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Influence of Processing Conditions on Mechanical Behaviours of Thermoplastic Natural Rubber/ Polyaniline Blend

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ABSTRACT

The blend fabrication of thermoplastic natural rubber (TPNR) and polyaniline (PANI) was carried out to determine the optimization of processing conditions by the mechanical testing (tensile, bending and Izod impact test). The TPNR matrix, made up of linear low-density polyethylene (LLDPE), natural rubber (NR), and liquid natural rubber (LNR) as compatibilizer with the composition ratio at 40:50:10. TPNR/PANI (90 wt % / 10 wt %) blends was prepared via a melt blending method using an internal mixer with various processing parameter conditions. The influence of processing conditions including the processing temperature (°C), speed of rotation (rpm) and processing time (min) on the mechanical properties of blend were investigated. The results showed that the optimum processing conditions for preparing the TPNR/PANI blend was obtained at 130 °C, 30 rpm and 13 min. The morphological test has been done on TPNR, and TPNR/PANI blends using SEM characterization. The SEM micrographs confirmed the good dispersion of PANI within TPNR matrix.

Keywords: *Polymer Blend, Polyethylene, Conducting Polymer, Tensile Test, Impact Test*

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Introduction

Polymer blends functionally produce new polymeric materials which have better properties compare to neat polymer materials. The polymer blends systems which made up of two or more pure polymers, could cause an alteration of properties and affect the mechanical properties of the end composites. In recent years, the thermoplastic natural rubber (TPNR) which is a blending of natural rubber and polyolefin has been developed by some researchers [1, 2, 3, 4]. For examples, NR/LLDPE/LNR and NR/polypropylene (PP)/LNR in the ratio 50:40:10 were fabricated in order to study the compatibility of the blends with the addition of LNR as compatibilizer into blend systems[5]. LNR has a good potential to be an effective compatibilizer in thermoplastic natural rubber blends as stated by Dahlan et al. [6] and Azizan et al. [7] who proved that the addition of LNR acted as an effective way to compatible the immiscible blend between NR and polyolefins blends. Besides that, the addition of LNR also contributed to reduce the interfacial tension which could improve the interaction between the phases of the blends [6]. The compatibility or toughness of polymer blends can be improved in several ways: 1) toughen the matrix phase; 2) use coupling agents or compatibilizer to optimize the interface between the filler and matrix; 3) optimize the properties of filler by altering the filler content and the particle sizes; 4) orientation and distributions of filler within matrix [8,9]. Commonly, TPNR has been prepared via melt blending method. In addition, TPNR was used as a matrix in various composites systems, such as the addition of nickel zinc ferrite nanoparticles in TPNR (PP/NR/LNR in the ratio of 70:20:10) and LNR-compatibilized NR/LLDPE blend in ratio 60:40 [13, 8].

Polyaniline (PANI) is one of infusible conductive polymers in a blend of a composite system which indicates to have a better dispersion in the thermoplastic matrix polymer [16]. It also contributed to lower the particles surface tension, formation of aggregates that ease the mixing with thermoplastic polymer where the preparation of blends containing PANI is normally focused on solution blending [12]. The utilization of PANI as a matrix in blend of NR/PANI-dodecylbenzene sulfonic acid (DBSA) and LLDPE/nanorod-PANI showed that the incorporation of PANI improved the mechanical and electrical conductivity properties of blends [16, 19]. However, a homogeneous mixture of blend containing PANI is one of critical factor to determine the enhancement of blend performance [16]. The two main aims of this research were to investigate the influence of processing condition on mechanical behaviours of TPNR/PANI blend, and to determine the optimum processing condition for the fabrication of TPNR/PANI blend.

Materials And Methodology

Materials Preparation

Linear low density polyethylene (LLDPE) was purchased from Exxon Mobile Chemical Corporation, and used as a thermoplastic resin in this study. It has a density of 0.918 gcm^{-3}, melt flow index of 1.0g/10 min and melting temperature between 120-160ºC. SMR-L grade natural rubber (NR) was obtained from Malaysian Rubber Board (MRB) and used to prepare LNR. Polyaniline (PANI) needle-like powders, was purchased from E-TEK Co. Ltd, Kyengki-Do, Korea.

