

Effect of LLDPE on Impact, Flexural and Morphological Properties PP/NR Blend.

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Abstract.

One of the most successful methods developed for modifying polymer properties is the rubber-toughening process by blending rubbers with plastics. Blends of polypropylene (PP) with elastomers are developed with the objective to overcome the inherent brittleness of PP at low temperatures and to enhance the impact strength at room temperature. In this study, a new impact-modified PP ternary blends based on PP/ natural rubber (NR)/linear low density polyethylene (LLDPE) is developed; the NR content ranged from 0 to 30%. The blends were prepared in a laboratory scale twin screw extruder. After mixing and pelletising, the samples were injection moulded and tested for mechanical properties. Impact, flexural and morphological properties of the blends were studied. An increase in impact strength but a decrease of flexural modulus was observed with increasing NR contents. The partial replacement of PP with LLDPE as the third component in PP/NR/LLDPE ternary blend had enhanced the impact strength with a slight decreased in flexural modulus. From morphology features, LLDPE addition improves the dispersion of NR, affecting mainly the larger particles.

1.0 Introduction

Blending of various rubbers with polypropylene (PP) to enhance the impact has been widely studied (1-3). Physical blends of natural rubber (NR) and PP, to form a thermoplastic natural rubber (TPNR), have been developed into a semirigid and impact-resistant plastic. These materials are often used in automotive applications when low temperature impact strength is required, especially where the vehicles are subject to very cold climates. In this respect, NR based materials offer advantages over PP/EPDM materials on account of NR inherent low temperature performance (4).

The disadvantage of rubber toughening of thermoplastic is the decrease in the flexural properties. The addition of a suitable third polymer may be a better way to get an impact modified PP which possess satisfactory impact strength and rigidity. Therefore, part of the rubber is sometimes replaced by polyethylene (PE) to improve such properties in PP rubber blends. It has been reported by many researchers that the addition of small amounts of HDPE to the blend of PP and NR would improve adhesion between the disperse rubber phase and the polyolefin matrix (5-7). The resulted blends achieved better rubber dispersability and stiffness compared to the binary blend. Holz *et al.* also reported that addition of LLDPE as the third component resulting ternaryblend with more homogeneous and a finer disperse phase particle diameter compared to HDPE (7). This work deals with the particle changes and morphology of PP/NR blends by the addition of LLDPE and their effect on impact, flexural and morphological properties. The blends were mixed in a twin-screw extruder and the samples were prepared by injection molding.

2.0 Experimental

2.1 Materials

The PP used in this study was injection molding grade polypropylene homopolymer 6431 with a specified melt flow index of 7.5 g/10 minutes. The LLDPE grade was LF5011 with a specified melt index of 2.0 g/10min. These resins were supplied by Titan Himont Polymers (M) Sdn. Bhd. The natural rubber (NR) used was viscosity stabilized grade of Standard Malaysian Rubber (SMRCV) obtained from the Rubber Research Institute of Malaysia.

2.2 Preparation of Blends

The NR, which was received in a bale form, was first sliced into small pieces to allow subsequent pressing into thin sheets using a two-roll mill. The rubber sheets were then cut into long strips to facilitate easy loading into the twin screw extruder.

Extrusion was done in a Brabender PL2000 twin-screw extruder with $L/D = 30$ and $D = 2.5$ cm. The extrusion was conducted at a speed of 45-48 r.p.m. and at a barrel temperature of 190 °C, 200 °C and 210 °C from feeding zone to die zone, respectively. The residence time of the blends in the extruder was kept at about 60 seconds by adjusting the extrusion rate. The compounds were extruded via a twin 4 mm rod-die.

