The Effect of Polypropylene Grafted Maleic Anhydride on the Polypropylene / Natural Rubber Blends Filled with Cyperus Odoratus

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Abstract A new thermoplastic blend was developed by using polypropylene (PP) with natural rubber (NR) as the base material. The natural filler is added to enhance the properties of PP/NR blend. Two series of blends under varying conditions were prepared and investigated. The first series was to compare the properties of PP/NR blend with different filler loading. Second is to investigate the effect of polypropylene grafted maleic anhydride (PP-MAH) on the properties of PP/NR blend filled with Cyperus Odoratus. Process development, tensile properties, thermal analysis, FTIR analysis and morphological characterization of blends were investigated with the variation of the conditions of the blend. The increasing filler loading decrease the tensile properties of the PP/NR blend as support by morphology study of the PP/NR blends. Incorporation of PP-MAH was resulted in improved tensile and thermal properties compared to uncompatibilized counterparts. The increment in tensile strength was confirmed by the SEM study that showed better dispersion of NR in the PP matrix and improved adhesion between the two phases.

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1 Introduction

*Cyperus Odoratus* can be considered as natural filler which contain lignocellulosic fibers. The major source of the lignocellulosic fibers or similar feedstock can come from recycling fiber based products, such as paper, waste wood and agricultural residues. The main advantages of using lignocellulosic fibers as an additive in thermoplastics is the low density, biodegradable, abundant, low cost, high specific stiffness and strength, desirable fiber aspect ratio, less abrasive nature to the equipment during process renewable, high filling levels possible, low energy consumption and wide variety of fibers available throughout the world [1-5]. Moreover, they can attract considerable interest as reinforcing fillers for thermoplastics especially those with a relatively lower melting point like polypropylene, high and low density polyethylene [6-8]. The properties deterioration of incorporation of *Cyperus Odoratus* into PP/NR blends is due to the difference between the surface properties of the natural filler and matrix. The natural filler is highly polar and hydrophilic while the matrix is generally non-polar and relatively hydrophobic [9-11]. Without compatibilizer, natural fillers embedded in a polymeric matrix generate unstable interfaces and the stress applied to the filler/polymer composite is not efficiently transferred from the matrix to the filler remains underexploited. The poor ability of the polymer to wet the filler hinders the homogenous dispersion of fillers within the polymeric matrix [12]. Therefore it is important to improve compatibility of the two polymeric phases of the blend to achieve better homogeneity and morphology for improved and desired mechanical properties [13-15]. Compatibilizing system that use polypropylene grafted maleic anhydride (PP-g-MAH) and carboxylated acrylonitrile butadiene rubber (NBR-RCOOH) as a compatibilizer was investigated by Soares and co workers [16] and found that there is an improvement in tensile and swelling properties of PP/NBR blends.

2 Experimental

2.1 Materials

The raw material that were used in mixing and compounding used in this study such as PP, NR, *Cyperus Odoratus*, ZnO, CBS, stearic acid, sulphur and PP-g-MAH are listed completely with the function and supplier in the Table 1.
Table 1: List of raw materials, their functions and suppliers

| Raw materials  | Function       | Supplier                        |
|----------------|----------------|---------------------------------|
| SMR L          | Elastomer      | RRIM Guthrie Group Sdn. Bhd.    |
| Polypropylene  | Plastic        | Titan Polymer Sdn. Bhd          |
| Cyperus Odoratus | Natural filler | Paddy field                     |
| Zinc oxide     | Activator      | Anchor Chemical Co (M) Ltd.     |
| CBS            | Accelerator    | Anchor Chemical Co (M) Ltd.     |
| Stearic acids  | Activator      | Anchor Chemical Co (M) Ltd.     |
| Sulphur        | Vulcanizing agent | Anchor Chemical Co (M) Ltd. |

2.2 Preparation of the sample

2.2.1 Preparation of PP/NR/ Cyperus Odoratus composites

Blends were prepared using heated two roll mill. Mixing was done at temperature 170°C and rotor speed 13rpm and 10 rpm for front and back mill for 12 min. The effect of compatibilizer of polypropylene grafted maleic anhydride (PP-g-MAH) on developed PP/NR composite. 3 wt% of the compatibilizer will be added. The mixing was carried out by using heated two roll mill with temperature 170°C for 12 min. Samples of the blends were compression molded in an electrically heated hydraulic press. Procedure of moulding of all blends mentioned above except blends of PP/NR involved preheating of the sample for 3 min at 170°C, followed by compressing (pressure of 10 MPa) of the mould for 7 min at the same temperature and subsequently cooling under pressure for another 5 min.
3 Characterization and Testings