Preparation of Liquid Natural Rubber (LNR)

Liquid natural rubber (LNR) was synthesized using the photochemical degradation or oxidation technique on the natural rubber (NR). About 1.5 kg of NR was cut into small pieces and soaked in the 60 cm^3 glass flask with toluene for 24 hours. After that, 0.3 g methylene blue, 0.39 g rose Bengal and 15 ml methanol were added into the mixture. The mixture was stirred continuously with a mechanical stirrer at 10 rpm under the exposure of fluorescent light for 10 days.

Samples Preparation

Indirect mixing technique (IDT) was applied in order to prepare the composites which involved a pre-mixing of PANI particles with LNR that are manually stirred using a glass rod, before it was melt blended with LLDPE and NR. The TPNR from NR/LLDPE/LNR (50:40:10) with 10 wt % PANI particle were compounded by using an internal mixer (Haake Rheomix 600P) with various processing conditions such as processing temperature (120-150 °C), rotor speed (20-50 rpm) and processing time (13-15 min). Note that for the processing temperature investigation, the speed of rotation and processing time are kept constant at 50 rpm and 13 min, respectively. The same approach was used for the rotor speed and processing time investigation where the other processing conditions were kept constant for each investigation. For rotor speed investigation, processing temperature was kept constant at 130 °C and processing time was 13 min. Finally, for the processing time investigation, the temperature and speed of rotation were kept constant at 130 °C and 30 rpm, respectively. For the preparation of all blends, NR was first placed into the mixer and allowed to melt for about 3 min, then the pre-mixture of LNR and PANI was added in and LLDPE pellets were added after 5 min. The whole mixing process took 13 min. After the blending process, the samples were prepared by compression moulding via hot and cold press (LP50, LABTECH Engineering Company LTD) under the pressure 6.9 MPa at 130 °C.

Characterization

Tensile test of the samples was carried out by using a tensile machine (model Testometric M350-10CT) with a 5kN load cell according to ISO 37-2 standard specification procedure, where the test samples were cut at 1 mm thickness and a crosshead speed of 50 mm min^{-1}. At least five samples were tested for each formulation of samples. A three-point bending test and a tensile test was performed on the same *Testometric* machine. A flexural test is highly influenced by the behaviours of samples on top and the bottom surfaces. The samples with dimensions of 127 mm (length) × 12.7 mm (width) × 3.0 mm (thickness) were prepared according to ASTM D790-96. Crosshead speed of 1.35 mm/min and span length of 50 mm were fixed. To determine impact strength, Izod test was carried out using the *Digital Impact Testing Ray Ran* according to ASTM D256 test method. At least five samples in the shape of rectangular each having dimensions of 64 mm (length) × 12.7 mm (width) × 3.0 mm (thickness), with a V notch at the centre were used for this testing. All mechanical testing were performed at room temperature. The morphology characterization of the TPNR and TPNR/PANI blend sample was examined under the scanning electron microscope (SEM) (model LEO 1450 VP) by using the fractured surfaces of blend sample obtained from the tensile test. Before the examination, the samples were sputter-coated with a thin layer of gold to avoid electrostatic charging during the morphology examination.

Results And Discussion

Figure 1 (a) shows the influence of processing temperature parameters on tensile strength where, the highest tensile strength of TPNR/PANI blend was achieved at 1.61 MPa when mixing temperature was at 130°C. The tensile strength value was then gradually dropped when the higher processing temperature than 130°C was applied, due to the oxidation of NR and the aging of the blend which led to the strength degradation of the blend's [14]. Figure 1 (b) show the influence of rotation speed on the tensile strength, where the highest tensile strength of 1.81 MPa was obtained at 30 rpm. In fact, the rotor speed of the processing can be related to the rubbery properties of TPNR and PANI particles (micro size). The rotation processing speed at 30 rpm also promoted a well dispersion of PANI with the aids of LNR due to the achievement of better interaction between amorphous NR and LLDPE with PANI. Similar finding has been reported by [3]. Finally, the highest tensile strength of 1.81 MPa was measured during 13 min of mixing as shown in Figure 1 (c). The longer processing time (more than 13 min), the more the mixture was exposed to the heat and thus may lead to the oxidation of NR which will cut off the polymer chain [18]. Therefore, it was not suitable for this blend mixing.

