



COMPARISON OF RHEOLOGICAL AND MECHANICAL PROPERTIES OF MODIFIED POLYPROPYLENE – SHORT GLASS FIBER COMPOSITES

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Short glass fiber (SGF) reinforced composite materials were principally fabricated using polypropylene (PP) as thermoplastic matrix. Short glass fiber and polypropylene frequently suffer from lack of adequate fiber-matrix adhesion. This problem was addressed by grafting polypropylene (PP) with maleic anhydride (MA) in the presence of benzyl peroxide (BPO) as an initiator. The results revealed that by increasing fiber contents from 5 to 40 %, tensile strength increases while elongation at break decreases. Rheological behavior was found to be pseudoplastic, whereas viscosity increases by increasing SGF contents. A decrease in die swell was observed with increase in SGF contents.

Keywords: Short glass fiber, Adhesion, Grafting, BPO, Recycle polypropylene, Die swell

1. Introduction

Thermoplastic composites consisting of PP filled with short glass fiber (SGF) covered with EILs (Engineered interphase layers) can be designed to achieve more stiffness and toughness than the virgin PP [1]. In addition to the effect of fiber content and particle shape, interphase thickness, elastic moduli relative to those of the matrix and adhesion to the matrix play a crucial role in deciding the composite response to mechanical loading. The thermodynamic forces are determined by the surface free energy of components and the system tends to acquire morphology with minimal total free energy. In a majority of the PP composites, the free energy of the filler is significantly greater than that of the soft and rigid interphases used, which is again greater than that of the PP bulk.

During the last few decades, reinforced thermoplastic polymers have emerged as versatile, high performance and economical materials in automotive, transportation, aeronautical and marine industries [2]. Furthermore due to their higher impact properties these composites are considered as suitable for composite armor structures. More recently, short glass fiber (SGF) composites with polypropylene (PP) have been

commercialized (Saint Gobain Vetrotex's Twintex, Baycomp). These new SGF/PP composites present the general advantages of semi-crystalline thermoplastic matrix composites with respect to molding processes, low volatile organic compound emissions, damage tolerance, resistance to chemical environment and recycling possibilities.

Several studies have been reported on the modification of SGF/PP composites. Laura D.M. et al. [3] focused on surface modification of polypropylene and short glass fiber (SGF) for better adhesion. Wang et al. [4] have reported the mechanical properties and morphological structures of short glass fiber reinforced PP composite. Bureau and Denault [5] studied the fatigue resistance of continuous glass fiber/polypropylene composites.

E. Ségard et al. [6] focused attention on damage analysis and the fiber-matrix effects in polypropylene reinforced by short glass fibers. Fua et al. [7] focused attention on tensile properties of short-glass-fiber and short carbon fiber reinforced polypropylene composites. Rheological properties of short fiber filled polypropylene were investigated by Sepehri et al. [8]. In these structures although the reinforcement was different but the same

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polymer (polypropylene) matrix was employed.

Die swell is a flow phenomenon which commonly occurs when polymer melt emerges from a confined boundary. This phenomenon can be easily demonstrated by extruding a polymer melt through a capillary die. Die swell normally occurs due to memory effects of polymeric fluid. Die swell varies with shear rate, temperature, die length and filler content [9-13].

In the present work, we have made a comparison of mechanical and rheological properties of polypropylene filled with short glass fiber (SGF/PP), short glass fiber and maleic anhydride grafted polypropylene composite (SGF/PP-g-MA) and short glass fiber and maleic anhydride grafted polypropylene through addition of recycled polypropylene (SGF/PP-g-MA/RPP). Plastograph (Torque versus Time curve) and die swell behavior of the blends were also studied.

2. Experimental

2.1. Materials

Polypropylene (PP) used in this study was purchased from Reliance Industries Jamna Garh, with MFI value of 16 g/10 min (ASTM D1238). Short glass fiber (SGF) was donated by Fiber Craft Industries, Pakistan. The recycle injection molding grade PP with MFI value of 12 g/10 min. was obtained from a local Polymer Processing Lab. University of Engineering and Technology, Lahore. The maleic anhydride and benzyl peroxide were supplied by Akzo Nobel, Taiwan.

2.2. Preparation of PP-g-MA

Polypropylene-grafted-maleic anhydride (PP-g-MA) was prepared by melt extrusion. The grafting reaction was carried out in a Brabender Plasticoder (PLE 330) at 180 °C and screw speed of 80 revolutions per minute (rpm). Sample containing 2 parts per hundred (phr) maleic anhydride, 1 phr benzyl peroxide and PP was dry blended before charging to the mixer and mixing was continued for 7 min.