Tensile test were carried out according to ASTM D638 using the Instron tensile testing machine. A cross head speed of the tensile machine was maintained at 10mm/min and tests were performed at 25± 3°C. Stress at peak (MPa), Young’s modulus (MPa) and elongation at break (%) were automatically calculated by the software. The average properties were calculated after taking the statistical average value of at least five measurements for each blends. Series of Fourier-transform infrared spectroscopy (FTIR) spectra were recorded with the IR spectrometer in the range of 550-4000cm⁻¹ at resolution of 4 cm⁻¹ using a Perkin-Elmer 2000 series instrument. All spectra were scanned for four times before the spectrum is confirmed. Thermogravimetric analysis (TGA) was carried out by using Perkin-Elmer Pyris 6 TGA analyzer with temperature range from 30ºC to 600ºC at a nitrogen flow of 50 ml/min and at a heating rate of 10 °C/min. Lost of weight in the sample was then recorded automatically from the analyzer. Morphology analysis for the blends tensile fracture surface was carried out using a scanning electron microscope (SEM) model JEOL JF6460LA. Samples that had already undergone tensile test were collected and subjected to the scanning electron microscope (SEM). All the test specimens were taken from tensile fracture with maximum care to avoid any damage and contamination that would affect the result. Fractured surfaces of the specimens were coated with a thin gold layer of about (1.5-3.0nm) thickness to avoid electrostatic charging during examination and poor image resolution. Differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. DSC measurements were carried out under nitrogen on samples of 5-10 mg using a Perkin-Elmer DSC-7 apparatus. The samples were placed in standard aluminium pans with pierced lids. The scanning rate was of 10 °C/min. The first heating scan was carried out from 30-190ºC and hold for 5 mins then 190-30 ºC and hold for 5 mins then 30-230 ºC for the determination of the glass transition temperature, T_g.

4 DISCUSSION

4.1 Structural analysis

Fourier transform infrared is used to determine the functional group in PP/NR blend with ratio (70:30). The FTIR spectra analysis of PP/NR blend is shown in Figure 1 below. From the figure, it can be seen several bands that indicates the functional group in the blend system. First, the shoulders observed in the region of 3100-3010cm⁻¹ shows the =CH stretch and due to the presence of alkene groups in natural rubber. A strong absorption band appears at the range of 2950-2800cm⁻¹ corresponds to the stretching vibration of C-H bonds that indicates
alkanes groups which is dominantly by polypropylene structure in the blend system [17]. Finally, the existence of strong peak at range of 1465-1537 cm⁻¹ represents the CH₂ bending. The different bands at 1712 and 1637 cm⁻¹ which are associated with the stretching vibrations of the C=O and C=C groups of the acrylic, respectively [18]. The broad shape of the C=O peak suggests that this group is in interaction with the surface through hydrogen bonds with the hydroxyl groups [19]. The extent of carbonyl groups is observed in the region of 1712-1860 cm⁻¹ with small peaks and shoulders detected in the spectra of the blend system [20]. Figure 1 shows the FTIR spectra of PP/NR-MAH with 10 wt% filler loading. The spectrum of grafted polypropylene (PP-g-MAH) compared to the one without compatibilizer, shows the appearance of an absorption band at 1790 cm⁻¹. This band which attributed to the symmetric and asymmetric stretching vibration of C=O group, proves that the grafting took place.

Fig. 1. FTIR spectra of PP/NR-MAH with 10 wt%

4.2 Tensile properties

The properties of thermoplastic rubber blends are dependent on the material properties of individual phases, blend ratio, the phase morphology and the interactions at the interface [21]. The tensile properties of immiscible polymer blends are affected by the addition of compatibilizers. The tensile properties namely tensile strength, Young’s modulus and elongation at break of uncompatibilized blends of PP/NR filled with *Cyperus Odoratus* and compatibilized blends of PP/NR with maleic anhydride are demonstrated in Figures 2(a) (c) respectively. The tensile properties are found to be improved with addition of PP-g-MAH into the blends. The trend of the tensile strength when there is higher in filler loading is
increasing from 14.99 MPa to 15.87 MPa. Then the tensile strength decreases as higher loading filler to 12.08 MPa and 11.5 MPa. The highest tensile strength is when 10 wt% of filler loading is incorporated into the blend system. The tensile strength of blend system that is added with compatibilizer is higher compared to PP/NR blend with filler loading. The increasing in tensile properties is due to the increased dipolar interaction between the PP-g-MAH and NR phase, which causes reduced in interfacial tension between the PP and NR phases [22-23]. However, the tensile strength is at highest value when 10 wt% of natural filler is added into the blend. This shows the highest value of natural filler into the blend system. As the filler loading increases, the tensile strength decreases because the filler doesn’t interact with the matrix. The filler does not facilitate the stress transfer to the matrix. The effect of compatibilizer on the Young’s modulus can be seen from Figure 2(b). From the graph, the highest Young’s modulus is at 10 wt% filler loading with the presence of compatibilizer which is 596.3 MPa. The lowest is 400.8 MPa when 30 wt% filler loading. Studies by Pukansky [24] said that Young’s modulus was measured during the process of elastic deformation in the composites where the movement of at the filler-matrix interfaces was very limited. When the polymer is filled with rigid particles, the polymer itself will contribute to the elasticity of the composites. The increase in the modulus of the composites due to the alignment of the polymer, bonding of the filler to the matrix and the fraction of filler packing. The effect of PP-g-MAH on elongation at break of PP/NR blend filled with Cyperus Odoratus is illustrated in Figure 4.16. Generally, adding a rigid filler into the PP/NR will decreased the elongation at break. From the Figure 2(c), that unfilled PP/NR exhibits ductile failure with the elongation at break 29.05%. However, with the incorporation of PP-g-MAH into filled PP/NR blend, the elongation at break has slightly improved compared to filled PP/NR without compatibilizers. The addition of PP-g-MAH into the same composition has increased the elongation at break from 17.76% to 26.5% and 27.4% respectively. Enhancement in ductility could be due to the presence of maleic anhydride in PP-g-MAH which acts as dispersing agents for Cyperus Odoratus into the matrix. Consequently, the ductility of Cyperus Odoratus filled PP/NR blend can be improved.
Fig. 2. Tensile properties of PP/NR and PP/NR-MAH composites.
4.3 Morphological Study