Impact bars (3mm x 13mm x 125mm) and dumbbell tensile specimens (ISO/ R 527, type I) were injection-molded on an Arburg Allrounder 750-310D. The barrel temperature ranged from 170-210 °C. The injection pressure was 1100 bar. While the mold temperature was 40°C. For 3 mm thick samples the injection moulding cycle time could be as short as 50 sec. The compositions of the blends prepared in this study were listed in Table 1. PP/NR blends were prepared in the following weight ratios: 100/0, 90/10, 80/20 and 70/30. Then, the LLDPE would be added for replacement of PP in the PP/NR binary. The amounts of LLDPE added for replacement of PP were 5, 10, 20 and 30 % of total weight of PP.

Table 1: Blend Formulation

Sample Code	NR(%)	PP(%)	LLDPE (%)
A1	0	100	0
A2	10	90	0
A3	20	80	0
A4	30	70	0
B1	0	95	5.0
B2	10	85.5	4.5
B3	20	76	4.0
B4	30	66.5	3.5
C1	0	90	10
C2	10	81	9
C3	20	72	8
C4	30	63	7
D1	0	80	20
D2	10	72	18
D3	20	64	16
D4	30	56	14
E1	0	70	30
E2	10	63	27
E3	20	56	24
E4	30	49	21

2.3 Testing and Characterization

The impact strength of the blend was measured using a Rosand Instrumented Falling Weight Impact (IFWI) Tester Type IV. Samples for impact testing were injection molded to the size specified in 'BS 2782: Part 3: Method 359 specimen type 4 mode'. The samples were notched 45° and the notch depth was fixed at 2.6±0.02 mm.

Flexural test was carried out according to ASTM D790-97. The test procedure used was Test Method 1, Procedure A, i.e., three-point loading utilizing center loading. The distance between the spans was 4.96 cm and the strain rate (compression speed) was 3mm/min. Five samples were tested for each composition.

SEM Philips ZL40 was used to obtain the microstructures of the different blends. The blends were first freeze fractured under liquid nitrogen. The cryogenically fractured surfaces were etched in chloroform for 48 h to remove the NR phase. The samples were then coated with a layer of gold to facilitate examination under the SEM. The domain dimensions were measured by image analysis. About 150 particles were analyzed for the diameter measurement.

3.0 Results and Discussion

3.1 Mechanical Properties

The effect of NR contents on the impact strength of PP/NR blends at 27 and 0 °C is given in Figure 1, which shows that the impact strength increases with natural rubber content. At both temperatures (27 °C and 0 °C), the increase of impact strength is more significant as the NR content increases from 20 to 30 % compared to the increase of NR contents from 10 to 20 %. The results are quite similar with that obtained from the blend of PP with EPDM (8). In another research on PP/EPDM blend by Choudhary *et al.*, the addition of up to 15 % EPDM content only improved the impact strength of PP slightly. A greater enhancement of impact strength was observed at EPDM contents in excess of 20 % (9).

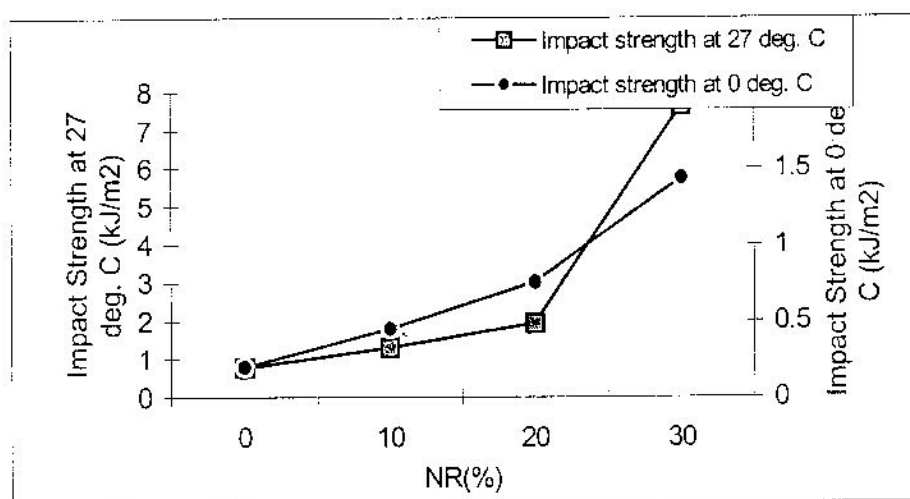


Figure 1: Effect of NR contents on impact strength of PP/NR binary blends
At 0 °C and 27 °C