2.3. Blend Preparation

Fiber-plastic blends have generally been prepared by melt mixing techniques. Melt mixing is an easy and economical way of blending to avoid problems of contamination and solvent or water removal etc. Here three types of blends (PP/SGF,

PP-g-MA/SGF, and PP-g-MA/SGF/RPP) were prepared. Different samples of the blends were prepared through varying the SGF and PP contents. The maleic anhydride and benzyl peroxide contents were kept constant in the blends. All these blends were prepared in a Brabender Plasticoder Mixer (PLE-330) at a temperature of 180 °C. The rotor speed was 100 rpm and time of mixing was 5 min. The products were ground to powder form. Composition of the blend is outlined in Table 1.

2.4. Mechanical testing

The samples for mechanical testing were prepared by compression molding at 170 °C in a hydraulic press. The tensile property measurements were performed on TIRA universal testing machine (Model 2810 E6) using dog-bone specimens in accordance with ASTM D638.

2.5. Rheological testing

The test apparatus used in the study was Melt Flow Indexer (Karg industritechnik) with die diameter 2.095 mm and length 4, 10, 30 mm. Experiments were performed at 220 °C in accordance with ASTM D1238. Test loads were varied from 2.16 kg to 21.6 kg for the development of rheograms. Extrudate diameter was measured with vernier caliper.

3. Results and Discussion

3.1. Plastograph studies

The processing characteristics of the blends have been studied from time-torque curves obtained during mixing in Plasticoder. Torque - time plots for different compositions of the blends are shown in Figure 1. The figure clearly indicates that torque increases as the cold material is introduced to the hot chamber due to resistance offered by unmelted beads of polypropylene (PP). Once the material attains the set temperature and gets melted, the torque decreases. Again torque increases with addition of SGF and decreases steadily as mixing proceeds. Leveling off can be observed in the torque value which corresponds to homogeneous blend formation. The two peaks in all the figures for all compositions correspond to addition of PP and SGF into the mixer respectively. The highest value of the torque is observed for the blends containing RPP. This observation can be

Table 1. Blend composition for PP/SGF, PP-g-MA/DGF and PP-g-MA/SGF/RPP composites.

Composites	PP /SGF Blend Compositions		PP-g-MA / SGF (MA 2 phr and 1 phr BPO)		PP-g-MA / SGF (2 phr MA and 1 phr BPO and 30% RPP)	
	PP %	SGF %	PP %	SGF %	PP %	SGF %
1	95	5	95	5	65	5
2	90	10	90	10	60	10
3	85	15	85	15	55	15
4	80	20	80	20	50	20
5	75	25	75	25	45	25
6	70	30	70	30	40	30
7	65	35	65	35	35	35
8	60	40	60	40	30	40

attributed towards intrinsically higher viscosity of RPP.

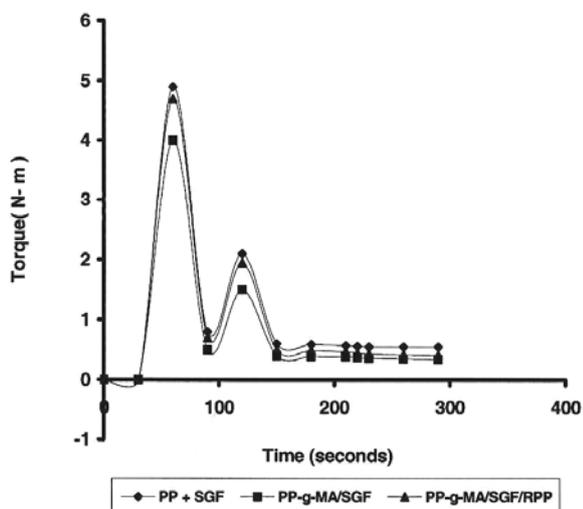


Figure 1. Torque-time plots for PP and SGF blends containing different contents of SGF as given in Table 1.