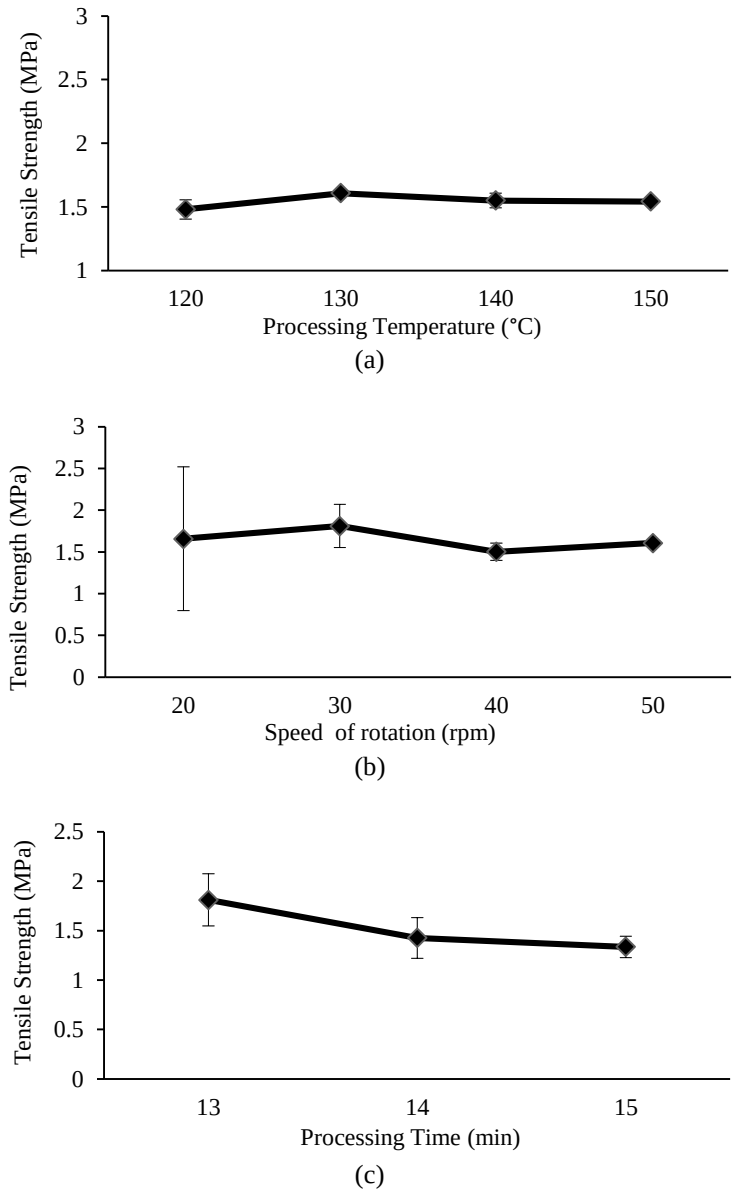
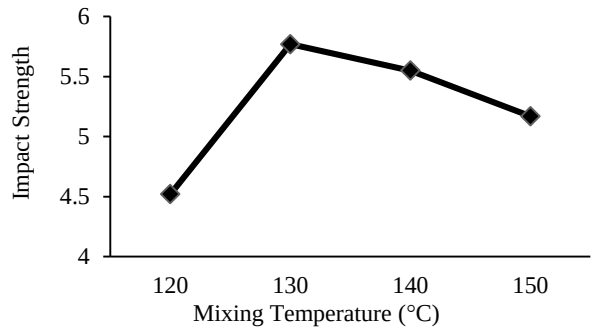
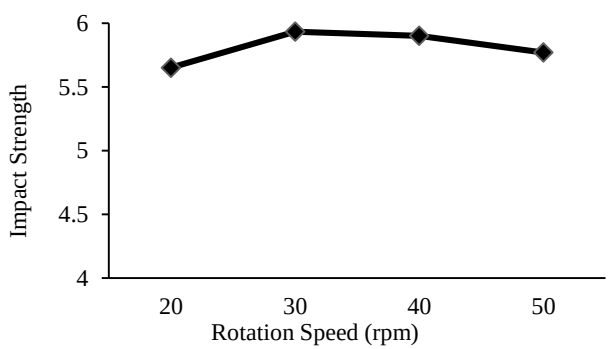


