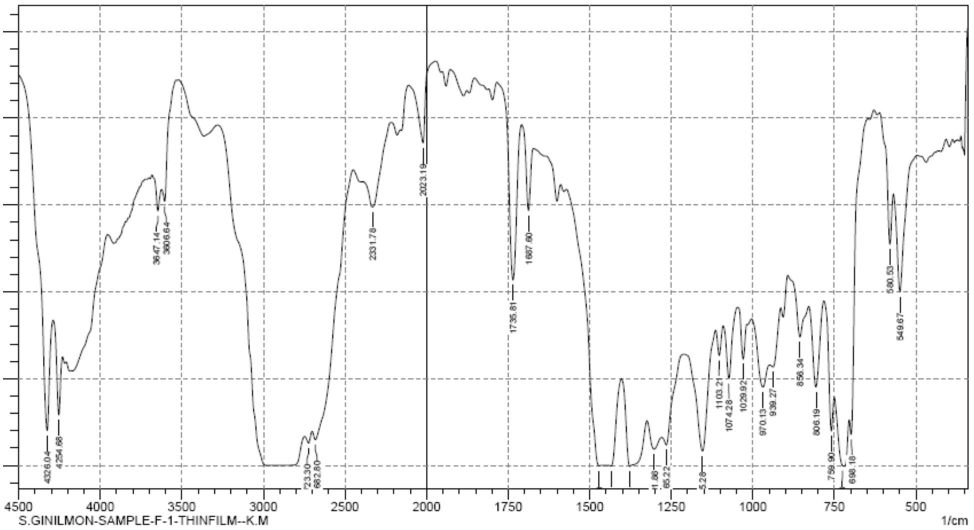


Figure 1: FT-IR Spectrum of EPDM Rubber Film

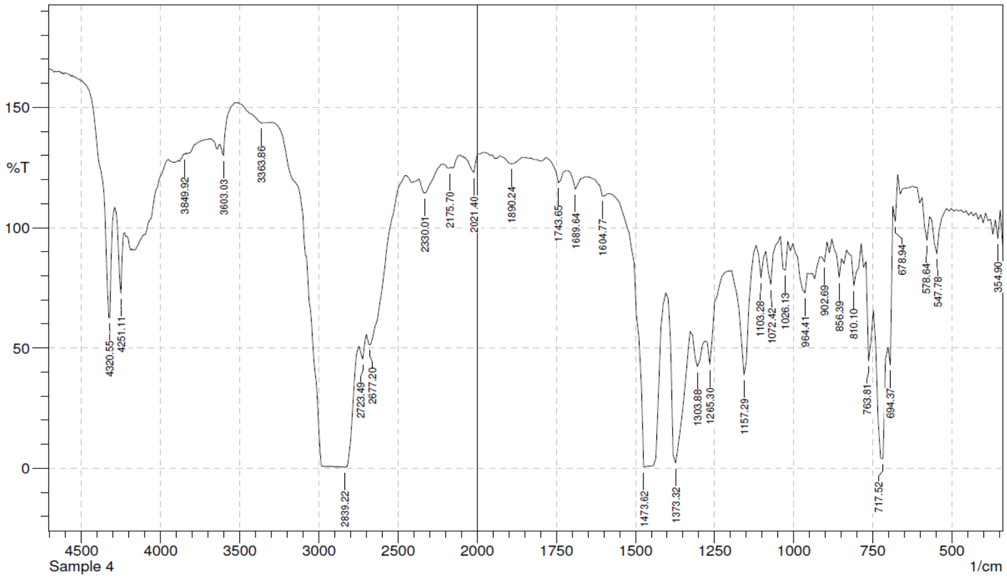


Figure 2: FT-IR Spectrum of EPDM/LLDPE Blend

The peak at 732 cm-1 is indicative of the C-H rocking vibration in long methylene sequence, typically found in polyethylene chains of LLDPE [17]. The absorption band at 856 cm-1 can be used to confirm the butene-1 copolymer of LLDPE [18]. It is well observed that on addition of LLDPE in EPDM, the peak at 2330 cm-1 appears due to -CH2 stretching group in LLDPE. Moreover, the peak intensity increases with increase in LLDPE content which can be seen in EPDM/LLDPE (15phr).