Figures 2 and 3 show the effect of NR and LLDPE contents on the impact properties of ternary blends of PP/NR/LLDPE blends at 27 °C and 0 °C respectively. Figure 2 illustrates generally the impact strength at 27°C increases with increasing NR and LLDPE contents. The increase in impact strength values with increasing LLDPE content was also observed by Holz *et al.* in the study of PP/EPDM/LLDPE.(7). A very interesting observation in the present study is the sharp increase in impact strength values for the samples containing 20 % NR as LLDPE content in PP increases from 20 to 30 %.

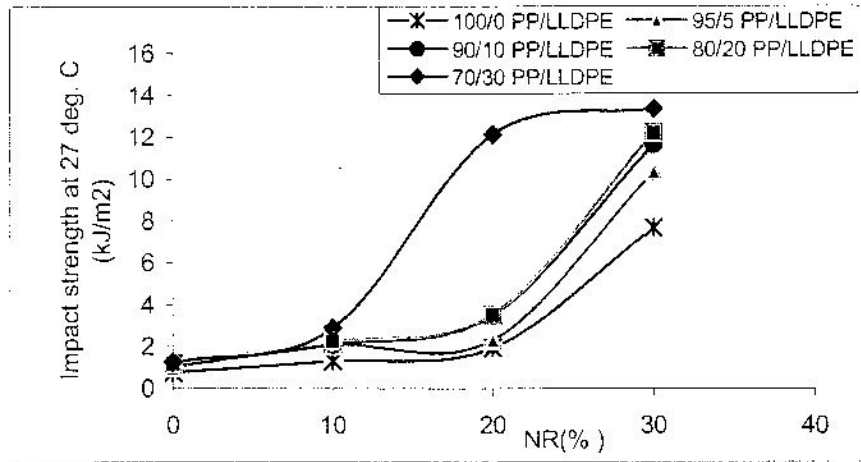


Figure 2: Effect of NR and LLDPE contents on impact strength at 27 °C in PP/NR /LLDPE ternary blends.

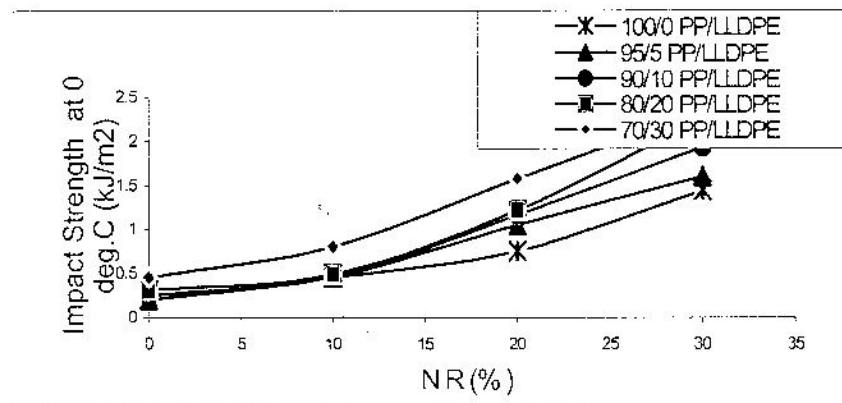


Figure 3: Effect of NR and LLDPE contents on impact strength at 0°C in PP/NR /LLDPE ternary blends.

It was observed that at 27°C the 10% LLDPE replacement of PP resulted in around 50% increase in impact strength compared to around 70% when 10% NR was added to PP. However, the ternary blend with 10 % replacement of PP with LLDPE at 10% NR content resulted in a relatively large increase (around 170%) in the impact strength compared to the pure PP.

