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Tensile and Thermal Properties of Natural Rubber/ Ethylene Propylene Rubber Waste/Linear Low-Density Polyethylene Blends

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ABSTRACT

Natural rubber (NR) is an isoprene polymer and non-polar rubber obtained from Hevea brasiliensis tree. NR has superior mechanical properties but poor resistance to heat and ozone due to its unsaturation in backbone chain. Ethylene propylene rubber (EPDM) is non-polar rubber which is highly in demand especially in automotive industries because it has high oxidation and ozone cracking resistance since the double bond does not exist in the main backbone chain, leading to high amount of scrap or waste accumulated by time. Thus, this research embarks to use the blend of NR/EPDM in addressing green environment. However, the blend of this material leads to phase separation and poor interfacial adhesion, resulting in a heterogeneous blend that possesses poor compatibility. Hence, linear low-density polyethylene (LLDPE) is used as a compatibilizer and additive in this blend. The ternary blends NR/EPDMw/LLDPE blend were prepared in an internal mixer at approximately 160 °C. The amount of EPDMw was fixed at 60 phr, but NR and LLDPE were manipulated. The blend compositions of the ternary blend were 40/60/0, 35/60/5, 30/60/10, 25/60/15, and 20/60/20 (phr) of NR/EPDMw/LLDPE, respectively. The effects of the partial replacement of NR by LLDPE on compatibility, tensile and thermal properties were studied using tensile testing, DSC and TGA. The results showed that the ternary blend was partially miscible, and the 30/60/10 blend composition had better compatibility compared to other *compositions, which was indicated by an increment of tensile strength and elongation at break, with 11.33 MPa and 270.66%, respectively than that of the control sample. Adding LLDPE to an NR/EPDMw blend increased the Tm, but further increasing LLDPE from 10 to 20 phr and it did not significantly affect the Tm, which remained unchanged. It also showed that the crystallinity and thermal stability of the blend increased as LLDPE content in the blends increased. This was because the presence of LLDPE improved the melting enthalpy and crystallinity of the blend. As the LLDPE content increased, it restricted the mobility of polymer chains and lowered thermal vibrations in C-C bonds, enhancing thermal stability. Overall, the addition of LLDPE content improved the compatibility and thermal stability of NR/EPDMw blends.*

Keywords: NR; EPDM Waste; LLDPE; Compatibility; Tensile Properties; Thermal Properties

INTRODUCTION

In the domain of polymer blends, the combination of natural rubber (NR) and ethylene propylene rubber (EPDM) has gained significant interest in addressing the low resistance of NR to heat, ultraviolet (UV) light, oxygen, and ozone, which is due to its highly unsaturated polymeric backbone [1]. Over time, the accumulation of EPDM waste rubber, which takes decades to decompose due to its crosslinked molecular structure, has led to significant environmental challenges, such as soil and water contamination [2]. Therefore, EPDM waste (EPDMw) is utilized in this research to promote environmental sustainability. However, the NR/EPDM blend has poor compatibility caused by poor interfacial adhesion between phases [3]. To overcome this compatibility issue, this research incorporates linear low-density polyethylene (LLDPE) into the NR/EPDMw blend. Ibrahim and Dahlan [4] discovered that the adhesion between the NR and PE phases increased after the addition of EPDM as a third component. This improvement in interphase interaction among EPDM, NR, and PE is attributed to the structural similarities between them. NR, PE, and EPDM share similar hydrocarbon structures with few or no polar functional groups. This similarity in chemical composition means they all have low polarity, resulting in compatible surface energies that allow for better interfacial adhesion when combined.

LLDPE demonstrated the highest compatibility with NR compared to other polyethylene (PE) groups such as low-density polyethylene (LDPE) and high-density polyethylene (HDPE) [5]. LLDPE is a type of polyethylene with linear chains and low density, while NR is a natural polymer with a highly flexible and elastic structure. The physical entanglement of the polymer chains of LLDPE and NR can lead to mechanical interlocking and improved compatibility. Dahlan *et al.* [6] noted that NR and LLDPE interacted even in the absence of Liquid Natural Rubber (LNR), as evidenced by a gel content of 3.5%. This interaction was attributed to the similar structures and solubility parameters of NR and LLDPE. The formation of gel served as an indicator of interaction between the components of the blend, occurring only when a strong interaction existed. Moreover, LLDPE has good compatibility with NR due to its low melting temperature, which aids in the prevention of thermal degradation of rubber [7].