The effect of PP-g-MAH as a compatibilizer on the morphology of the PP/NR blends was investigated by scanning electron microscopy and the micrographs of tensile fractured surfaces of PP/NR with filler loading at 10% and 30% are illustrated in Figure 3 and 4. From the figure we can see that the blend system with PP-g-MAH as compatibilizer exhibit better dispersion of the fiber in the matrix. The fiber is well embedded in the continuous phase of the matrix. This shows a good adhesion between the natural filler and the matrix, PP. Generally polypropylene is categorized as a non-polar molecule while *Cyperus Odoratus* is polar molecule. PP becomes polarized by grafting with maleic anhydride. The addition of PP-g-MAH into the blend caused to increase dipolar interaction between the filler and matrix. Therefore, it could be achieved better adhesion and better dispersion of PP/NR and natural filler by compatibilizing the blends with PP-g-MAH.
Fig. 3. Scanning electron micrograph of surface of PP/NR-MAH blend with 10 wt% filler loading at (a) x150 magnification (b) x300 filler magnification
4.4 Thermal stability

The Figure 5 (a) and (b) illustrated the TGA and DTG curves of PP/NR blend with filler loading and filled PP/NR blend with the presence of filler loading. The degradation process starts at 20 °C and complete at 580 °C. From the graphs, it can be seen that filled PP/NR with the presence of compatibilizer have more resistance against degradation and have a better
thermal stability compared to filled PP/NR blend. The control specimen has the highest weight loss followed by PP/NR blend with 10 wt% filler loading without the presence of compatibilizer. At the final decomposition point, total weight loss for of PP/NR blend with 30 wt% filler loading with the presence of PP-g-MAH lower compared to PP/NR blend with 10 wt% of filler loading. With the addition of compatibilisers, PP-g-MAH, the end degradation temperature were improved further. In this point of view, it can be concluded that the thermal stability of PP/NR blend filled with Cyperus Odoratus was improved with the addition of compatibilisers.

Fig. 5(a). The TGA curves of PP/NR blend with filler loading and PP/NR-MAH with filler loading
4.5 Differential Scanning Calorimetry (DSC)

The effect of compatibilisers (PP-g-MAH) on the blend can be seen as illustrated in Figure 6 (a) and (b) respectively. The effect of compatibilisers on thermal properties of PP/NR blend with filler loading been analysed in isothermal DSC experiments. In this study, details of thermogram obtained for various compositions of filler loading with and without PP-g-MAH have been plotted. Compared to the virgin PP/NR blend the PP/NR blend with filler loading have lower crystallinity. Among the filled PP/NR blend composition the addition of PP-g-MAH has significant effect on increasing the crystallization and melting temperature, while the filled PP/NR blend without PP-g-MAH does not show significant effect on melting and crystallization temperatures of composites. Judging from the decreasing height of the peaks compatibilised filled PP/NR blend as compared to control, it appears that the incorporation of the compatibilisers reduce the level of crystallinity of PP/NR blend. Slower crystallisation rate of compatibilised filled PP/NR blend is observed by broadening of the crystallisation peak and reduction of the melting point. Other reason for the reduction of the melting temperature of all compatibilised filled PP/NR blend due to the disturbance of crystallinity formation induced by the filler in the system during coolong process.

Fig. 5(b): The DTG curves of PP/NR blend with filler loading and PP/NR-MAH with filler loading
Fig. 6(a): The heating curve of PP/NR blend with filler loading and PP/NR-MAH with filler loading

Fig. 6(b): The cooling curve of PP/NR blend with filler loading and PP/NR-MAH with filler loading
5 Conclusions

The properties analyzed from the tensile properties shows that the increasing of filler loading decreased the tensile strength. The Young’s modulus also decreased with the increasing of filler loading however the elongation at break increases. Morphology of the blends indicates the filler is does not dispersed well in the PP matrix. Since PP/NR blends and natural filler are incompatible, an attempt was made to compatibilize in order to improve the morphology and the properties of the blends. Polypropylene graft maleic anhydride (PP-g-MAH) were used to compatibilize the blend. The compatibilizing of filled PP/NR with PP-g-MAH resulted in better tensile properties better than the uncompatibilized blends. A finer morphology with improved interfacial adhesion is obtained with all compatibilized blends.

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