Flexural test was done to determine the rigidity of the blend. It may be seen that the flexural modulus of the blends decreases with increasing NR content (Figure 4). Pure PP has a flexural modulus of 1,300 MPa. On adding NR, there is initially a gradual reduction in the flexural modulus values until 20 % NR content followed by a sharper decrease at 30 % NR content. This is due to the fact that NR is a very low modulus material.

The effects of increasing NR and LLDPE contents for ternary blends as shown in Figure 5 indicate that the flexural modulus decreased with increasing NR and LLDPE content as expected for the ternary blends. Since the primary determinant of the flexural modulus of these blends was the PP content, anything that lower the amount of PP would cause the resultant blend to have a lower flexural modulus. So, when the replacement of PP with LLDPE increased, the flexural modulus decreased as expected. This drop in the flexural modulus indicates a slight softening of the material with the increase of both NR and LLDPE.

Besides contributing to the large improvement in impact strength, another advantage of the partial replacement of PP with LLDPE is the decrease in the rigidity is only slightly. For example, the flexural modulus for blend C2 (blend with 10 % replacement of PP with LLDPE at 10% NR content) only decrease around 25% compared to the pure PP. So, it is an advantage to have a blend with combination of PP, NR and LLDPE to enhance the enhance impact strength with only a slight decrease in rigidity.

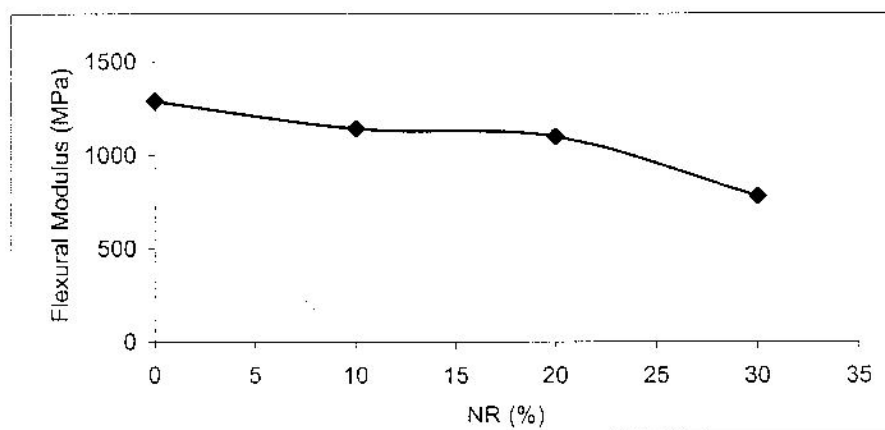


Figure 4: Effect of NR contents on flexural modulus in PP/NR binary blend

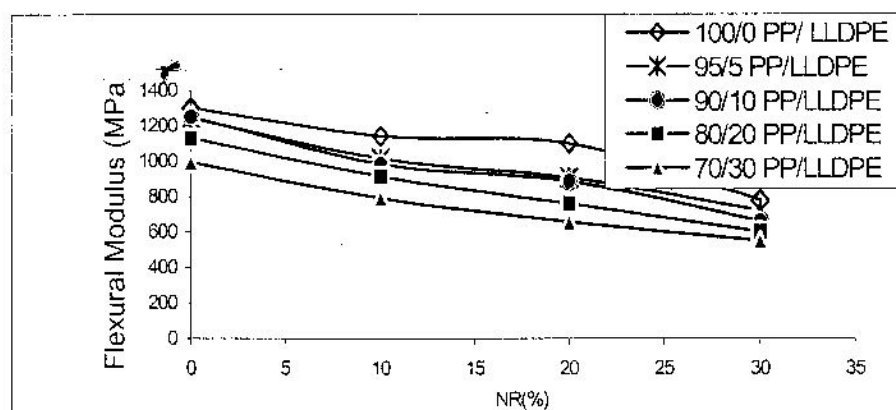


Figure 5: Effect of NR and LLDPE contents on flexural modulus in PP/NR/LLDPE ternary blends

