Fabrication process and optimization of hybrid MWCNTS/GF reinforced polypropylene

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***Abstract*—**In this study, polypropylene (PP)/random discontinuous glass fiber/multi-walled carbon nanotubes (MWCNTs) composites were synthesized and processed using mould injection technique. Chopped strand E-glass with an alkali content less than 1% and coated with polyvinyl acetate with Silane coupling agent were used as reinforced materials. Aspect ratio of glass fiber embedded is 450. Multi-walled carbon nanotubes were mixed in a masterbatch to improve the physico-mechanical properties of polypropylene/glass fiber composites. Glass fiber was mixed with thermoplastic-MWCNTs as master batch (1- **15**%) and neat PP in co-rotating twin extruder at 185 and 200 ^oC & 300 r.p.m. It is found that MWCNTs distribution in PP can be improved in the presence of coupling agent. Dispersion of GF and MWCNTs in polymer matrix showed a significant improvement at 200 ^oC. Mechanical properties of PP-GF composites can be enhanced in the presence of MWCNTs up to 8% wt/wt. Hybrid $MWCNT_S$/GF reinforced polypropylene has a potential application for manufacturing high mechanical PP composites.

***Keywords*—**Fabrication process, optimization, hybrid MWCNTS/GF reinforced polypropylene.

I. Introduction

POLYPROPYLENE (PP) is manufactured by addition reaction of propylene having CH_3 group attracted to its linear molecular chains, PP is stronger and rigid to polyethylene (PE). Polypropylene (PP) is saturated polymer (polyolefin) with linear hydrocarbon chain and is expressed as CnH_2n [1-4]. It is relatively easy material to process due to low melt viscosity in spite of its semicrystalline nature. Its pseudoplastic nature enhances its flow at high shear rates. Its melt temperature for injection molding is between 200 °C to 250 °C. Three types of PP grade are available naming Homopolymer, Block copolymers and Random copolymers. Homopolymer is general purpose grade with good strength and stiffness, Block copolymer incorporates 5-15% ethylene with good impact resistance and their toughness can be increased using elastomers. Random copolymers are relatively low melting point grade and it includes of 1-7 % ethylene. PP can be processed by all thermoplastic processing methods i.e. injection molding, extrusion blow molding and general purpose extrusion. Injection molded polypropylene articles can be made with all types of PP i.e. homopolymer, random, impact copolymer and filled copolymer. Since melts exhibits shear thinning properties, it requires high injection pressure and shear rate to fill the mold [5-10]. PP is used in packaging materials, automotive parts i.e. dash boards and bumpers and industrial applications i.e. pipes and sheets. PP is flexible, heat resistant, having good fatigue resistant and have good resistance to acids and alkalis [11-15]. Some drawbacks of PP are brittle properties at low temperature, poor resistant to UV, translucence and flammable. PP is reasonably economical with melting point in the range of 160°C to 160°C. Melt flow index (MFI) value of PP allows to use it in engineering products like wind turbine. PP is liable to chain degradation if exposed to UV or sunlight. In external applications especially in the case of wind turbines it can show cracks and crazes on the surface of blades, these cracks can be deeper with the passage of time and can cause complete failure of wind turbine blades. To overcome this problem UV absorbents or carbon black can be added, these materials provide good resistance to cracks propagation. PP can also be oxidized at high temperature; this problem can also be overcome by adding anti-oxidants. All GFs in common have good insulating properties, elastic modulus (50-90 GPa), low thermal coefficient expansion and high density. GFs are generally chosen for flexibility of sizing, dimensional stability, low cost of raw materials, thermal conductivity, insensitivity to putrefaction. Some constraints in the use of GFs reinforcement in thermoplastic composites are lack of surface conductivity for electrostatic discharge and abrasion wear. Dispersion of GFs in polymer matrix depends upon fiber contents, aspect ratio, and sizing of fibers and real length of fibers in final products. Glass fiber reinforced composites consist of glass fibers of high strength and modulus embedded in polymer matrix. The new material has combine properties of both fiber and matrix i.e. load carrying property of fibers and transferring stress properties of matrix]. The influence of reinforcement is very much evident in GF/PP composites. Storage modulus (E') of GF reinforced PP was found to be 14 GPa as compared to 4.6 G Pa of pure PP.The adhesion between polypropylene and glass fibers can be increased by modifying glass fibers with aluminum alkyl and hydroxy-α-olefin PP chains were grown directly on GF using metallocenic copolymerizaton, three times increase in strength and toughness was found [16]. The interfacial strength between GF and PP can be increased using many methods i.e. using silane as coupling agent which makes covalent bond with glass fibers and increase interfacial strength, using film formers for filament, using lubricants to reduce fuzz, using antistatic agents to reduce static generation, and using

