Identification of the Best Blend Composition of Natural Rubber-High Density Polyethylene Blends for Roofing Applications

W. V. W. H. Wickramaarachchi, S. Walpalage, S. M. Egodage

Abstract—Thermoplastic elastomer (TPE) is a multifunctional polymeric material which possesses a combination of excellent properties of parent materials. Basically, TPE has a rubber phase and a thermoplastic phase which gives processability as thermoplastics. When the rubber phase is partially or fully crosslinked in the thermoplastic matrix, TPE is called as thermoplastic elastomer vulcanizate (TPV). If the rubber phase is non-crosslinked, it is called as thermoplastic elastomer olefin (TPO). Nowadays TPEs are introduced into the commercial market with different products. However, the application of TPE as a roofing material is limited. Out of the commercially available roofing products from different materials, only single ply roofing membranes and plastic roofing sheets are produced from rubbers and plastics. Natural rubber (NR) and high density polyethylene (HDPE) are used in various industrial applications individually with some drawbacks. Therefore, this study was focused to develop both TPO and TPV blends from NR and HDPE at different compositions and then to identify the best blend composition to use as a roofing material. A series of blends by varying NR loading from 10 wt% to 50 wt%, at 10 wt% intervals, were prepared using a twin screw extruder. Dicumyl peroxide was used as a crosslinker for TPV. The standard properties for a roofing material like tensile properties tear strength, hardness, impact strength, water absorption, swell/gel analysis and thermal characteristics of the blends were investigated. Change of tensile strength after exposing to UV radiation was also studied. Tensile strength, hardness, tear strength, melting temperature and gel content of TPVs show higher values compared to TPOs at every loading studied, while water absorption and swelling index show lower values, suggesting TPVs are more suitable than TPOs for roofing applications. Most of the optimum properties were shown at 10/90 (NR/HDPE) composition. However, high impact strength and gel content were shown at 20/80 (NR/HDPE) composition. Impact strength, as being an energy absorbing property, is the most important for a roofing material in order to resist impact loads. Therefore, 20/80 (NR/HDPE) is identified as the best blend composition. UV resistance and other properties required for a roofing material could be achieved by incorporating suitable additives to TPVs.

Keywords—Thermoplastic elastomer, natural rubber, high density polyethylene, roofing material.

I. INTRODUCTION

BLENDING of polymers is the widely used technology to develop new polymers because blends possess better properties than respective virgin polymers [1]. It is cheaper, energy effective and less time consuming compared to synthesizing a new polymer. Polymer blend is a physical mix of two or more polymers with or without other property enhancing materials like fillers, compatibilizers, etc. [2].

TPEs, a kind of polymer blend consists of a thermoplastic like polyethylene (PE), polypropylene, polystyrene, polyvinylchloride (PVC), etc. and a natural or synthetic rubber [3]. TPEs can be classified as TPO and TPV. TPO consists of non-crosslinked rubber phase and a thermoplastic phase, and is preferably used at lower temperatures. It has a low density, transparent structure and produce at an attractive price. TPV has partially or fully crosslinked rubber phase and a thermoplastic phase. Light weight, high toughness, durability, reduced material and energy costs, recyclability, extended the service temperature range, resistant to chemical, fire and weather, etc. are the economic and property advantages of TPOs or TPVs than synthesizing a new polymer, for the same application [4].

Large numbers of different roofing materials namely clay, wood, metal, concrete, asphalt contained shingles, slates, single ply membranes, asbestos and plastics (PE, PVC) are used worldwide with their inherent drawbacks [5], [6]. Among them, single ply membranes and plastics are from polymers and their application is limited. Single ply membrane cannot be placed directly in the roof like a sheet or a tile. It should be adhered to the existing roof. Plastic is light weight and transparent. Adding fillers to produce a usable roofing material is not cost competitive.

During the first 11 months of 2018, the world demand of NR observed a growth at 5.2%, amounting to 14.017 million tonnes. The world production accounted 13.960 million tonnes, an increase of 4.6% from 13.350 million tonnes during the same reference period [7]. Though, NR has increased demand and production and possesses excellent rubbery properties, due to its low chemical and weather resistance, applications of NR are still confined to limited products. Further, NR cannot be used alone for outdoor applications having long service life. Therefore, blending of NR with a thermoplastic currently uses in roofing applications like PE would facilitate to use NR in outdoor applications. It was proven that HDPE compared to low density PE is more suitable for roofing applications [8]. This paper presents the effect of NR/HDPE blend composition on properties of the blends prepared using twin screw extruder and the identified best blend composition to match with requirements for roofing materials.

W. V. W. H. Wickramaarachchi is a PhD student at Department of Chemical and Process Engineering, University of Moratuwa, Sri Lanka (e-mail: wathsalauom@gmail.com).