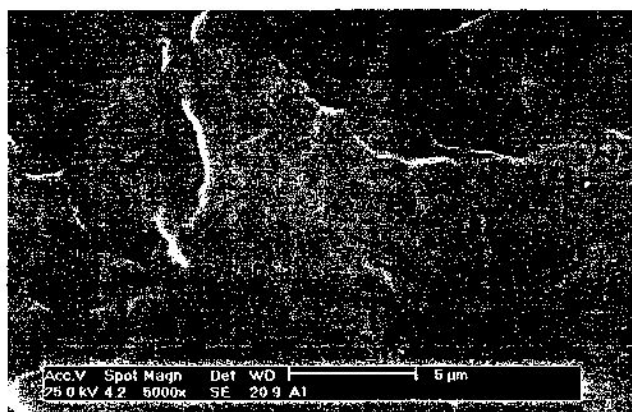
The addition of LLDPE to PP/NR blend enhances the impact strength because firstly LLDPE is more ductile than PP. The second possibility is that LLDPE improved the dispersion of the NR.

3.2 Morphology Analysis

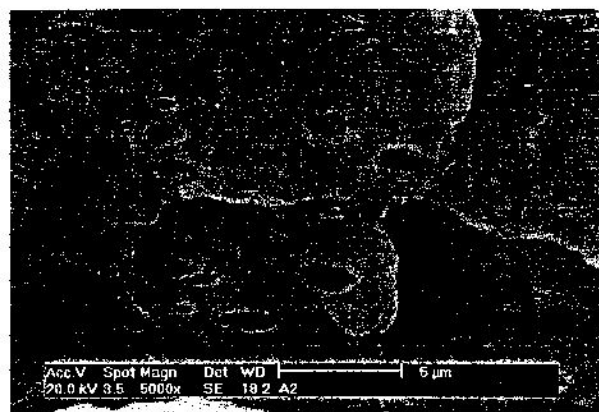
The morphology of liquid nitrogen-fractured surfaces of pure PP homopolymer is shown in Figure 6(a). It clearly shows as expected that no voids are present. The micrograph of 90/10 PP/NR (A2) binary blends shows dark phases due to the voids left by the extracted rubber (Figure 6(b)). This observation showed that there seemed to be no evidence of miscibility between the dispersed rubbery phase and PP matrix. The particles size distribution of elastomer was quite broad ranging from 0.01 to 3 μm .

It has been shown by many previous researchers that blending of PP and NR would result in a heterophase system with PP as the continuous phase and NR as the particles (5,10). In the present study, the minor phase of NR was coarsely dispersed in continuously PP matrix in essentially spherical domains. Continuity of a phase was favored by both a high volume fraction and low viscosity relative to that of the other components (11,12). Therefore the continuity of the PP phase in the blend may be attributed to PP being the major component in the blend and the viscosity of the PP is considerably lower than that of the natural rubber at the shear rates prevailing during blending (5).

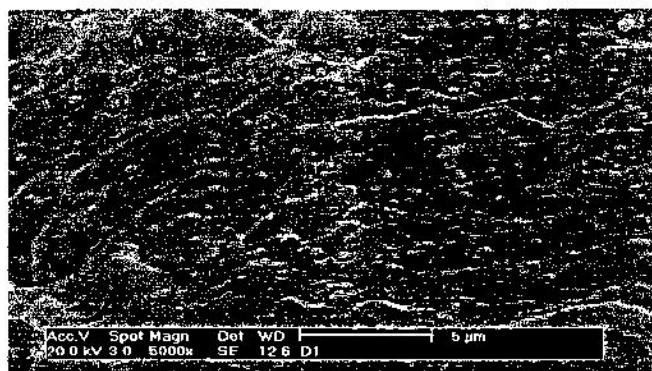
Figure 6(c) shows micrograph of etched surface of the 90/10 PP/LLDPE binary blend. Discrete phase of LLDPE as domains sticking to the surface of the PP matrix was observed. These droplets were quite uniformly distributed inside the PP matrix. Polymers of PP and LLDPE were immiscible with each other and thus they were microscopically separated in the blends. Generally, one of them, depending on the ratio between the two components of the blend, was dispersed rather than dissolved in the matrix of the other (13,14). In the previous work by Oscar and Carley, these researchers revealed that the PP/PE blends were heterogeneous two phases systems and the components were crystallized separately into discrete phases (15).



