Dynamic Vulcanization of Polypropylene / Natural Rubber Blends Filled with Cyperus Odoratus

Norfatulikmah Zainal Abidin¹, and Mohamad Kahar Ab Wahab¹,*

¹School of Materials Engineering, University Malaysia Perlis, 02600, Arau, Perlis, Malaysia;

Abstract. A new thermoplastic blend was developed using polypropylene (PP) with natural rubber (NR) as the base material. The natural filler is added to enhance the properties of PP/NR blend. The first series was to compare the properties of PP/NR blend with different filler loading. Second series was to investigate the effect of dynamic vulcanization on the properties of PP/NR blend filled with Cyperus Odoratus with the intention of improving the blend properties. 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 and it shows in the morphology study of the blend. Dynamic vulcanization of the blend resulted in improved tensile and thermal properties compared to unvulcanized counterpart. This result is confirmed by the SEM study that showed better dispersion of NR in the PP matrix and improved adhesion between the two phases.

1 Introduction

Thermoplastic elastomers (TPEs) are materials that are processed by the same method used for a rigid thermoplastic such as injection molding and extrusion, yet have the properties and performance normally describe to conventional thermoset rubber. The importance of TPEs has been gained due to their wide range of application in such as automotive parts, industrial supplies, electrical equipment, household appliances, food contact systems and medical apparatus [1-5]. It already started replacing many other conventional materials in various applications and have become a highly demanding class of polymeric materials. Some of the properties of TPEs which may not be found in any other materials are low cost and attractive properties such as light weight, superior mechanical strength, applicability at elevated

* Corresponding author: kaharwahab@unimap.edu.my
temperatures, corrosion resistance, ability to be tailored for specific engineering applications. The most important feature of TPEs is the repeated recyclability up to several times without significant loss of properties [6-8]. TPEs can be classified into two major groups which are block copolymers and rubber plastic blends. A class of TPEs based on rubber and thermoplastic compositions where the rubber phase is dynamically vulcanized is known as thermoplastic vulcanizates (TPVs) or dynamic vulcanizate. Dynamic vulcanization is the process of mixing a thermoplastic and rubber which is later cross-linked under dynamic conditions. In order to activate and to complete the vulcanization process, the process is performed at high shear rate above the melting temperature of the thermoplastics and also at sufficiently high temperature [9-10]. Due to the advantages of being low in both density and the cost, the product based on PP are very significantly commercial. Moreover, its crystalline structure and high melting point results in resistance to solvent and high temperature [11-13]. While natural rubber (NR) exhibits outstanding properties such as green strength and tensile strength because it can crystallize spontaneously when it is strained. However, for some specific applications, the properties of natural rubber such as modulus, hardness and abrasion resistance need to be improved [14-15]. The best choice of polyolefin to be blended with NR is polypropylene (PP) due to its high softening temperature 150ºC and the low glass transition temperature of the blend [16].

2 Experimental

2.1 Materials

The raw materials that were used in mixing and compounding used in this study such as PP, NR, Cyperus Odoratus, Zinc oxide, CBS, stearic acid, sulphur and PP-g-MAH are listed completely with the function and supplier in the Table 1.

| 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 blends via dynamic vulcanization approach

Blends were prepared using heated two roll mill. Mixing was done at temperature 170°C and rotor speed 13 rpm and 10 rpm for front and back mill for 12 min. The effect of dynamic vulcanization (DV) on PP/NR blends filled with *Cyperus Odoratus* is determined. The curatives is added to the compounding based on the formulation given in Table 2 below. The mixing is still 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.

Table 2: Formulation table for dynamic vulcanization on PP/NR blends filled with *Cyperus Odoratus*

| Ingredients               | Compositions (wt%) |
|---------------------------|--------------------|
| PP/NR (70/30)             | 100                |
|                           | 95                 |
|                           | 90                 |
|                           | 80                 |
|                           | 70                 |
| *Cyperus Odoratus*        | 0                  |
|                           | 5                  |
|                           | 10                 |
|                           | 20                 |
|                           | 30                 |
| Curatives                 |                    |
| Zinc oxide*               | 1.5                |
| Stearic acid*             | 0.6                |
| CBS*                      | 0.75               |
| Sulphur                   | 1.0                |

*phr based on weight of NR

3 Characterization and Testings

Tensile test were carried out according to ASTM D638 using the Instron tensile testing machine. One millimeter thick dumbell tensile specimens were cut from the molded sheets with a Wallace die cutter. 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 blend. 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 30°C to 600°C at a nitrogen flow of 50 ml/min and at a heating rate of 10 ºC/min. Loss 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 ºC/min. The first heating scan was carried out from 30-190ºC and hold for 5 mins then 190-300ºC and hold for 5 mins then 30-230ºC for the determination of the glass transition temperature, Tg.

