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MECHANICAL AND THERMAL PROPERTIES OF GRAPHENE OXIDE REINFORCED POLYPROPYLENE/PINEAPPLE LEAVES FIBRE COMPOSITES

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ABSTRACT

Polypropylene (PP) has many interesting properties and widely used in many applications. Natural fibres such as pineapple leaf fibre (PALF) have been used to improve the mechanical properties of PP due to various advantages such as low cost and low density. The objective of this study is to investigate the effect of graphene oxide (GO) content on mechanical and thermal stability of PP/PALF composites. The effect of PALF on mechanical and thermal properties of neat PP was also investigated. The PP/PALF and PP/PALF/GO composites compatibilized with polypropylene-grafted-maleic anhydride (PP-g-MAH) were melt-blended using co-rotating twin-screw extruder and injection moulded into test samples. Throughout the study, the weight ratio of PP: PALF: PP-g-MAH was fixed at 85:10:5 weight percent. PP/PALF/GO with different GO contents (0, 0.5, 1.0, 2.0 phr) were prepared. Mechanical properties of the polymer composites were studied through tensile and impact tests while thermal properties were investigated through thermogravimetric analysis (TGA). All mechanical properties with the exception of elongation break improved with the incorporation of 10 % PALF into PP. The addition of 1.0 phr GO increased the impact strength of PP/PALF from 44.85 to 49.49 J/m, which is about 10 % increase. However, the tensile strength and Young's modulus did not significantly change with GO content. The study has demonstrated that simultaneous incorporation of GO and PALF into PP has enhanced the mechanical strength of PP. The thermal stability of PP/PALF/GO composites as indicated by T_{max} at 0.5 phr GO content was significantly higher than neat PP and PP/PALF composites.

Keywords: polypropylene, pineapple leaf fibre, graphene oxide, mechanical and thermal properties

1.0 INTRODUCTION

Polypropylene (PP) is one of the most widely used semi-crystalline thermoplastics due to low density, relatively low cost and ease of processing [1]. Although PP has many good properties, there is a need for constantly improving the properties to make it competitive compared to other engineering polymers through the addition of additives and blending with other polymers [2, 3]. The polymer is being used in various applications such as packaging, automotive parts and bottle manufacturing [4].

The utilization of natural fibres in the manufacture of polymer-matrix composites is gaining importance worldwide. Natural fibres like banana, hemp, oil palm, jute, bamboo, henequen, and pineapple are rich in cellulose and are abundantly available in tropical countries. There are a number of advantages in using natural fibres for reinforcing polymer composites which include low cost, low density, low energy consumption and eco-friendly [5]. In this study, pineapple leaf fibre (PALF) was used as reinforcing agent in PP composites. The utilization of PALF in polymer composites will increase its usage and reduce waste product from pineapple cultivation.

Graphene, one-atom-thick nanosheet of sp2-hybridized carbon atoms arranged into a hexagonal lattice has emerged as a new interesting material in 21st century [6] This fascinating novel nanomaterial has shown a great potential for various applications which include polymer composites, supercapacitors and lithium ion batteries [7-9]. Many studies have shown improvement in electrical conductivity, mechanical, thermal stability, and flame retardant properties of neat polymer with the incorporation of graphene [10-12].

In this research, graphene oxide (GO) was used to reinforce the PP/PALF composites. Graphene oxide contains reactive oxygen with functional groups such as carboxylic, hydroxyl, and epoxy groups [13]. The epoxy and hydroxyl groups are attached on the GO basal plane, while the carboxylic groups are present on the edges of GO. Due to these functional groups, GO is strongly hydrophilic in nature and disperse easily in water. Incorporation of GO into polymers has the potential to significantly improve the thermal stability and mechanical strength due to the large specific area [14]. Polypropylene-g-maleic anhydride (PP-g-MAH) is used as the compatibilizer to increase the adhesion properties of hydrophobic PP with a more hydrophilic GO and PALF.