Moreover, LLDPE and EPDM blends exhibit a reduction in crystallinity and heat of crystallization as the EPDM content is increased [8]. This suggests that LLDPE and EPDM may have some level of compatibility, as the presence of EPDM affects the crystallization behavior of the blends. The compatibility between LLDPE and EPDM in the blends leads to enhanced mechanical and thermal properties. It was observed that 90/10 LLDPE/EPDM blend has partial miscibility [9]. Moreover, the co-continuous morphology of the LLDPE/EPDM blend increases the adhesion between the component polymers, further enhancing the compatibility of the blends [10].

Therefore, LLDPE was used as a compatibilizer in NR/EPDMw blend in this research and the effects of the partial replacement of NR by LLDPE on compatibility, tensile and thermal properties were studied.

EXPERIMENTAL METHODOLOGY

The EPDMw that was collected from NT Rubber-Seals Sdn. Bhd. in Jitra, Kedah was initially crushed before being grounded into a powder (1.0 mm) using rubber cutting mill. The formulations shown in Table 1 were used in this study. The blending process was conducted using an internal mixer at approximately 160 °C. The process started by mixing NR (SMR20), which was provided by Kilang Hevea Bukit Perak in Gurun, Kedah, for 1 minute. Subsequently, zinc oxide (ZnO) and stearic acid were incorporated into the mixture and blended for 1 minute. Following this, EPDMw was added for 1 minute. Then, LLDPE was added for 3 min. Next, 2,2,4-trimethyl-1,2-dihydroquinoline polymer (TMQ) was added and mixed for 30 seconds. Finally, mercaptobenzothiazole disulfide (MBTS) and sulphur were added and mixed for another 1 minute. After that, the dough form of compounded material from the internal mixer process was withdrawn and sheeted out by using the two-roll mill. LLDPE pellets were supplied by Pengerang Petrochemical Company Sdn. Bhd. The ZnO, stearic acid, TMQ, MBTS, and sulphur were supplied by Zarm Scientific and Supplies Sdn. Bhd., Pulau Pinang. The blending process was conducted using an internal mixer at 160 °C, similar temperature of molding by using hot press to get 150 mm x 150 mm x 2 mm rubber slab sample. The rectangle test specimen of 150 x 15 x 25 mm dimension was cut from a rubber slab using a cutter knife. Then, the tensile test was conducted at 500 mm/min and a 2 kN load. Then, the Differential Scanning Calorimeter (DSC) analysis was conducted using Netzsch DSC 200F3. The 10 mg of vulcanized rubber was carried out between -100 and 200 °C, at a heating rate of 10 °C/min, with nitrogen gas purged at a 50 mL/min flow rate. The percentage crystallinity (X_c) was then determined using the following Equation (1).

$$X_c = \frac{\Delta H_m}{w \cdot \Delta H^\circ} \times 100 \tag{1}$$

where X_c is the percentage crystallinity, ΔH_m is the melting enthalpy from the DSC curve, w is the weight fraction of the crystalline polymer in the composite (in this case, only LLDPE have a crystalline part), and ΔH° is the theoretical melting enthalpy for 100% crystalline polymer. The theoretical melting enthalpy of 100% crystalline polyethylene is $\Delta H^\circ = 293$ J/g [11].

Thermogravimetric Analysis (TGA) analysis was conducted using Netzsch TG 209F3. A 7-10 mg vulcanized rubber sample was placed in a nitrogen atmosphere from 30 to 800 °C. The heating rate was set at 10 °C/min.

Table 1: Compound Formulation for Different Blend Compositions.

Ingredients (phr)	NR/EPDMw/LLDPE (phr)				
	40/60/0	35/60/5	30/60/10	25/60/15	20/60/20
NR (SMR20)	40	35	30	25	20
EPDMw	60	60	60	60	60
LLDPE	0	5	10	15	20
ZnO (activator)	5	5	5	5	5
Stearic acid (co-activator)	2	2	2	2	2
TMQ (antioxidant)	2	2	2	2	2
MBTS (accelerator)	0.6	0.6	0.6	0.6	0.6
Sulphur (curing agent)	3	3	3	3	3

Notes: phr is an acronym for "parts per hundred rubber"

RESULTS AND DISCUSSION

Tensile Properties

Table 2 depicts the tensile strength (TS) and elongation at break (%) (EB) of the different NR/EPDMw/LLDPE blend compositions.