3.2. Mechanical testing

It has been observed that tensile strength of all three types of blend increases by increasing the fiber content. The results are shown in Figure 2. The increase in tensile strength with increase in fiber content is obvious. The tensile strength of fiber is of the order of MPa and it is expected to confer the higher tensile strength in composites. Some of the fiber strength is transmitted to matrix through the interface developed. This is due to the stress bearing capacity of the fiber at the interface. Figure 2 illustrates that for the same level of filler loading; tensile strength for PP-g- MA/SGF blend is more than the ungrafted PP/SGF. The increment can be attributed towards the achievement of

greater wettability and dispersion of the fiber and improved adhesion at the fiber-matrix interface as a result of grafting. Tensile strength of PP-g-MA/SGF/RPP composite is less than PP-g-MA/SGF because of incorporation of RPP in which the properties have deteriorated. The above is true upto 30 % of filler loading, above 30 % the tensile strength of grafted composites decreases. We believe that this is due to fiber agglomeration that reduces the adhesion between the phases and hence reduces the properties. Blends containing SGF and virgin PP modified with maleic anhydride give better strength than the blend containing RPP.

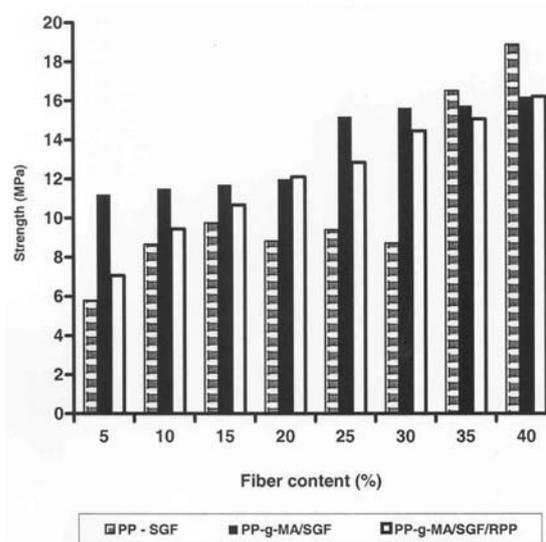


Figure 2. Variation in tensile strength of blends of (PP/SGF, PP-g-MA/SGF, PP-g-MA/SGF/RPP) containing different contents of SGF.

Figure 3 illustrates the effect of fiber loading on elongation at break of three types of the blends. A steady decrease in elongation at break is observed

with increase of filler loading. It has been observed that elongation at break for untreated blends is greater than that of the treated blends which is a significant indication of good degree of adhesion at fiber-matrix interface in treated blends. The deformation capacity of the matrix is restricted by good fiber-matrix adhesion in both elastic and plastic zones. Figure 3 also reveals that PP/SGF blends show greater elongation at break than the other two types. The elongation at break for PP-g-MA/SGF/RPP blends is greater than its counterpart containing virgin PP, because RPP reduces the adhesion.

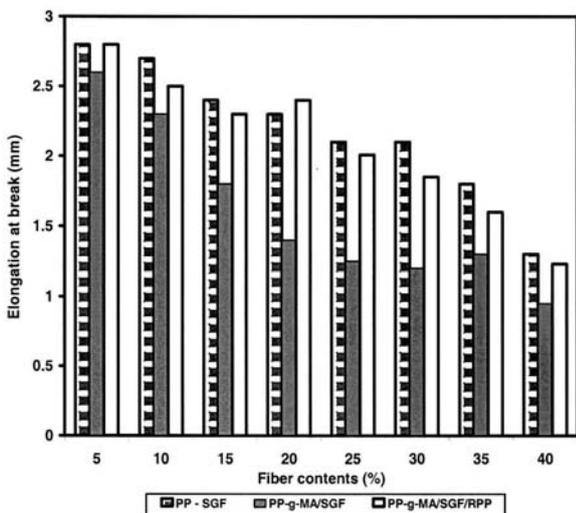


Figure 3. Variation of elongation at break with fiber contents.

3.3. Rheological studies

3.3.1. Development of rheogram

Melt Flow Index (MFI) is an important parameter that is widely used to characterize the flow property of resins due to its easy measurement and manufactures usually supply a value of MFI measured under standard conditions for each resin. Figure 4 shows the changes in the MFI as the fiber content in the composites changes.

From the definition of MFI

$$MFI = 10.60 \cdot w \tag{1}$$

where, w is weight rate of flow (in g/sec). It is evident from Figure. 4 that the MFI values for PP-g-MA/SGF and PP-g-MA/SGF/RPP composites are much greater than the corresponding MFI values for PP-SGF composite. This behavior is

due to the improve adhesion at the interface of PP and fiber blend containing MA that is not present in the PP-SGF blend. Also the addition of the RPP reduces the union between matrix and fiber.