Previous studies have reported on the use of graphene based nanofillers with natural fillers. However, the study on the use of hybrid GO and PALF in polymers has not been reported. The objective of this research is to enhance the mechanical properties and thermal stability of PP by incorporating two different reinforcing agents, which are GO and PALF through melt blending technique

2.0 METHODOLOGY

2.1 Material

Heterophasic polypropylene (PP) copolymer, SM 240 grade of density of 0.96 g/cm^3, and melt flow index 35 g/10 min (230°C and 2.16 kg load) was purchased from Lotte Titan Chemicals, Malaysia. Polypropylene-grafted-maleic anhydride (PP-g-MAH) compatibilizer of melt flow index 150 g/10 min (230°C and 2.16 kg load) and melting temperature 167°C was purchased from Dupont, Dow Elastomers, and Wilmington DE, USA. Pineapple leaf fibre (PALF) was obtained from Biopolymer Research Group, School of Chemical Engineering and Energy Engineering, Universiti Teknologi Malaysia and UGOX^{TM} United Graphene Oxide (Graphite Generated Nano Materials) powder (purity: 99%), supplied by United Nanotech Innovations Private Limited, India, with average thickness of 0.8 to 2.0 nm, average number of 3 to 6 layers and lateral dimension of 5 to 10 µm, was used in this experiment.

2.2 Composites Preparation

PP/PALF/GO composites were prepared with different amount of GO (0, 0.5, 1 and 2 phr) whereas the amount of PP, PALF and PP-g-MAH were fixed at 85:10:5 wt% with neat PP as the control. All the composites were melt intercalated using Brabender PL 2000 Plastic Coder co- rotating twin screw extruder at temperature of 185–200°C from the feed zone to the die head zone. After melt intercalation, the extrudates were subsequently pelletized before being injection moulded into standard test specimens using JSW model NIOOB 11 Muraron-Japan injection molding machine at temperature range of 185–200°C

2.3 Mechanical Testing and Thermogravimetric Analysis

Two types of mechanical tests were performed, which are tensile and impact. Tensile tests were performed on dumbbell shaped PP/PALF/GO and PP/PALF samples at a cross head speed of 50 mm/min using Universal Testing Machine, Shimadzu's AG-X plus according to ASTM D638. Notched impact strength for PP/PALF/GO composites samples was tested on a Zwick Roell HIT25P Impact Tester according to ASTM D256. The notch was milled with 45° angle and 9 mm depth with an Automatic Notch Machine. The results presented were the average of five samples. Both tests were done at ambient temperature of about 25^{o}C.

The thermal stability of PP/PALF/GO composite was investigated using thermogravimetric analysis (TGA) Mettler Toledo Star^e system with an alumina crucible using 10 mg of sample as probe. The analysis was conducted from ambient temperature to 600°C at air flow of 50 ml/min in nitrogen atmosphere. Finally, the chemical interactions of PP/PALF and PP/PALF/GO composites at various GO content were analyzed by FTIR using attenuated total reflectance (ATR), on a Perkin Elmer FTIR spectrometer. The spectra were recorded in the range from 850 to 4000 cm^{-1}.

3.0 RESULTS AND DISCUSSION

3.1 Mechanical Properties of PP Composites

Figures 1-3 show the effects of PALF and GO content on the tensile properties of PP/PALF composites. It can be seen that the modulus of PP/PALF composite has improved about 21% as compared to neat PP which is quite significant. However, Young's modulus of PP/PALF/GO did not increase with increasing GO content. The Young's modulus of PP/PALF/GO at all GO content, nevertheless, are still higher than pure PP. Among the PP/PALF/GO composites, the Young's modulus increased with GO content.

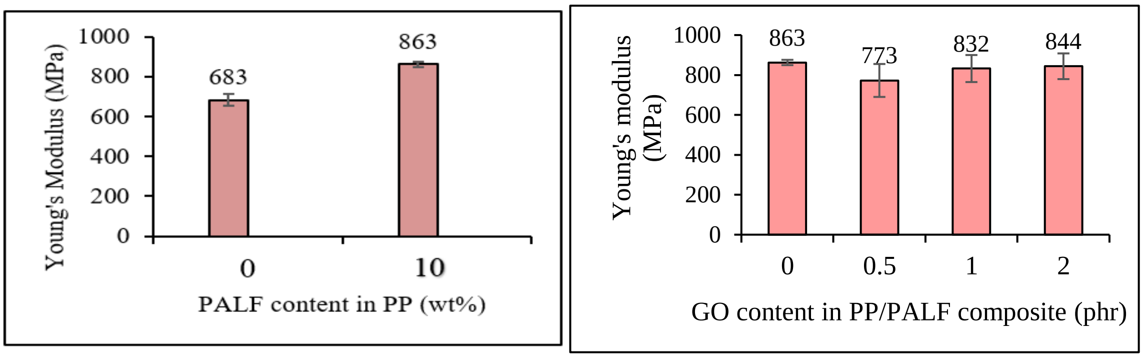


Figure 1 Effect of PALF and GO content on Young's Modulus of PP composites

A decrease in elongation at break from 16 to 12% was observed when 10 wt% of PALF was incorporated into the neat PP. This is because the mobility of the PP chains has been restricted with the addition PALF. Not much change in ductility of PP/PALF/GO was observed with increasing GO content. Similar behaviour has been widely reported in previous work in which the elongation at break of PP reinforced with GO decreased as compared to neat PP [15].