(a)



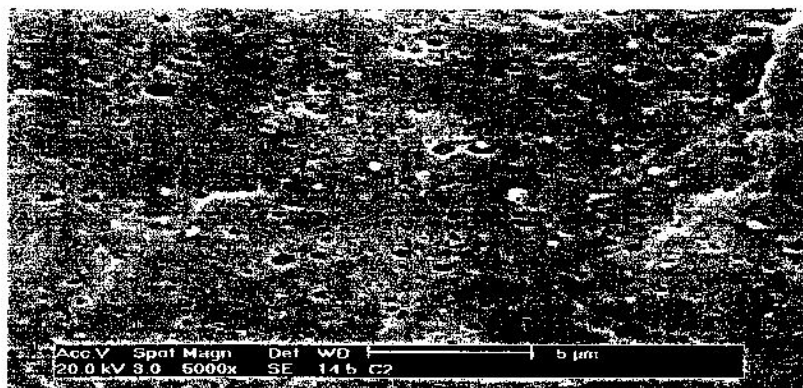
(b)



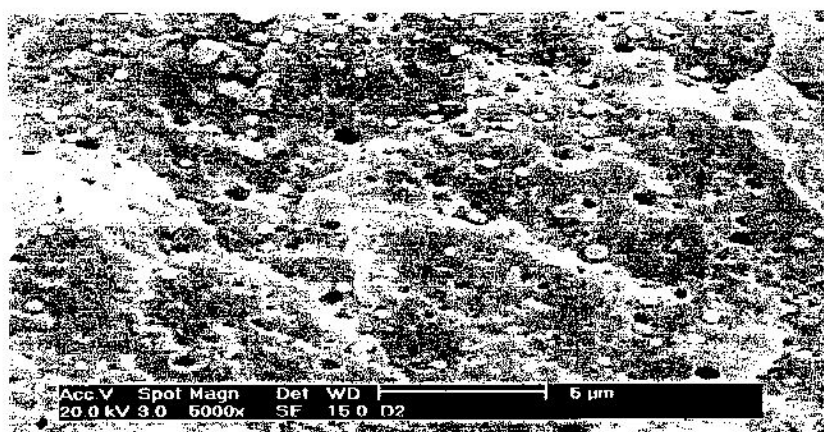
(c)

Figure 6: SEM photograph of extracted surfaces of a) PP homopolymer, b) 90/10 PP/NR and c) 90/10 PP/LLDPE.

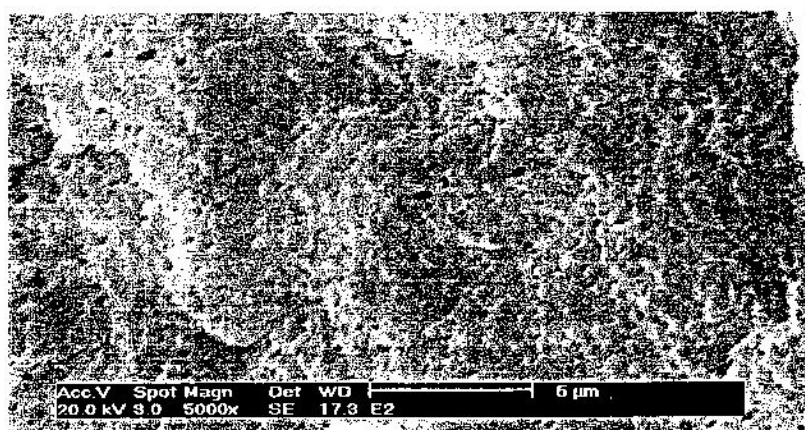
The morphology of the PP/NR/LLDPE ternary blends with different content of LLDPE are shown in Figures 7(a) –(c). Figure 7(a), 2(b) and 2(c) corresponded to the ternary blends with 10 %, 20 % and 30 % LLDPE for the replacement of PP respectively at 10 % NR content.