Figure 1: Influence of mixing conditions such as a) temperature, b) speed of rotation and c) time on tensile strength

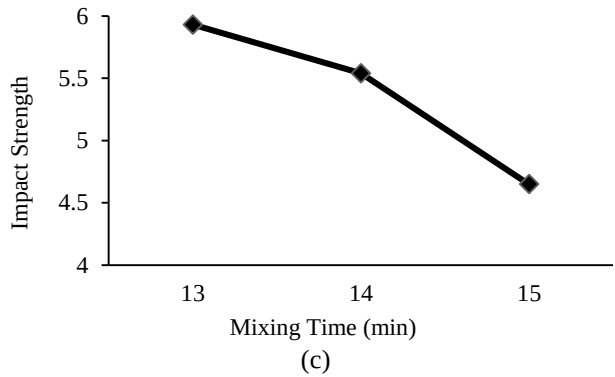
Figure 2 shows the influence of processing conditions on the impact strength. The result exhibited a similar trend as tensile strength as obtained in Figure 1. Generally, impact strength is one of the test that was used to measure the toughness which defined by the ability of samples to absorb the applied energy [11]. Therefore, the addition of PANI into the TPNR blend showed 1.33 % decrease in the impact strength from 6.01 kJm^{-2} to 5.93 kJm^{-2}. This indicates that the added PANI caused the TPNR blend to have lower ductility, more brittle and easy to fracture which led to poor impact fracture toughness or impact properties [20].



(a)



(b)



(c)

Figure 2: Influence of mixing conditions such as: a) temperature, b) speed of rotation and c) time on the impact strength

Figure 3 shows the influence of: (a) processing temperature, (b) rotation speed and (c) time of processing on the bending strength. The processing parameters could affect the blending strength which is dependent upon the compatibility between the hydrophobic TPNR blend [12]. Cote et al. (2009) proved higher compatibility promoted better interaction between PE and PANI particles which led to better stress transfer thus enhanced the properties [15]. The previous studies claimed that the bending properties were affected by many factors such as: the fiber-fiber interactions, the alignment of the fiber-matrix system, the presence of voids, dispersion and the resin-rich areas [6]. Based on Figure 3, the highest bending strength was achieved at 130°C processing temperature, 30 rpm speed of rotation and 13 min time of mixing. The highest bending strength of 1.65 MPa can also acted as a reference for the suitable processing condition for TPNR/PANI blends which responded to the synergistic effect. The synergism proved that the blend had a better fiber particles arrangement and thus may reduced the empty space between the fiber and matrix TPNR with micro PANI particles [6]. Therefore, the effects have increased the mechanical properties of the composites.

From the mechanical test results, it can be concluded that the optimum processing conditions for TPNR/PANI are 130°C, 30 rpm, 13 min for processing temperature, speed of rotation and processing time, respectively. The values for each parameter (i.e. processing temperature, speed of rotation and processing time) gave the highest strength in terms of tensile, impact and bending at 1.81 MPa, 5.93 kJm^{-2} and 1.65 MPa, respectively. Generally, the interfacial interaction of more than two polymer components in blend is one of the important factors to determine the optimum mechanical properties of the blends.