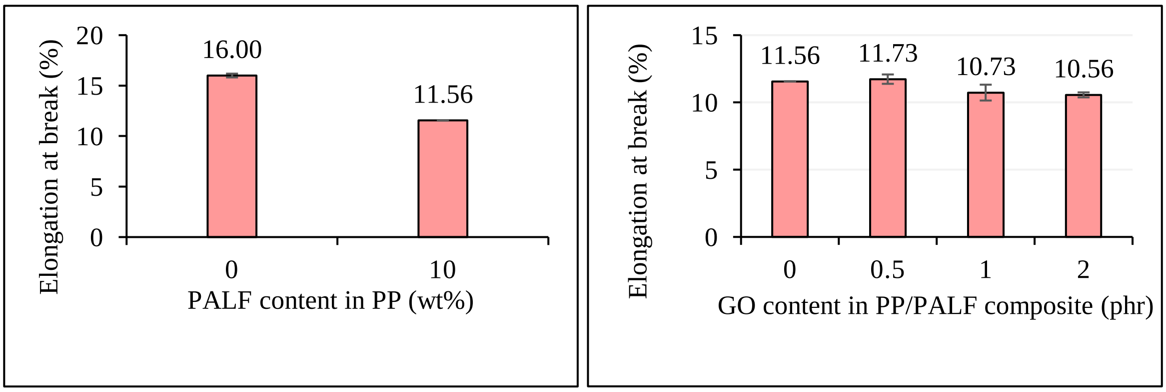


Figure 2 Elongation at break of PP composites

From Figure 3, the tensile strength increased by 6% with the incorporation of 10 % PALF into PP. This shows that there is good interfacial interaction between PALF and PP, with PP-g-MAH as the compatibilizer. A slight increase in tensile strength was observed with the incorporation of 0.5 phr GO into PP/PALF composites. No further increase in tensile strength was observed with increasing GO content. Similar behaviors have been previously reported where the incorporation of GO at different content has no significant changes on the tensile strength of neat PP [16]. Thus, the highest tensile strength achieved was 32.73 MPa upon the addition of 0.5 phr GO into the PP/PALF composites.

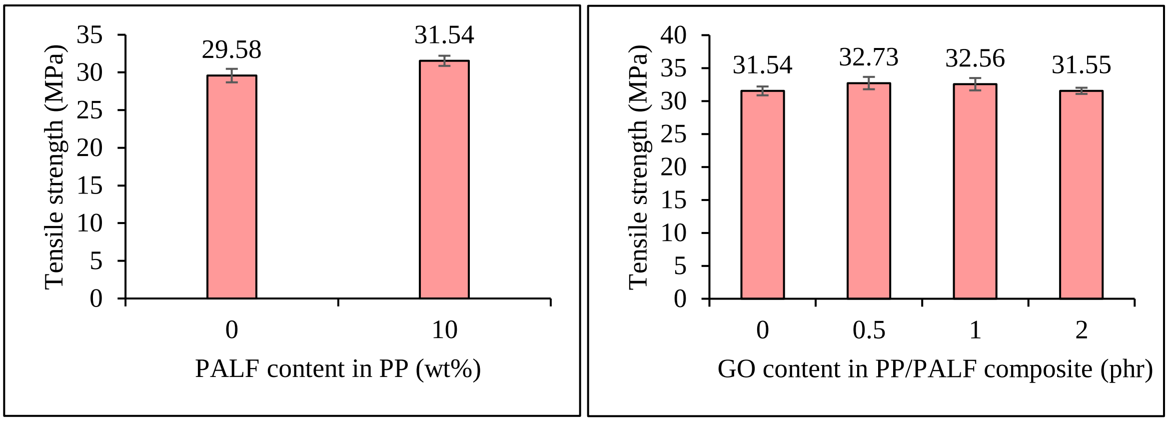


Figure 3 Tensile strength of PP composites

The overall results show that there is no significant increment in both modulus and tensile strength of PP/PALF/GO composite as compared to PP/PALF. One plausible factor is the formation of voids in the PP/PALF/GO composites due to the addition of hybrid fillers in the composites. The formation of voids in the PP/PALF/GO composite maybe due to the poor distribution of GO during processing of the hybrid composites resulting in poor adhesion with PP matrix [17].