4 Discussion

4.1 Structural analysis

Fourier transform infrared (FTIR) 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 1465-1537cm⁻¹ represents the CH₂ bending [18]. From the Figure 2, it shows the FTIR spectrum from the PP/NR blend filled with 10wt % of filler loading which is Cyperus Odoratus. 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 [19]. 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 [20]. 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 [21]. The FTIR spectra analysis of and vulcanized PP/NR blend with 10 wt% filler loading can be seen from the Figure 3. From the figure we can see the stretching of CH3 at the region 2950-2800 cm⁻1. The peaks appeared in nearly 1715 cm⁻1 and 3345 cm⁻1 indicate the presence of carbonyl and hydroxyl/hydroperoxides group, respectively. However, it can be seen from the FTIR spectra between unvulcanised PP/NR with filler loading with PP/NR-DV with filler loading are almost identical indicating that there is no significant effect of vulcanization on the chemical
changes during the processing. In the sulphur-cured system, S-S linkage are formed due to the presence of sulphur as vulcanizing agent [22].

Fig. 1. FTIR spectra of virgin PP/NR (70:30) blend

Fig. 2. FTIR spectra of PP/NR blend with 10 wt% of filler loading

Figs 3. FTIR spectra of vulcanized PP/NR blend with 10 wt% of filler loading
4.2 Tensile properties

Figure 4 (a) shows comparison of tensile strength between unvulcanised PP/NR blend with filler loading and vulcanized PP/NR blend with filler loading. For PP/NR blend with 5 wt% filler loading, the tensile strength is 13.09 MPa and further decrease with filler loading 10 wt% that is 11.40 MPa. The lowest tensile strength is 9.66 MPa with incorporation of filler loading 30 wt%. From the graph, it can be seen that the vulcanized blend has higher tensile strength compared to unvulcanised blend system. The incorporation of 5 wt% of filler loading has shown slight increment compared to unvulcanised system which is 13.12 MPa. When the blend is vulcanized with 10 and 20 wt% filler loading the tensile strength decrease from 11.74 MPa to 11.38 MPa respectively. When dynamic vulcanization is performed during the mixing process, the viscosity of the mixture will increase. This will cause higher increment of friction during the mixing process so that particle will become smaller and the dispersion of NR phase in PP matrix are evenly distributed. Small size dispersion and the nature of cross-linked particles distribution facilitate the further initiation and movement of the matrix flow. Even though the tensile strength of vulcanized system is higher compared to unvulcanised system but the tensile strength for both systems decreased with the increasing amount of filler loading. This is due to the occurrence of filler agglomeration in the blend system. The second reason is the difficulty of achieving homogenous blend system by using roll-mill at higher filler content [23].

Similar trend was observed for the Young’s modulus as shown in Figure 4 (b). It also decreases as the filler loading. The Young’s modulus for vulcanized system is higher compared to the unvulcanised system. The Young’s modulus for 5 wt% filler loading without vulcanization is 367.4 MPa while 385.1 MPa for unvulcanised system. The 30 wt% shows lowest Young’s modulus with 305.6 MPa and 328.2 MPa for unvulcanised and vulcanized system respectively. This is due to the rubber-filler interaction decreases with increasing filler loading [24]. The dispersion of filler in the matrix poor in unvulcanised system hence the tensile strength and Young’s modulus decreases as the filler loading increases. This will promote the discontinuity of the blends and at the end contributes to the reduction in tensile properties. The enhancement of tensile strength in vulcanised blend is due to the increased crosslink density in dynamically vulcanized PP/NR blend filled with Cyperus Odoratus. Formation of cross links in the elastomer phase facilitates better stress transfer which is the major contributing factor to such enhancements [25]. George et al. [26] reported that a large number of small, uniformly distributed cross-linked rubber particles can be observed in vulcanized samples and those entangled rubber molecules cannot slip past each other during loading and thereby resulting in higher tensile strength and Young’s modulus. The effect of filler loading has increased the stiffness of the specimen and dynamic vulcanization has improved the stress transfer between the matrix and the filler hence increase the Young’s modulus for the blend. Figure 4 (c) shows elongation at break for vulcanized PP/NR with filler loading compared to unvulcanised PP/NR blend with filler loading. The elongation at break correlates with the measures of the strain before it ruptures. It can be seen that the elongation at break is directly proportional to the Young’s modulus of the blend system. The elongation at break for PP/NR-DV blend with 30 wt% shows the highest elongation at break which is at 16.4% due to the stress transfer between the filler and the matrix. The fine dispersion of NR in PP matrix and the cross-linked rubber particles helps the flow of the stress transfer and improved the interaction between filler-matrix.
Figs 4 (a) – (c): Tensile properties of PP/NR blend with natural filler and PP/NR-DV with natural filler
4.3. Morphological Study