Table 2: Tensile Properties of Different NR/EPDMw/LLDPE Blend Compositions.

NR/EPDMw/LLDPE Blend (phr)	Tensile Strength (MPa)	Elongation at Break (%)
40/60/0	5.56	173.64
35/60/5	7.76	204.48
30/60/10	11.33	270.66
25/60/15	9.52	229.42
20/60/20	7.25	169.18

The result shows an increment of TS and EB in the blends containing up to 10 phr LLDPE, with data of 11.33 MPa and 270.66 %, respectively. This suggests that up to this composition, the LLDPE contributes to enhancing the TS and EB of the blends due to improved compatibility and effective stress transfer between the constituent's materials in the blend. Makmud *et al.* [5] have reported that LLDPE demonstrates the highest compatibility with NR compared to other PE groups such as LDPE and HDPE. 10 phr of LLDPE enhances the flexibility and stretchability of the blend sample.

However, further increasing the LLDPE content beyond 10 phr reduces its TS and EB. This reduction trend can be attributed to the poor interaction between the components and leads to phase separation which negatively affects the TS. This could be due to the poor wetting of LLDPE by the NR. As further increased amount of LLDPE and decreased amount of NR incorporated in the blend sample leading to lower TS. According to Abu-Abdeen and Elamer [12], poor wetting can cause poor interfacial adhesion between thermoplastic and rubber matrix that leads to weak interfacial region. Abdelsalam *et al.* [13] stated that low compatibility in rubber blends can cause phase separation, which in turn affects mechanical properties and thermal properties.

Thermal Properties

To prove that a decrease in material compatibility correlated with reduced tensile properties, three samples were selected for compatibility evaluation which were 40/60/0 (control), 30/60/10 (the highest tensile properties), and 20/60/20 (the lowest tensile properties of the blends). These three samples were also analyzed for thermal properties using both DSC and TGA. Figure 1 and 2 present the exotherms scan patterns and TGA thermogram, respectively. Table 3 depicts the melting enthalpy and initial degradation temperature of the ternary blends.

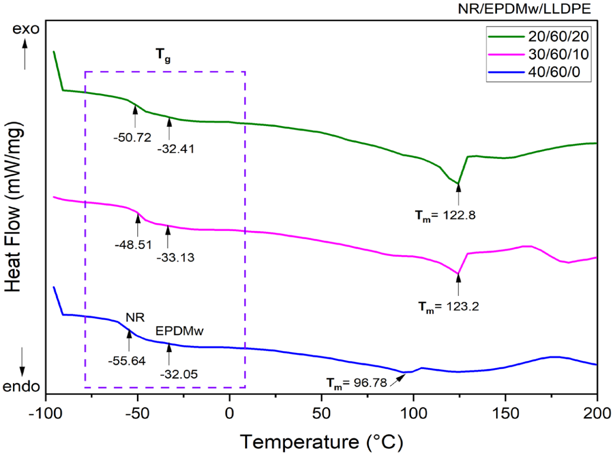

Figure 1: The Effects of Partial Replacement of NR by LLDPE on DSC Exotherms of NR/EPDMw/LLDPE Blends.

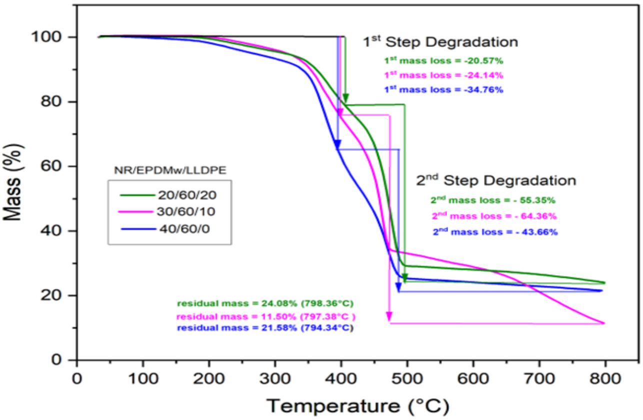

Figure 2: The Effects of Partial Replacement of NR by LLDPE on TGA Thermal Transition of NR/EPDMw/LLDPE Blends.