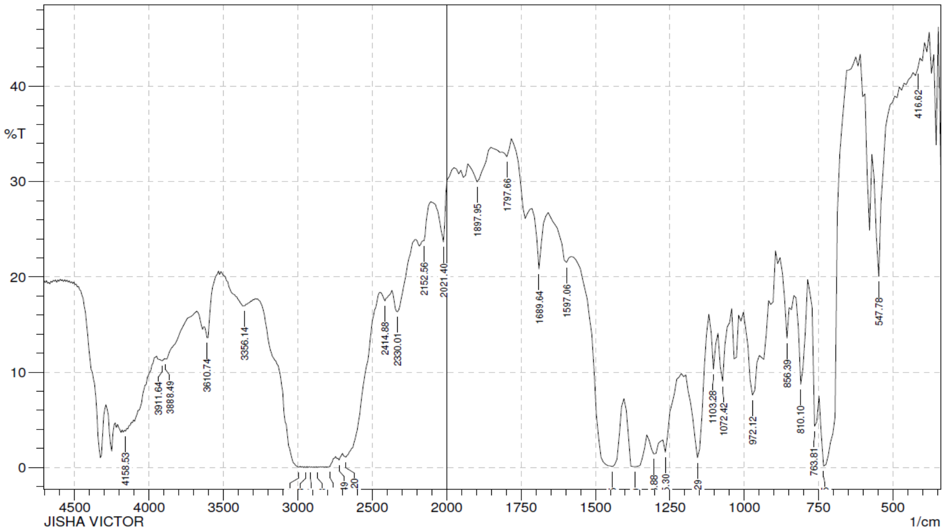


Figure 3: FT-IR Spectrum of EPDM/LLDPE/GO Nanocomposites

The strong peaks around 2960-2850 cm-1 are characteristics of C-H stretching vibrations, present in both EPDM and LLDPE. The presence of multiple peaks in this region indicates different types of C-H bonds (methyl, methylene). The peak at 1442 cm-1 corresponds to the C-H bending vibration in methyl groups, present in both rubbers. The peak at 1365 cm-1 attributed to the C=H bending vibration in methylene group again found in both polymers. The peak at 732 cm-1 is indicative of the C-H rocking vibration in long methylene sequence, typically found in polyethylene chains of LLDPE. The around 810 cm-1 represents the C-H out of plane bending vibration, specific to the double bond in the diene monomer of EPDM. This is a distinguishable feature of EPDM compared to LLDPE. The peak around 854 cm-1 is characteristics of C-H out of plane bending vibration in alkene group.

The peak at 1265 cm−1were corresponding to the asymmetric and symmetric stretching of C-O -C group, respectively. Moreover, three significant peaks around 1365, 1442 and 1597 cm−1 were in order contributed to C- H and C-H2 bonds of chain branch and C-C band stretching vibrations [19, 20]. In addition, the strong peak appeared around 1735 cm−1was corresponding to C= O stretching absorption, this could be due to the presence of oxidised functional group on graphene oxide. Furthermore, two significant peaks appeared at 2800 and 2916 cm−1 were contributed to the symmetric and asymmetric stretching vibration of methylene in saturated hydrocarbon back bone [21]. Spectrum (c) in Fig. 5 represents the vibrations resulted from nanocomposite containing 5 phr graphene oxide. The effect of the graphene oxide presentation appeared in the combination of C- H deformation vibration to one significant peak around 732 cm−1. In addition, the peak at 1103 cm−1was corresponding to C- O stretching vibration. The presence of nano filler also affected the vibration peaks of methylene in hydrocarbon backbone and consequently the rubber structure. This behaviour can be addressed to formation of additional bonds between the surface of graphene oxide and the rubber backbone during blending.