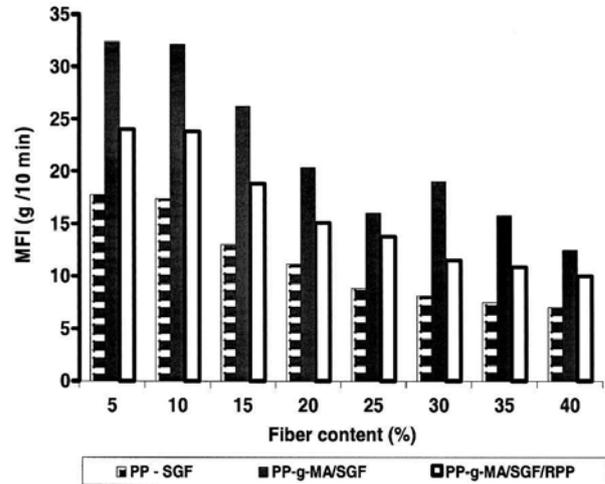


Figure 4. Variation in MFI (2.16kg) value with fiber contents.

In melt flow indexer, the shear stress is determined from the pressure applied by a piston. The shear rate is determined from the flow rate. As the geometry of melt flow indexer remains constant so the expressions reduces to [14, 15].

$$\tau = 9.13 \times 10^4 L \tag{2}$$

$$\gamma = 1.83 \frac{MFI}{\rho} \tag{3}$$

where τ is a shear stress (Pa), γ is a strain rate; L is test load (Kg). To evaluate viscosity using Power Law model we have to calculate power law parameters.

Power law exponent;

$$n = \frac{\log(HL) - \log(LL)}{\log(HLMI) - \log(MI)} \tag{4}$$

consistency index;

$$m = \frac{9.13 \times 10^4 L}{1.83 \frac{MFI}{\rho}} \tag{5}$$

where LL is standard load (usually 2.16 kg) and HL the high load (usually 21.6 kg). MI (melt flow index refers) to standard weight of 2.16 kg and $HLMI$ to "High Load" melt index 21.6 kg. Hence, the shear

thinning behavior is frequently expressed by power-law model, which yields good data fit for large number of thermoplastic composites. The relation relates the viscosity with shear rate.

$$\eta_a = m\dot{\gamma}^{n-1} \quad (6)$$

where η_a is the apparent viscosity and 'm' is the melt consistency index. Figures 5 and 6 indicate the flow properties of polypropylene composites filled with short glass fibers as a function of shear rate and fiber content respectively. The apparent viscosity decreases quite sharply with increasing shear rate for all the composite systems (PP/SGF, PP-g-MA/SGF, PP-g-MA/SGF/RPP), which implies a shear-thinning behavior of the materials. It is apparent from the data in Figure 5 that there is a sharp decrease in the viscosity of PP/SGF composite with shear rate because polymeric chains and fibers orient in the flow direction at the higher shear rate. PP-g-MA/SGF, PP-g-MA / SGF/RPP composites also show a decreasing trend of viscosity with shear rate but the magnitude of change is small.

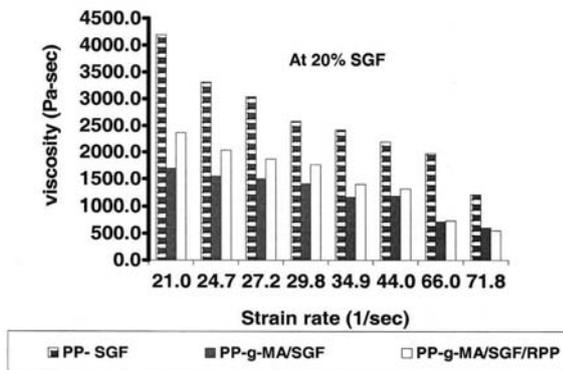


Figure 5. Development of rheogram using power law model for (PP/SGF, PP-g-MA/SGF, PP-g-MA/SGF/RPP).