3.2 Impact Strength

As shown in Figure 4, the impact strength increased significantly from 37.75 to 44.85 J/m, with the incorporation of 10 % PALF into PP which indicates that there is enough adhesion for the impact stress to be transferred from PP matrix to PALF. This means that PP-g-MAH is an effective compatibilizer which contributes to the increase of compatibility between PP matrix and PALF. Interestingly, it was also shown that impact strength of PP/PALF/GO composites were significantly higher at 1.0 phr GO content (49.49 J/m) compared to PP/PALF composite and neat PP. The improvement was about 23% compared to neat PP. The proposed interactions between GO with PALF and GO with PP are given in Figure 5. However, the impact strength of PP/PALF/GO composites decreased from 49.5 to 43.0 J/m at 2.0 phr GO content. This is because there was a higher tendency for the GO to agglomerate at higher GO content in PP/PALF/GO [18].

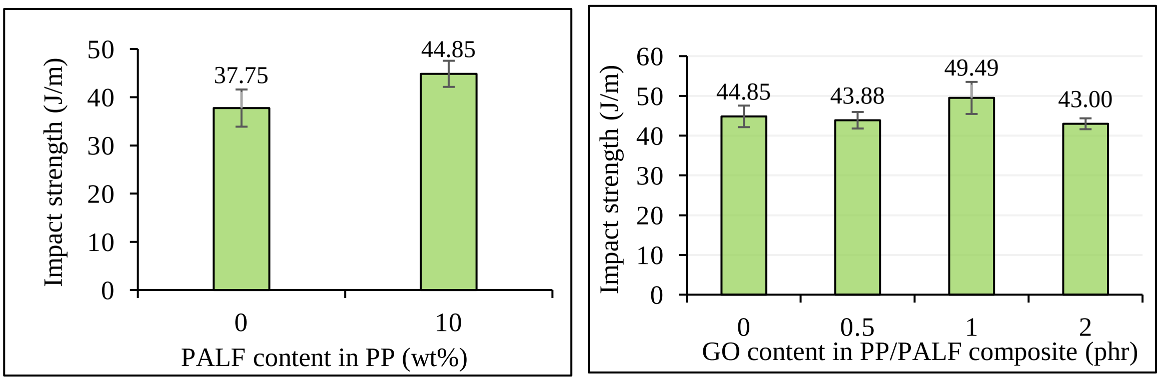
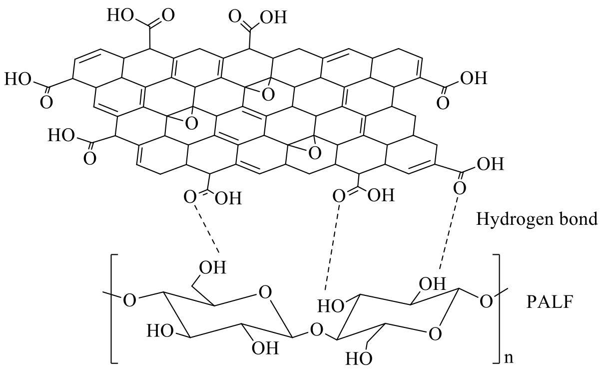
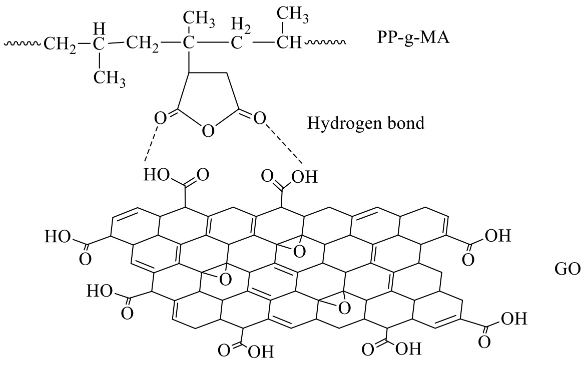


Figure 4 Impact strength of PP composites



a) Formation of hydrogen bond between GO and PALF.



b) Formation of hydrogen bond between PP-g-MAH and GO.

Figure 5 Formation of hydrogen bond a) between GO and PALF b) between PP-g-MAH and GO.