MECHANICAL PROPERTIES OF EPDM/LLDPE/GO FILMS

Tensile strength measures the maximum stress a material can withstand before breaking. The pure EPDM film has a tensile strength of 5.17, which increases with the addition of LLDPE up to 15phr (9.46)). This indicates that LLDPE enhances the film’s ability to resist tensile forces. Incorporating GO into the EPDM/LLDPE blend further enhances the tensile strength. As GO content increases from 0.5

to 5 phr, the tensile strength rises from 13.65Mpa to 15.44Mpa, indicating that GO act as a reinforcing filler [7]. The tensile strength values of EPDM/LLDPE/GO are 13.65(0.5phr), 14.55(1phr), 15 (3phr), and 15.44 (5phr), respectively. Similarly, adding GO to pure EPDM, the tensile strength gradually increases from 9.8Mpa to 12.12 mpa with increasing GO content from 0.5 phr to 5 phr. The tensile values for various compositions of EPDM/GO are 9.8(0.5phr), 11.03(1phr), 11.58(3phr), and 12.12(5phr) respectively. This drastic improvement in mechanical properties was due to the better dispersion of nanofiller along with the penetration of LLDPE and EPDM chains in between GO layers [8] shows the effect of graphene oxide sheets on the tensile strength. As can be seen, the addition of graphene oxide to the EPDM/LLDPE blend increased the tensile strength due to the uniform distribution of graphene oxide in the EPDM/LLDPE matrix in these samples.

Table 1: Mechanical properties of EPDM/LLDPE/GO composites with varying compositions.

Sample	Composition(phr)	Tensile strength (Mpa)	Tensile strain	Modulus
EPDM	100	5.17	8.225	1.84
EPDM/LLDPE	15	9.46	13.26	3.98
EPDM/LLDPE/GO	0.5	13.65	15.01	4.25
EPDM/LLDPE/GO	1	14.55	16.08	4.91
EPDM/LLDPE/GO	3	15	16.83	5.14
EPDM/LLDPE/GO	5	15.44	17.24	5.25
EPDM/GO	0.5	9.8	10.07	2.91
EPDM/GO	1	11.03	11.59	3.76
EPDM/GO	3	11.58	11.71	4.1
EPDM/GO	5	12.12	12.19	4.12

Tensile strain represents the maximum elongation a material can undergo before breaking. Pure EPDM exhibits the highest strain at 8.225., indicating good elongation before breaking. Adding 15 phr LLDPE increases the tensile strain to 13.26., suggesting improved flexibility and ductility compared to pure EPDM. Incorporating GO into the EPDM/LLDPE matrix results in a gradual increase in strain. The strain values for