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surfactants for size stability [Global Wind 17-20]. Adhesion between phases is also degraded in severe environmental conditions like high temperature, high stress conditions and elevated moisture [21-27]. The GF/PP composites are preferred due to high availability and low cost. The main difficulty in GF/PP composites is the high melt viscosity and poor wettability of fibers. Polar character of PP leads to the limited wetability and poor fiber matrix interface. Because of low polarity and lack of reactive groups, Silane can be used as effective coupling agent. Another way to improve GF/PP interphase is to add polar functional groups in PP chains keeping in view non polar nature of PP. Polar functional group facilitates homogeneous spreading of additives and fillers. In GF/PP composites polar functional groups are introduced by reaction of PP with esters, carboxylic acids or anhydride groups [28]. GF/PP composites offer good specific strength and modulus make them good candidates for wind turbine blades manufacture [29].

II. Experiment

A. Polypropylene

Polypropylene (PP) QURAIN® PP HM110, EQUATE/ PIC was selected as a matrix. PP homopolymer (density 0.9 g/cm^3) is developed for excellent mold filling, good gloss, high stiffness and antistatic.

B. Glass Fiber

Chopped glass fiber was used to reinforce polypropylene. Discontinues chopped glass fiber (3313) was supplied by (PPG industries, UK). Composition and physical properties of chopped glass fiber are listed in table 1

TABLE I
COMPOSITION AND PHYSICAL PROPERTIES OF CHOPPED E-GLASS

Composition	length	Density	Chopped glass fiber
- Alkali content less than 1% N_2O - Coupling agent: Polyvinylacetate with silane	4.5 mm	2600kg/m^3	

C. Multi-walled carbon nanotubes

The MWCNTs were purchased from Grafen (Turkey). Figure 1 illustrates a SEM image of the received MWCNTs. According to the specification of the supplier, carbon nanotubes dimensions are 9.5 nm (diameter) and 1.5 µm (length) as listed in table 2. They were synthesized by catalytic chemical vapor deposition method. The samples produced from this method were nanotubes with approximately 90% nanoparticles and metal oxide.

TABLE II
SPECIFICATIONS OF MWCNTS

Multi-walled Carbon Nanotubes	
Surface Area	250-300 m2/g
Carbon Purity	> 90 %
Diameter	~ 9.5 nm
Length	~1.5 µm
Metal Oxide	10%

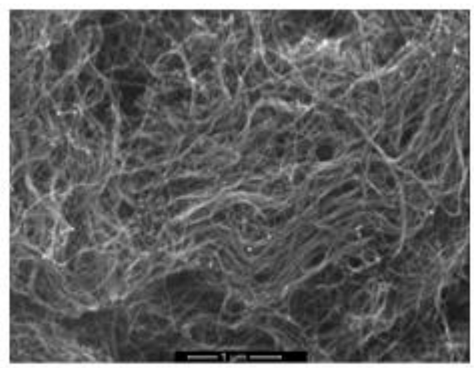

Fig. 1 SEM image of MWCNTs

D. Synthesis of polypropylene/E -glass composites

Samples of polypropylene/chopped glass fiber composites in the range 5–30 wt% fiber content were processed. Matrix and fiber are mixed using co-rotating twin-screw extruder (Labtech Engineering, Company LTD, Thailand) at 185 and 200^{o}C as illustrated in figure 2. The mixture was then shredded and injected into mould using injection moulding (Allrounder 220C, Arburg, Germany) at 220 ^{o}C under 506 atm into standard sample shape (ASTM D 638 I).