S. Walpalage is a professor and S. M. Egodage is a senior lecturer at Department of Chemical and Process Engineering, University of Moratuwa, Sri Lanka (e-mail: shanthaw@uom.lk and segodage@uom.lk).

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II. EXPERIMENTAL

A. Materials

Crepe rubber, a grade of NR in 3 mm size cut pieces and HDPE having specific gravity of 0.949 were used as the base polymers to prepare TPO and TPV blends. Dicumyl peroxide (DCP) was used as the reactive agent for TPV. All these materials were of industrial grade and were obtained from Samson Compounds (Pvt) Ltd, Sri Lanka.

B. Preparation of Blends

NR/HDPE TPO and TPV blends were prepared by melt blending in a co-rotating twin screw extruder (KTE 20) by varying the composition from 10-50wt% at an interval of 10wt%. 0.5 phr loading of DCP was added only for TPV blends.

NR and HDPE were first fed into the extruder, and taken away in pellet form. Obtained pellets were again fed into the extruder to get homogenize blends. For TPV blends, the pellets were mixed with DCP in the extruder in two additional times.

C. Preparation of Molded Specimen

Test specimens for tensile, tear, hardness and impact tests were prepared from TPO and TPV blends according to ASTM standard D3182-85, using an electrically heated hydraulic press operated at temperatures of 155°C and 160°C respectively, under 500 MPa pressure. Compression time for the blends was kept constant at 5 minutes. The molds were cooled to 40°C under the same pressure before the molded sheets were removed.

D. Determination of Mechanical Properties

Tensile properties and tear strength of the blends were determined using a Hounsfield H10KT tensile tester as per ASTM D638 and ASTM D1004, respectively. Dumbbell specimens and angle specimens were punched from of 2 mm thick molded sheets and used for determination of tensile properties and tear strength, respectively. Both tests were carried out at 28 ± 2°C under a strain rate of 50 mm/min. Extension was taken as the movement of crosshead. Hardness of blends was determined using a Shore D durometer, according to ASTM D2240. Impact strength of blends was determined using Charpy impact tester according to ASTM D6110. Average values for all the properties were taken out from six samples.

E. Determination of Thermal Properties

Thermal properties were determined using a differential scanning calorimeter (DSC) of model Q20 from TA instruments, USA according to ASTM D3418. Weight of approximately 5-10 mg of each blend was placed in a tzero pan and the test was run at a heating rate of 3 °C/min over a temperature range of -80 to 0°C and of 10 °C/min over a temperature range of 0°C to 160°C in nitrogen environment maintained at a flow rate of 35 ml/min. Glass transition temperature (T_g) and melting temperature (T_m) were obtained from the DSC curves. The degree of crystallinity was calculated using the expression:

$$\%crystallinity = \frac{\Delta H}{\Delta H_m^0} \times 100\% \qquad (1)$$

where ΔH is heat of fusion and ΔH_m^0 is heat of fusion for 100% crystalline PE. ΔH_m^0 for HDPE is taken as 293J/g.

F. Water Absorption

Test specimen of approximately 1 g of each blend was immersed in a water bath at room temperature. The specimen was removed from the water batch after 24 hours and gently wiped with a blotting paper to remove the excess water on the surface. The weight of each swollen sample was recorded. The degree of water absorption (Sw) was calculated using:

$$S_w = \frac{W_2 - W_1}{W_1} \qquad (2)$$

where, W_1 and W_2 are the weights of the specimen before and after the water absorption, respectively.

G. Sol-Gel Analysis

Sol-gel analysis was carried out using toluene as the solvent. Specimens, with dimensions, 15mm×15mm×2mm were cut from the molded sheets and weighed to record their initial weights. The specimens of TPO blends were immersed in toluene at 25°C for 72 hours. For TPV blends, specimens were immersed at 40°C for 7 days. A constant volume of 100ml of the solvent was used. After removal from toluene, the specimens were wiped with a tissue to remove any excess solvent from the surface. The specimens were then re-weighed to record their swollen weights. The swollen specimens were dried at 70°C for 2 hours using vacuum oven and weighed again to obtain the final dry weight. Swelling indices and Gel content were calculated using the expressions:

$$\text{Swelling index} = \frac{W_2 - W_3}{W_3} \qquad (3)$$

$$\%\text{Gel Content} = \frac{W_3}{W_1} \times 100 \qquad (4)$$

where, W_1, W_2 and W_3 are the initial weight the swollen weight, and the final dry weight of the specimen, respectively.

H. UV Resistance

UV resistance of the blends was measured by change of tensile properties using a UV chamber. Tensile specimens cut from the molded sheets were kept in the UV chamber for 20 hours and tensile strength was determined after that using the tensile tester as per ASTM D638.