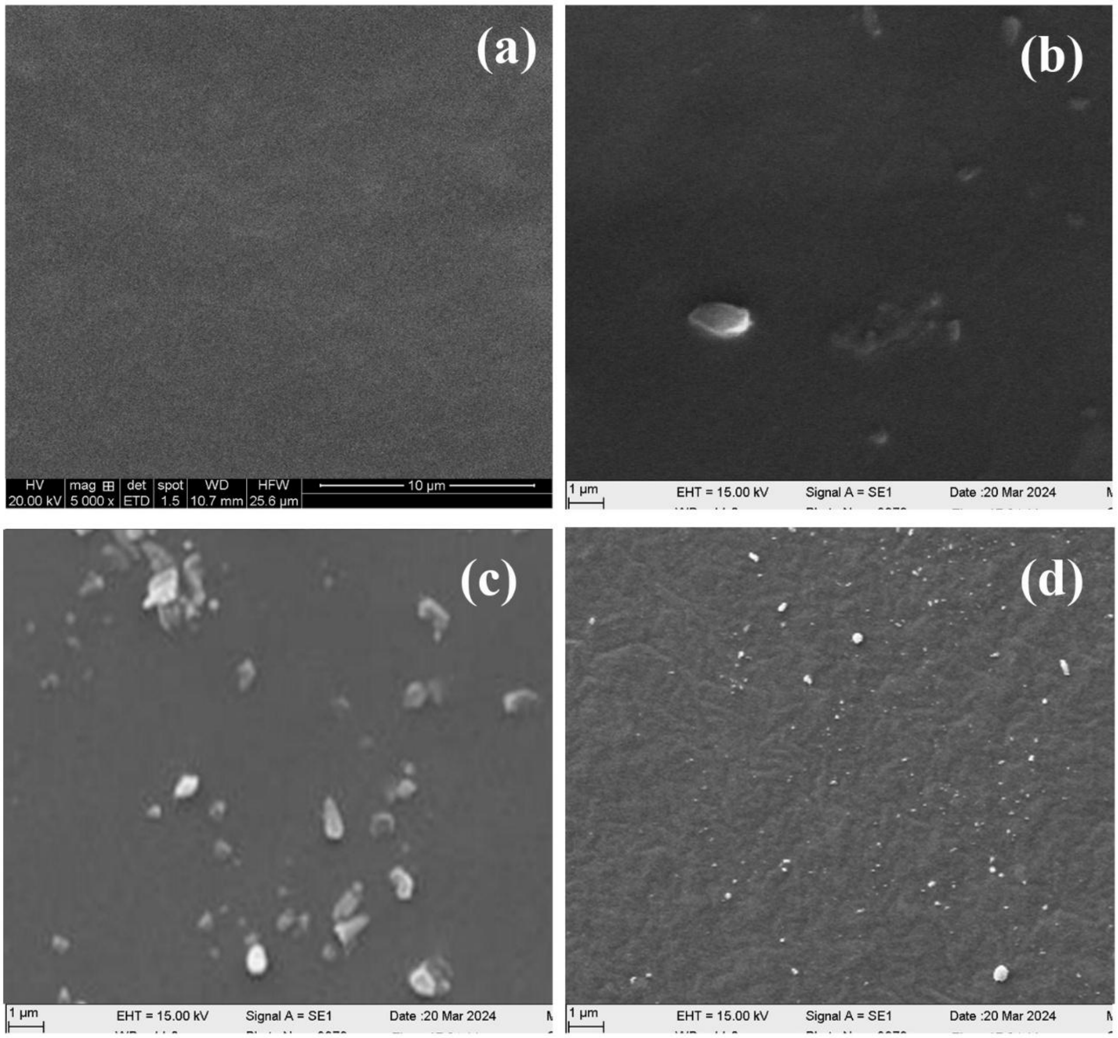
EPDM/LLDPE/GO composites increases with 0.5 phr (15.01), 1 phr (16.08), 3 phr (16.83) and 5 phr (17.24).This could indicate that a small amount of GO improves the materials ability to withstand deformation. Similarly, the addition of GO to pure EPDM shows similar trend. The tensile strain increases with increasing GO content with 0.5 phr (10.07), 1 phr (11.59), 3 phr (11.71), and 5 phr (12.19) respectively. Compared to EPDM/GO composites with the same filler loading, the elongation break of EPDM/LLDPE/GO composites are always higher, indicating the better dispersion of Graphite in EPDM matrix. The combination of EPDM/LLDPE and GO creates a synergistic effect, where the individual components work together to enhance the tensile strain of the films [9]. Graphene oxide play an important role in chemical bonding sites. As a result, graphene oxide can dramatically increase the mechanical properties by creating new chemical bonds and providing additional physical entanglements. [10]. Elongation at the break in the presence of GO increased because the GO sheets can interact with polymer chains very well due to their functional groups. Furthermore, they can suggestively serve as bridges between polymer chains on either side of a crack, absorbing stress and preventing further propagation. These effects collectively increase the energy required for crack growth, enhancing the material's elongation at break [11,12,13]