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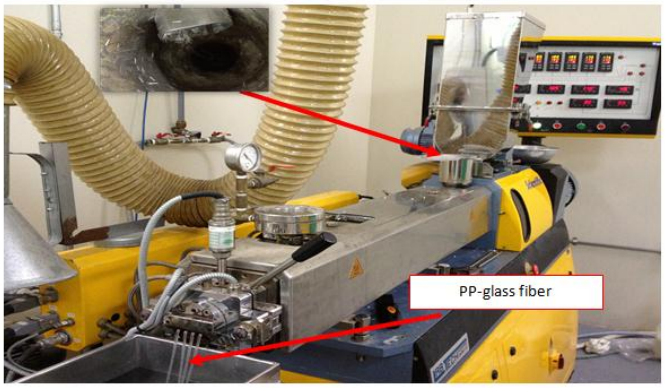


Fig. 2 Extrusion for PP-Glass fiber composites

E. Synthesis of polypropylene/E –glass carbon nanotubes composites

Chopped strand 3313 E-glass (PPG, UK) with an alkai content less than 1% and coated with polyvinyl acetate with Silane coupling agent were used. Glass fiber density is 2.56 g/cm^3, average fiber length 4.5 mm and diameter 10 µm respectively with aspect ratio 450. Chopped glass fiber was used as the reinforcing materials. Multi-walled carbon nanotubes were mixed in a masterbatch form (15-20%, Grafen, Turkey) as illustrated in figure 3. This particular thermoplastic-carbon nantubes masterbatch is defined as melting range starts at 165 ^{o}C and complete thermal degradation at 650 ^{o}C.

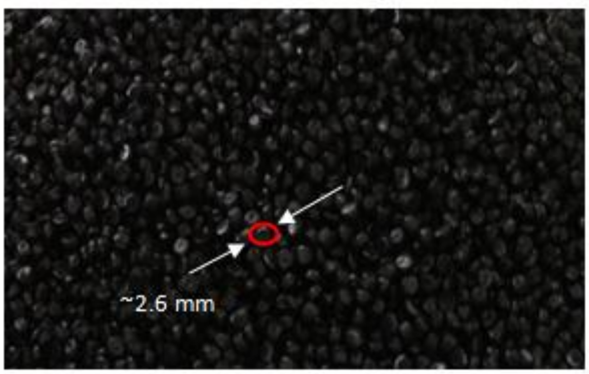


Fig. 3 Thermopastic multiwall carbon nanotubes masterbatch

F. PP Nano-composite processing

Glass fiber was mixed with thermoplastic-MWCNT as master batch (1-15 %) and neat PP in co-rotating twin extruder at 185 and 200 ^{o}C & 300 r.p.m. The compound is then shredded and processed using injection molding (Allrounder, Arburg, Germany) at 220^{o}C and 500 bar to produce tensile and sheet sample shapes as shown in figure 4. Injection molded specimens are processed according to D638 I. Tensile test was carried using ZWICK B066550 (Germany) universal testing machine. A 20-kN load cell was applied. Tension speed was 2 mm/s.

Fig. 4 PP/Chopped glass fiber/MWCNTs composites

G. Mechanical testing

Mechanical tests were carried out on samples of polypropylene composites to measure the static properties as shown in figure 5. Polypropylene specimens were manufactured according to D638I. Temperature for all the tests was 25 ^{o}C. Each datum of the tensile tests was the average of four repeated test values respectively.