3.3 Thermogravimetric Analysis

The thermal stability of neat PP, PP/PALF and PP/PALF/GO composites was analyzed using TGA. Figure 6 shows the variation of weight loss with increasing temperature for the PP/PALF and PP/PALF/GO composites. The temperature at 20% weight loss of sample (T_{20}), maximum decomposition temperature (T_{max}) and percentage yield of char are summarized in Table 1 and the effect of PALF on PP and the effect of GO content on PP/PALF composites can be determined. T_{20} denotes the initial decomposition temperature of the samples.

Table 1 Effect of GO content on thermal properties of PP/PALF composite

Sample	**T_{max} (°C)**	**T_{20} (°C)**	**Residue (%)**
PP	455.0	478.3	0.17
PP/PALF	455.0	480.0	0.51
PP/PALF/0.5 GO	459.3	480.0	1.67
PP/PALF/1.0 GO	457.3	480.3	1.68
PP/PALF/2.0 GO	455.3	479.0	2.55

There was no change with the addition of PALF into PP for the T_{max}. However, an increase of about 4°C was observed with incorporation of GO into PP/PALF composites. It became less effective above 0.5 phr due to the agglomeration of the GO. The increase in thermal stability of PP/PALF/GO composites as indicated by T_{max} results from the GO retarding the diffusion of oxygen into the PP matrix. Lim et al. reported a similar trend in their investigation on PP/MMT nanocomposites [19]. The char residues also increased with GO content.

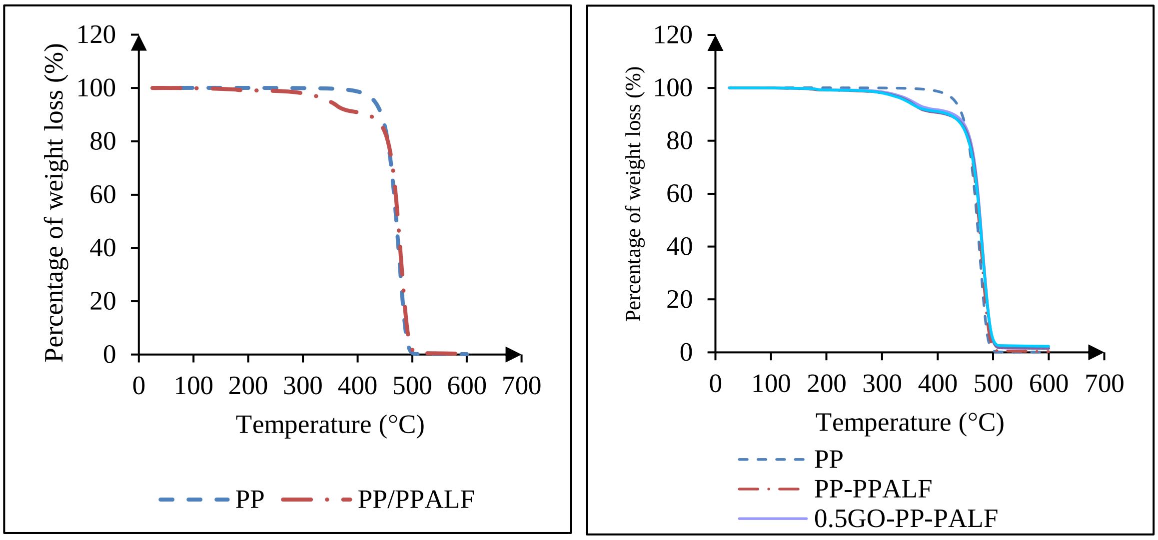


Figure 6 TGA curve of neat PP and PP/PALF/GO composites

3.4 Fourier Transform Infrared Characterization

Figure 7 shows the IR spectrum of the PP/PALF composite at different GO content. The emerging peaks of PP/PALF, PP/PALF/0.5 GO, PP/PALF/1.0 GO and PP/PALF/2.0 GO at 3359.31 cm^{-1}, 3361.07 cm^{-1}, 3360.73 cm^{-1} and 3359.95 cm^{-1} respectively were corresponded to the stretching vibrations of OH groups. Moreover, the appearance of four peaks at 2839 cm^{-1}, 2870 cm^{-1}, 2917 cm^{-1} and 2950 cm^{-1} for each of the IR spectrums represents the symmetrical CH_2 stretching vibration, CH_3 symmetrical stretching vibration, CH_3 asymmetrical stretching vibration and CH_2 asymmetrical stretching vibration respectively. These peaks formed due to the grafting effect of PP-g-MAH with GO [20]. The bands at 1454 cm^{-1} and 1376 cm^{-1} refer to deformation vibration symmetrical and asymmetrical of the CH_3 [21].