The shear viscosity of all composites increases as filler concentration is increased due to the restriction of the polymer chain motion by the filler particles (Figure 6). Interestingly, at low shear rate the addition of small amounts of SGF results in a significant enhancement in the apparent shear viscosity. At high shear rate, the magnitude of change in the shear viscosity for the composites is small. In other words, the viscosity of the composites tend to converge at higher shear rates due to the lesser pseudoplasticity of SGF filled systems, i.e. the power law exponent n is lower. Figure 7 shows the 'n' values for all the composites

studied. The n value for composites with higher fiber content is lower than the composites with lower fiber contents. The values of 'n' for PP-g-MA/SGF and PP-g-MA/SGF/RPP composites are comparable and also show a decreasing trend but the values are greater than PP/SGF composite because of the higher compatibility of phases so there is no significant effect of RPP on the power law index.

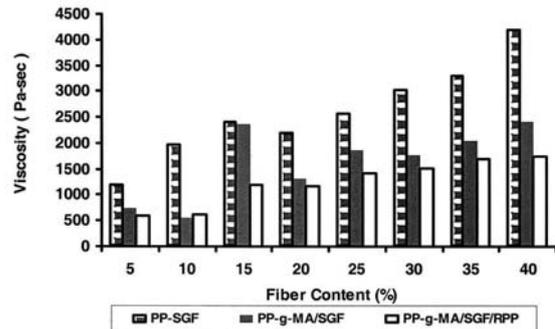


Figure 6. Variation in viscosity of composites with fiber contents.

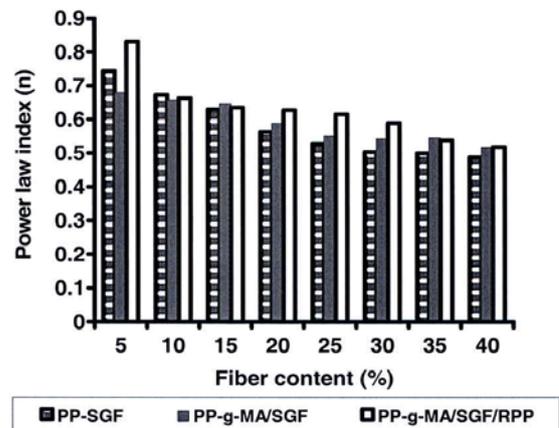


Figure 7. Variation of power law index(n) with fiber contents.

3.3.2. Die swell

Figure 8 shows the dependence of % decrease in die swell on the fiber content. Die swell occurs due to the recovery of elastic deformation imposed in capillary. The presence of the fiber can dissipate energy of the system by its movement which can be easier than that of polymeric chains for the given shear rate. Hence the elastic recovery of the filled system is less than that of unfilled system. Die swell is reduced because the percentage of polypropylene decreases and that of glass fiber increases. PP-g-MA/SGF composite shows minimum die swell as the melt undergo chain

scission and also the increased grafting reduces the die swell. Die swell is primarily driven by the release of normal stresses at the die exit. Die swell can be expressed by the simple relation

$$\alpha = \frac{\text{Extrudated diameter}}{\text{Die diameter}} \quad (7)$$

where α is the die swell. It is clear from Figure 8 that die swell decreases as the fiber content in the composite increases. The behavior is same for all the composites but PP-g-MA/SGF/RPP shows maximum reduction in the die swell due to the presence of RPP. Recycling thus reduced viscoelastic property.

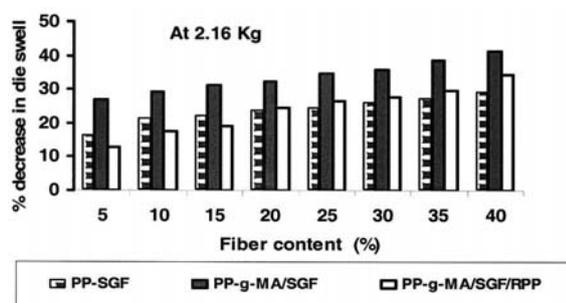


Figure 8. Variation of % decrease in die swell with fiber contents.

4. Conclusions

The results in this paper indicate that fiber contents significantly affect the mechanical and rheological properties of these three composite materials studied. The improvement in the tensile properties (TS) of PP-g-MA/SGF composite can be attributed to the increase in compatibility at interface and addition of RPP reduces the compatibility.

The rheological properties of blends of short glass fibers with PP, PP-g-MA and PP-g-MA/RPP have been studied in the molten state. The viscosity of these composite materials increases with fiber contents. Viscosity overshoot is observed in case of PP/SGF which makes the processing more difficult. Viscosity decreases with increasing shear rate and shear thinning behavior is observed. The die swell ratio decreases with increasing fiber contents but the effect is not very prominent.

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