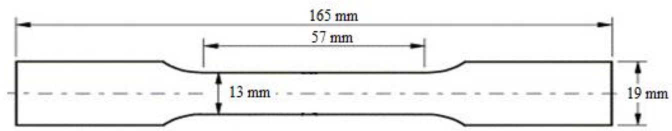


Fig.5 Dimensions of tensile test specimen

H. Surface morphology

Topography of fracture surface was investigated using Atomic Force Microscopy(AFM). Peak Force tapping mode - Bruker Dimension Icon Scanning Probe Microscope (SPM) was used to study PP-composites surface topography. Nominal tip radius (2-12 nm) was applied. The tip used was Scan Asyst-Air.

The fracture cross section of the PP-GF specimen was inspected by digital microscope (KEYENCE VHX-500F, Osaka, Japan) to study the interface morphology.

III. Results and Discussion

A. Effect of injection molding processing temperature on PP composites

Figure 6 (a) shows that the PP - MWCNTs-Thermoplastic masterbatch has a poor mixing with PP-Chopped glass fibers composites at 185 ^{o}C. Figure 6 (b) showed better mixing phase at 200^{o}C. This can be attributed to high adhesive force between the MWCNs and PP (masterbatch) in the presence of maleic anhydride coupling agents. Large amount of heat and pressure are required to melt the PP-MWCNTs in case of high matrix/dispersed phase adhesion bond as shown in figure 6(a). Increasing the melting temperature up to 200 ^{o}C was applied to obtain good mixing and MWCNTs distribution.

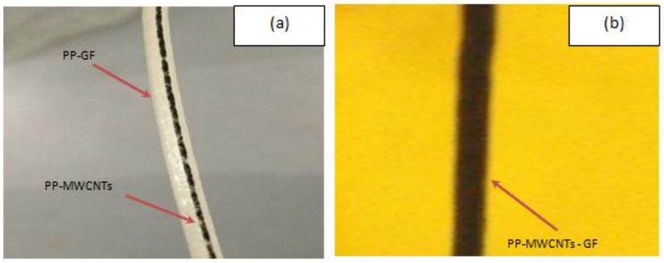


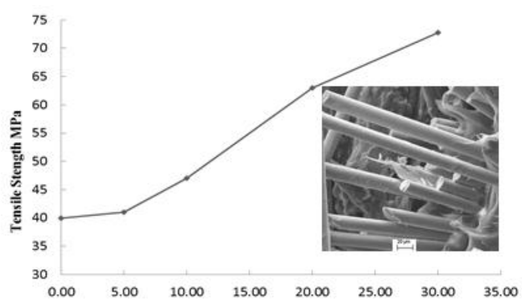
Fig. 6 PP-Chopped glass fiber and MWCNTs composites (a) at 185 ^{o}C (b) at 200 ^{o}C

B. Tensile properties of PP- Chopped glass fiber composites

Figure 7 shows the variations of the tensile strength with respect to chopped glass fiber weight fraction. It is depicted that the addition of glass fiber (GF) from 10 to 30 wt % effectively improves the tensile strength values from 40 to 72 MPa respectively. However, it can be observed from figure 7 that the tensile strength enhanced slightly at 5 wt % GF. This can be attributed to presence of voids at GF/PP intephase due to low melt flow around the GF [11]. The less improvement of tensile strength at the low concentration of GF (0-10 %) comparing with sudden improvement at higher fiber loading can be attributed also to lack of stress transfer at low fiber loadings.

C. Tensile strength properties of PP-GF-MWCNTs composites

Strength of PP has been improved in the presence of MWCNTs up to 95 % higher than neat polypropylene as shown in figure 8. PP-GF-MWCNTs composites can show higher tensile strength since partial stress can be transferred in to MWCNTs embedded in PP-GF composites. In addition, the MWCNTs can work as fiber bridging among the PP matrix and GF. This will lead to improve the stress transfer across the system components.