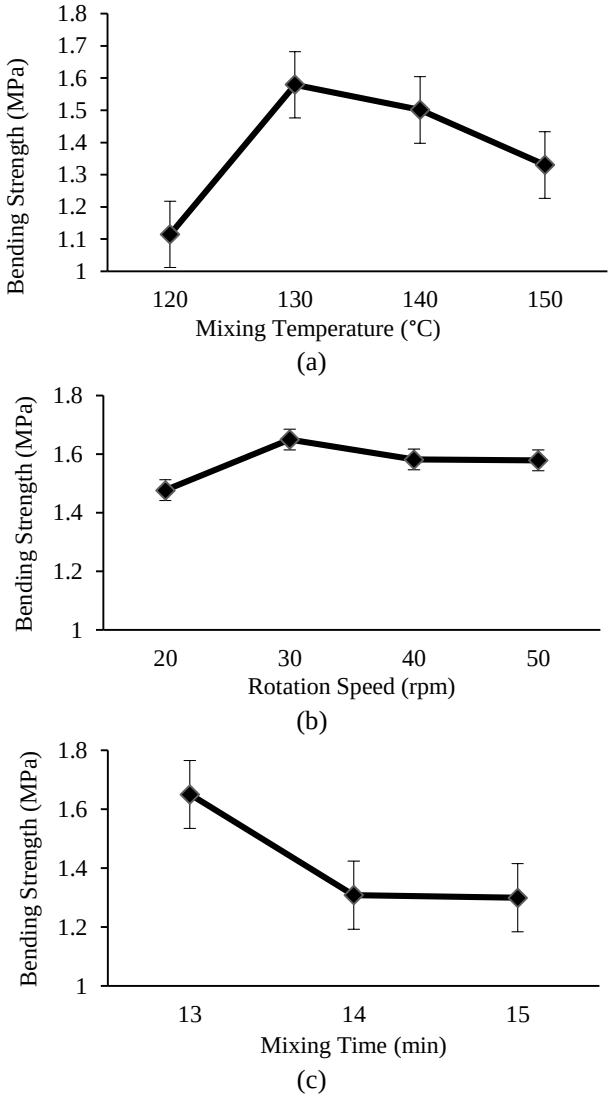


Figure 3: Influence of mixing conditions such as a) processing temperature, b) speed of rotation and c) time on bending strength

The SEM micrographs in Figure 4(a) and (b) showed the surface-fractured sample after the tensile test. Figure 4(a) shows a rough surface with large holes but overall homogenous surface morphology which indicates the rubber particles are well dispersed in the LLDPE matrix [14]. The white areas

are known as the incomplete melted plastics in the mixture. The less rough surface with small holes in Figure 4 (b) was due to the PANI propagation through the rubber domain in TPNR blend which led to a good interaction in a matrix system (Ozturk et al., 2001) as well as resulted in an efficient stress transfer to the rubber blends [5]. While the micrograph of TPNR/PANI in Figure 4(b) shows the noticeable uniform distribution of particles in the polymer matrix without the agglomerations of PANI and small holes than that appeared in the TPNR due to the filling of PANI particle. This indicates a good mixing of blend, as supported in enhancing the mechanical properties [15].

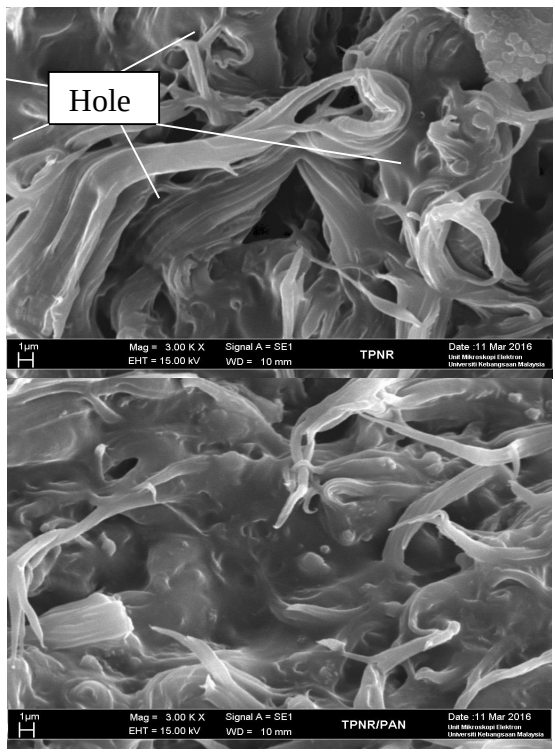


Figure 4: SEM micrographs of (a) TPNR, (b) TPNR/PANI blends.

Conclusion

The mechanical results showed that the optimum processing parameters conditions such as temperature, speed of rotation and processing time for the fabrication of TPNR/PANI are at 130°C, 30 rpm and 13 min, respectively.

These optimun parameters improved the mechanical properties of TPNR/PANI in terms of tensile, bending and impact strengths were confirmed by the captured micrograph by SEM that shows a good dispersion of PANI within the TPNR matrix, and thus led to good mechanical properties.

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