The phase morphology of a blend is determined by a several of factors including the relative concentrations of the polymeric components, the interfacial tension between them, the conditions used to process the mixture and the viscosity differences between the components [27-28]. The SEM pictures of tensile fractured surface of blends PP/NR (70:30) and PP/NR with 10% and 30% filler loading is shown in Figures 5(a) – (c). As shown in the figures, NR phase dispersed the continuous PP matrix. This is because the PP act as the domain to the system due to ratio 70:30. In Figure 5 (b), it can be seen that a number of voids and fiber pull outs on the tensile fractured surface of PP/NR blend with 10% filler loading. The presence of holes evidenced the retreat of particles, indicating low adhesion between the phases. The fiber is not wet by the PP matrix. In Figure 5 (c) shows the tensile fractured surface of PP/NR blend with 30% filler loading. There are more fiber pull out and voids that can be seen due to the incompatibility between the matrix and the fiber which is Cyperus Odoratus. This incompatibility is due to the difference between the surface properties of the natural filler that is highly polar and hydrophilic while matrix is generally polar and hydrophobic.
Figs 5: Scanning electron micrograph of surface of PP/NR blend (70:30) at (a) 0% filler loading, (b) 10% filler loading and (c) 30% filler loading at 300 X magnification.
Figure 6 (a) – (b) show the tensile fractured surface of PP/NR blend that undergoes dynamic vulcanization with 10% and 30% filler loading respectively. It can be observed in SEM pictures of tensile fractured surfaces of dynamically vulcanized blends has better dispersion of NR in the PP matrix and good adhesion between the natural fiber in the matrix compared to unvulcanised counterpart. The fiber shows good wetting and it is embedded in the matrix. The fiber is less agglomerate compared to the unvulcanised blend. This is a good indication to prove the improved tensile properties of vulcanized blends.

![SEM images of PP/NR blends]  
(a) 10% filler loading, (b) 30% filler loading at 300 X magnification.

**Figs 6**: Scanning electron micrograph of surface of PP/NR-DV blends (70:30) at (a) 10% filler loading, and (b) 30% filler loading at 300 X magnification.

### 4.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis or TGA is a standard procedure in which changes in the weight of a specimen is monitored as the specimen is progressively heated. The TGA and DTG curve of virgin PP/NR blend, PP/NR blend with 10 wt% and 30 wt% filler loading and vulcanized PP/NR blend with 10 wt% and 30 wt% filler loading is represented by the graph illustrated.
in Figure 7 (a) and (b) respectively. There are three stages of decomposition or weight loss happened on the system. The first stage is at range of 30-150 °C, the second stage is at the range of 150-300 °C and the third stage is at range of 300-490 °C. The initial weight loss between 30 °C and 150 °C is observed due to residual water. From the thermal degradation curves in the Figure 7 (a), the second stage of weight loss, it can be seen the initial degradation temperature for PP was 297.57 °C. Generally, the addition of filler has decreased the initial degradation temperature however when the PP/NR with filler loading is vulcanized the initial degradation were increased. This shows that the vulcanized PP/NR blend with filler loading have improved the thermal stability. The third stage weight loss can be seen is the end degradation temperature of PP was 457.25 °C. As the filler loading increase, the weight loss decreases as it needs more energy or high temperature to degrade the blends. From the Figure 7 (a) it can be seen that the weight loss of vulcanized PP/NR with 30 wt% filler loading is lower compared to unvulcanized PP/NR with 30 wt% filler loading. This shows that the dynamic vulcanization has increased the thermal stability of the blend system.

![Fig. 7 (a): The TGA curves of PP/NR blend with filler loading and PP/NR-DV with filler loading](image)

![Fig. 7 (b): The DTG curves of PP/NR blend with filler loading and PP/NR-DV with filler loading](image)
4.5 Differential Scanning Calorimetry (DSC)

The crystallization behaviour and melting characteristics of the composites were studied using differential scanning calorimetry (DSC). Figure 8 (a) and (b) shows the heating and cooling curve of PP/NR blend with filler loading and PP/NR-DV blend with filler loading. As shown in figure, the slight increased or remained essentially unchanged with increasing filler loading content. The melting point increased compared to unvulcanised system. It also can be observed that the use of lignocellulosic fiber can impart stability of the blend due to the presence of lignin as a natural oxidant. The increase in crystallinity is due to the arrangement of segmented molecules entangled molecules in the amorphous phase. When the dynamic vulcanization is done during the mixing process, the formation of carbonyl and hydroperoxides groups compete in the process of changing crystallinity. These chemical groups are attached to the molecular segments that cause and influx in disentangled chains, which it enabled the molecules to form a crystal structure, hence hindering the crystallization process.

Fig. 8(a): The heating curve of PP/NR blend with filler loading and PP/NR-DV with filler loading

Fig. 8(b): The cooling curve of PP/NR blend with filler loading and PP/NR-DV with filler loading
5 Conclusions

The first series of the study focused on the comparison between the PP/NR blends and PP/NR blends filled with different composition of Cyperus Odoratus. The characterization and 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 the PP act as dominant matrix and NR act the dispersed phase, dynamic vulcanization is done to crosslink the dispersed phase of NR. The tensile properties improved compared to the tensile properties of PP/NR blends filled with Cyperus Odoratus. The SEM studies revealed that better and uniform distribution of NR particles in the PP matrix when blends are subjected to dynamic vulcanization. The FTIR spectra analysis shows absorption bands that indicates that there is sulphur linkage due to the presence of crosslinking agent.

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