Modulus indicates a material's stiffness or resistance to deformation. The pure EPDM sample has the lowest modulus of elasticity (1.845). The addition of LLDPE increases the modulus to 3.98 Mpa, signifying a significant improvement in stiffness. Further addition of GO to the EPDM/LLDPE blend steadily increases the modulus. This indicates that GO act as a reinforcing filler, enhancing the composite's stiffness. The modulus increases with increasing GO content, The modulus of various compositions increases with 4.25 (0.5 phr), 4.91 (1 Phr), 5.14 (3 phr), and 5.25 (5 phr) respectively. Similarly in the absence of LLDPE, GO addition increases the modulus from 2.91 (0.5 phr) to 4.12 (5 phr). However, the values are generally lower compared to the EPDM/LLDPE/GO composites, suggesting that LLDPE plays a role in maximizing the reinforcing effect of GO. The dispersion of GO within the polymer matrix and interfacial bonding between the two phases significantly influence the modulus. The improvement in modulus can be anticipated that by an increase in the GO content, a more uniform and even distribution of nanosheets within the EPDM/LLDPE blend would be stabilized. Accordingly, this even distribution improves uniform stress transfer throughout the system. Additionally, interracially localized GO enhances the interfacial adhesion between the two phases, attributed to the amphiphilic and unique chemical structure of GO [14].

Both EPDM/LLDPE/GO blends and EPDM/GO blends exhibit higher tensile strength, strain, and modulus when GO contents increases. However, the EPDM/LLDPE/GO composites generally exhibit higher mechanical properties compared to EPDM/GO blends with the same GO content. Around 5phr both EPDM/LLDPE/GO and EPDM/GO shows peak tensile strength, strain and modulus. This suggests that the combination of LLDPE and GO provides a synergistic effect on the mechanical properties of EPDM. The strong interfacial bonding between the components, the uniform dispersion and distribution of LLDPE and GO within the EPDM matrix, the high aspect ratio and surface ratio of GO facilitate strong interaction with the polymer matrix, and the addition of LLDPE and GO can influence the crystallization and morphology of the EPDM matrix also contribute the enhanced mechanical properties of these composite films.

MORPHOLOGICAL ANALYSIS

The SEM images show good dispersion of LLDPE particles, indicating a homogeneous mixture. The smooth interface between EPDM and LLDPE phases indicates good interfacial adhesion, achieving desirable mechanical properties. The blend creates a homogeneous mixture with no significant phase separation, achieving desirable mechanical properties. The morphology of the blend with 15% of LLDPE shows good dispersion in the EPDM matrix, with lighter, smaller domains distributed throughout the darker EPDM phase. The interface between the LLDPE particles and EPDM matrix is smooth, with no voids or cracks. The Sem image c and d also shows a relatively smooth surface with some dispersed bright particles. These particles are likely the GO filler within the EPDM/LLDPE matrix. The distribution of GO appears to be reasonably uniform throughout, suggesting good dispersion within the polymer composite. There is no large-scale agglomeration of the GO, which is beneficial for the mechanical and physical properties of the composite. The composite's morphology is desirable for consistent properties the material, making it suitable for applications requiring flexibility, weather resistance, and impact resistance, such as automotive components, seals, gaskets, and roofing membranes.



Sem images of a) EPDM b) EPDM/LLDPE-15phr c) EPDM/LLDPE/GO-5phr

d) EPDM/GO-5phr

CONCLUSION

The addition of GO generally improves the tensile strength of the composites. This is likely due to the reinforcing effect of the GO, which enhances the stiffness of the material. GO incorporation also tends to increase the tensile modulus and also the elongation at the break. The improvement in mechanical properties, such as hardness, tensile strength, elongation at break, and modulus has been observed with the incorporation of GO. The extend of improvement depends on factors like GO content, dispersion and the interaction between the components.

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