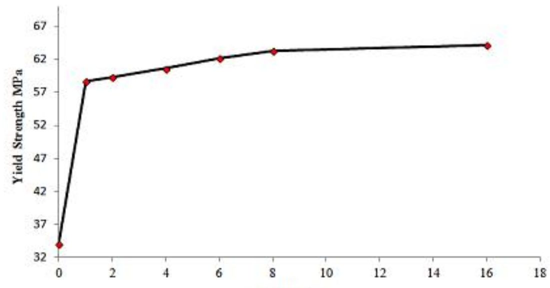


Fig. 8 Effect of MWCNTs on strength of neat PP

D. Surface analysis of PP-glass fiber

AFM 3-D surface images of PP-GF composites (figure 9 (a,b)) and neat PP are shown in figure 4.9 (c,d) . The glass fiber increases surface roughness but, at the same time, improves substantially the Modulus of elasticity.

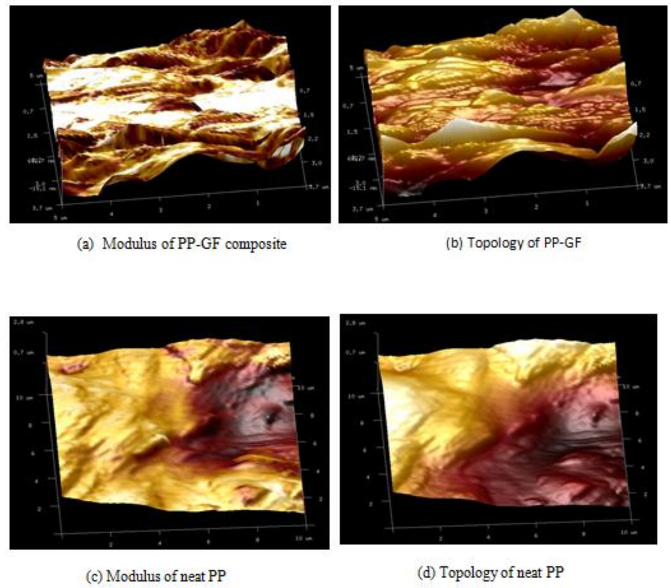


Fig. 9 AFM 3-D surface images

Figure 10 shows the glass fiber orientations and length using digitial microscopy (Keyence **VHX-500F).** The stress is assumed to increase linearly when the fiber length is greater than the critical length. Average fiber length for illustrated fibers in figure 10 is 0.14 mm. Fiber pull-out or matrix-fiber interfacial bond failure can be observed if the fiber length is less than critical length.

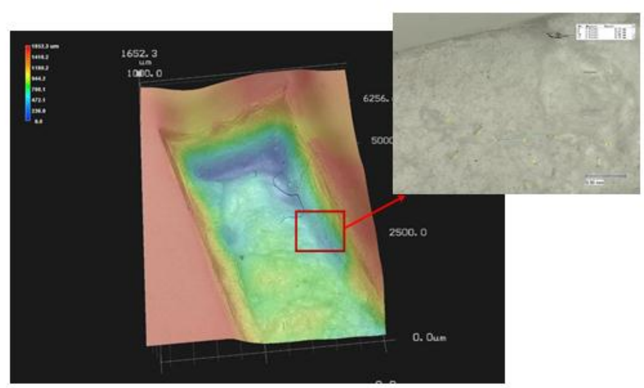


Fig.10 GF orientation and length using digital microscope-KEYENCE VHX-500F

IV. Conclusion

Temperature for mixing and compacting PP-GF-MWCNTs components is 200 ^{o}C in the extrusion process. The presence of MWCNTs can improve the tensile strength of PP-GF composites. Stress transfer across PP composites can be improved significantly as the GF loading above 10%..

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