Table 3: Thermal Properties of Different NR/EPDMw/LLDPE Blend Compositions.

NR/EPDMw/ LLDPE Blend (phr)	Thermal Properties			
	DSC		TGA	
	Melting Enthalpy, ΔH_m (J/g)	Percentage Crystallinity, X_c (%)	Initial Degradation Temperature, T_o (°C)	
			1st step	2nd step
40/60/0	0.92	0.00	344.34	414.34
30/60/10	3.60	12.29	347.38	427.37
20/60/20	6.50	11.09	348.36	443.36

The results from Figure 1 indicate that the 40/60/0 blend (NR/EPDMw without LLDPE) is immiscible, as indicated by two distinct transition temperatures (T_g) -55.64 °C for NR and -32.05 °C for EPDMw. This aligns with the findings of a prior study [14], which identified NR/EPDM as immiscible due to two distinct Tg observed in the blend. When LLDPE is added (in 30/60/10 and 20/60/20 blends), two Tg values are still present, but Tg becomes less distinct as they shift closer to each other, suggesting the improvement of compatibility and partial immiscibility. Both Tg of the 30/60/10 blend peaks move closer to each other compared to the 20/60/20 blend. This suggests that the 30/60/10 blend has better compatibility than 20/60/20 due to good interfacial interaction between the EPDMw and LLDPE phase at 10 phr LLDPE. A similar study by Pieroni *et al.* [15] on polypropylene/LLDPE/EPDM blends found that adding LLDPE improved elastomer dispersibility.

The melting temperature (T_m) of the LLDPE can be seen at 123.2 and 122.8 °C when 10 and 20 phr, respectively LLDPE is added to the blend as shown in Figure 1. Meanwhile the small peak T_m at 96.78 °C belongs to the partially crystalline elastomer of EPDM [16]. The higher T_m at 10 phr indicates the improvement in compatibility of phases among the blends [17] which aligned with the shifted of the T_g value. Other than that, the calculated percentage crystallinity according to melting enthalpy results from DSC for this sample is the highest i.e., 12.29% as compared to the 20/60/20 blend sample with the value of 11.09%. Thus, this also supports the finding of higher tensile strength for addition 10 phr compared to 20 phr LLDPE in the system.

The blend compositions of NR/EPDMw/LLDPE blends show a two-step degradation as shown in Figure 2. The 20/60/20 composition shows the highest thermal stability because it has the highest initial degradation temperature compared to other samples (Table 3). This indicates that adding more LLDPE improves the thermal stability of the blend. According to Iqbal *et al.* [10], this could be due to the use of LLDPE, which restricts the mobility of polymer chains and lowers thermal vibration in C-C bonds. Another explanation for the improved thermal stability of the blends could be the creation of a protective chain that functions as a physical barrier between the polymer and the combustion zone. Blending EPDM with LLDPE may improve its thermal stability and resistance to thermal degradation. According to Balakrishnan *et al.* [18], the increment of thermal stability might be due to kinetic effects, with the LLDPE particles retarding the diffusion of oxygen into the polymer matrix.

CONCLUSION

In conclusion, the amount of NR and LLDPE affects the compatibility, tensile properties and thermal stability of the NR/EPDMw/LLDPE blend. Gradual replacement of NR by LLDPE up to 10 phr (30/60/10) promotes better mechanical properties due to improved compatibility. The DSC thermograms support this statement by showing the T_g shifting close to each other as well as resulting in the highest value of crystallinity that contributes to the improvement of TS. The addition of LLDPE not only promotes elastomer dispersibility but also improves the thermal stability of the blends. The 30/60/10 blend showed good mechanical properties with higher Tm than 20/60/20 blend, making it a good option for development of rubber product, such as rubberized pavement. Although, 20/60/20 blend has shown better thermal stability than other blends, it resulted in poorer TS due to higher LLDPE content that led to phase separation, making it less favorable to be used in rubberized pavement.

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