(a)



(b)



(c)

Figure 7: SEM photograph of extracted surfaces of a) 81/10/9 PP/NR/LLDPE b) 72/10/18 PP/NR/LLDPE and c) 63/10/27 PP/NR/LLDPE blend.

It was observed that the ternary blend revealed a more homogeneous and a finer disperse phase particle diameter than the PP/NR binary blend. This shows that the addition of LLDPE as a third component improves the dispersion of NR and reduces the particle diameter. The result also shows that the particle phase size reduction increases with LLDPE content.

Other studies on plastics/rubber ternary blends also gave similar findings. Stehling *et al.* in their study on PP/PEP/HDPE blends reported that although PP, PEP and HDPE are insoluble, PEP and HDPE have an affinity for each other. As a result they tend to combine within PP to form composite PEP/HDPE particles. From their study, it was concluded that the addition of HDPE to PP/PEP rubber blends improves the dispersion of PEP rubber (6).

Similar results were obtained by Holz *et al.* in the studies of PP/EPDM/LLDPE (7). The researchers reported that the morphology of the ternary blend studied exhibited a more homogeneous and a finer disperse phase particle diameter. Based on the previous studies on plastics/rubber ternary blends, we are proposing the formation of NR/LLDPE composite particles within the PP matrix besides neat NR and LLDPE particles. Although PP, NR and LLDPE are essentially insoluble in each other at room temperature, NR is more soluble to

LLDPE than PP. This is due to the more compatibility of LLDPE/NR compared to PP/NR blend (16).

The SEM analysis showed that the PP and NR in the PP/NR blends are immiscible. NR was dispersed as domains in the continuous PP phase, with the number and size of dispersed droplets depending upon the blending ratio. The number of NR particles acts as stress concentration site and increase with increasing NR content.

SEM analysis for the PP/NR/LLDPE ternary blend showed that the dispersed domain sizes of the blends are reduced which indicates that the adhesion between the phases is enhanced with the addition of LLDPE as third component. The addition of LLDPE improves the dispersability of NR. In the PP/NR/LLDPE ternary blend, NR has a tendency to go in to the interface between PP and LLDPE and form an envelope around the LLDPE particles.

The NR/LLDPE combination demonstrated a synergistic interaction in its effect on the impact strength of PP. Generally, NR are good impact modifiers if the particle size and distribution can be optimized. In the PP/NR blend, NR cannot function as a good impact modifier because the material was poorly dispersed in the PP. This is due to the high viscosity of the NR compared to the PP. When LLDPE used in admixture with NR, the impact strength of the ternary blend is enhanced resultant, because the LLDPE improved the dispersion of the NR phase. There is only a slight decrease of flexural modulus with the addition of LLDPE. So, it is an advantage to replace the PP with small quantity of LLDPE in the ternary blend to enhance the impact strength but minimizing the decrease in the material's rigidity.

5.0 Conclusions

From the present study, it can be concluded that:

- Addition of LLDPE for the replacement of PP in the PP/NR/LLDPE ternary blends improved the impact strength and a slightly reduction in the flexural modulus.
- SEM analysis show that PP/NR and PP/LLDPE and PP/NR/LLDPE blends are immiscible (multiphase) systems in which NR and LLDPE phases remained as dispersed particles in the continuous PP matrix.
- The addition of LLDPE in the PP/NR/LLDPE improves the dispersability of NR. LLDPE reduces the particle diameter of NR resulting in an increase in the impact strength as shown by the SEM.

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