From the FTIR- ATR spectrum, it was observed the peaks formed at 3359 cm^{-1} for PP/PALF/2.0 GO are broader as compared to the peak of PP/PALF, PP/PALF/0.5 GO and PP/PALF/1.0 GO. This indicates that a large amount of OH group of GO presence on the surface of PP/PALF/2.0 GO. Higher OH group present in the PP/PALF/GO composites, increases the hydrophilicity and results in larger pore size [20]. Similar findings were observed in this research in which, PP/PALF/2.0 GO has the largest pore size as compared to other composites. Thus, it can be concluded that PP/PALF/2.0 GO has a higher amount of OH group which causes it to aggregate and exhibit poor mechanical properties. Additionally, there is also no significant shift observed in the peaks of IR spectrum for OH groups at different GO content of PP/PALF composite. Hence, this indicates that less interaction of hydrogen bonding occur when GO was incorporated at different phr into PP/PALF composite. In short, this finding supports the facts that the tensile strengths of PP/PALF/GO at 0, 0.5, 1.0 and 2.0 phr of GO were almost identical and has no effect.

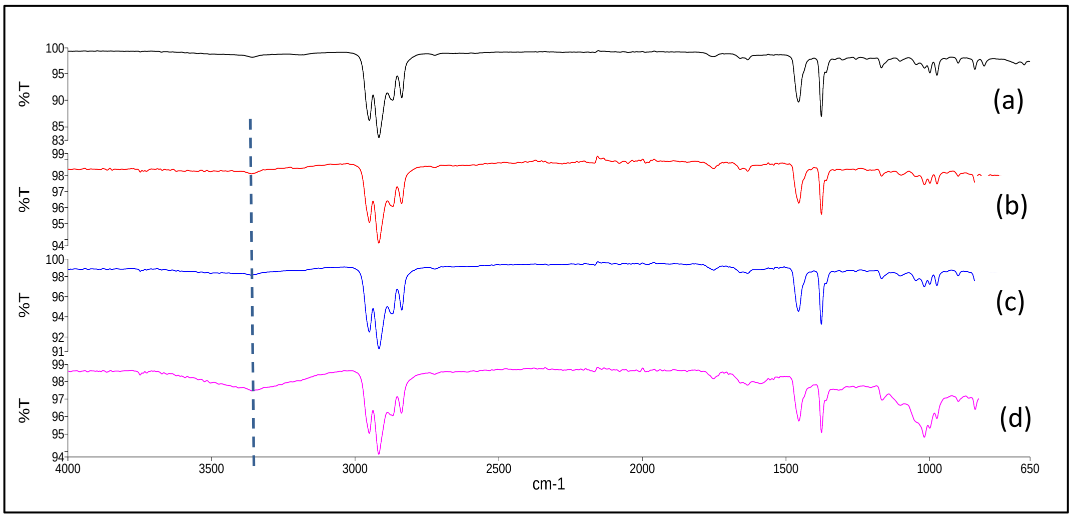


Figure 7 FTIR spectra of PP/PALF at different GO content (a) PP/PALF, (b) PP/PALF/0.5 GO, (c) PP/PALF/1.0 GO, (d) PP/PALF/2.0 GO

4.0 CONCLUSION

The main objective of this study is to investigate the effects of GO at various content on mechanical and thermal stability of PP/PALF composites. The effect of PALF (at a constant content of 10 % content) on mechanical and thermal stability of neat PP compatibilized with PP-g-MAH was also determined. The tensile strength, Young's modulus and impact strength increased with the incorporation of PALF. All mechanical properties with the exception of elongation break improved with the incorporation of 10 % PALF into PP. The addition of 1 phr GO increased the impact strength of PP/PALF from 44.9 to 49.5 J/m, which is about 10 %. However, the tensile strength and Young's modulus did not significantly change with GO content. The study has demonstrated that simultaneous incorporation of GO and PALF into PP has enhanced the mechanical strength of PP. The thermal stability of PP/PALF/GO composites as indicated by T_{max} at 0.5 phr GO content was significantly than neat PP and PP/PALF composites. The percentage of char residue gradually increased when GO was added into PP/PALF composite and at 2.0 phr of GO, the highest percentage of char residue at the final residue was observed.

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