III. RESULTS AND DISCUSSION

A. Mechanical Properties

Fig. 1 shows tensile strength variation against NR loading for TPO and TPV blends. Tensile strength of both blends decreases with increase in NR loading. The higher tensile strengths show for TPV blends compared to TPO blends at

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every loading. After 30wt% of NR loading, TPV blends show a drastic reduction. However, the variation of tensile strength against NR loading for TPOs shows a linear downward trend. Addition of NR caused to interrupt the degree of crystallinity of HDPE. Table I shows the variation of degree of crystallinity for both blends. According to the PE structures, HDPE has low degree of short chain branching and closely packed crystalline structures and hence, it shows a higher degree of crystallinity. With the addition of 10 wt% loading of NR the degree of crystallinity drastically decreases and further decreases with increase in NR loading in both blends. DCP makes crosslinks in both NR and PE phases. Generally, 4-5 phr loading of DCP is needed to vulcanize rubber, and 0.5 phr is enough for TPEs. The reduction of degree of crystallinity of TPV blends is higher than that of TPO blends. These results reveal that the crystalline structure of HDPE was influenced by NR, and further, by crosslinking of both NR and HDPE phases.
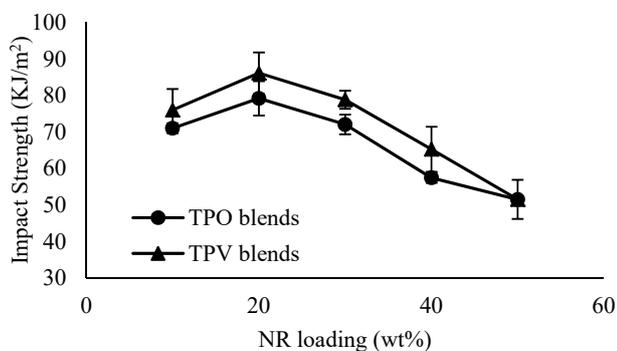

Fig. 1 Tensile strengths of TPO and TPV blends at different NR loadings

Ultimate tensile strength of the widely known concrete based roofing tiles is 3 MPa [9], and hence tensile strength of 3 MPa was chosen as the minimal acceptable strength for a roofing material. The tensile strengths of all blends are higher than the minimum and thereby confirmed that the blends could be used as a roofing material.
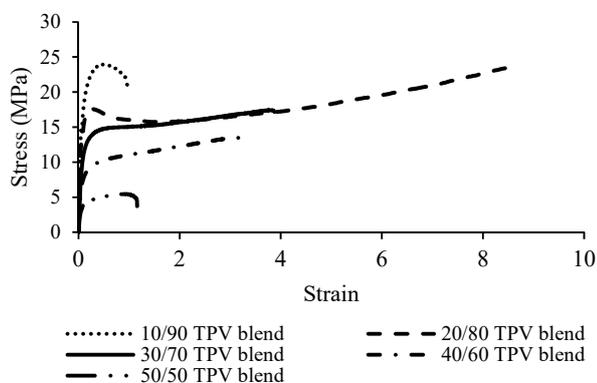

Fig. 2 Impact strengths of TPO and TPV blends at different NR loadings

Variation of impact strength against NR loading for both

blends is shown in Fig. 2. Highest impact strength for both blends is shown at 20wt% loading of NR, suggesting that highest toughness would occur at that composition. Addition of NR increases energy absorption by the blend due to the presence of smaller NR dispersed phases in the HDPE matrix, and increases in impact strength. Good adhesion between phases will promote stress transfer between the phases and therefore, TPVs show higher impact strength than TPOs. However, due to reduction of tensile strength of HDPE by addition of NR, and to formation of larger NR dispersed phases, impact strength decreases with NR loading after the optimum loading. Fig. 3 shows the stress-strain curves for TPV blends at different NR loadings. The area under the stress-strain curve also relates to the toughness of a material. The highest area is shown by the 20/80 TPV blend, which has the highest toughness and confirmed the impact strength results. For roofing applications, it is needed to withstand high loading and sudden impacts and therefore a roofing material should be strain hardening.
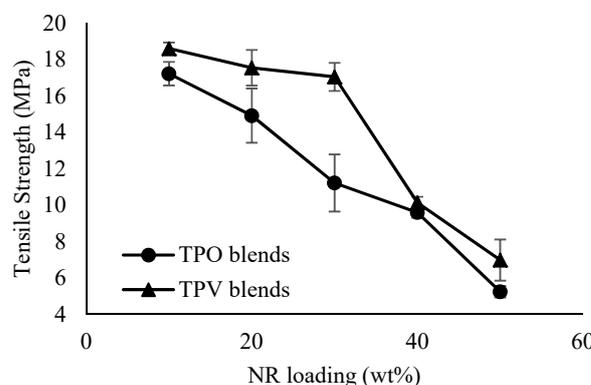

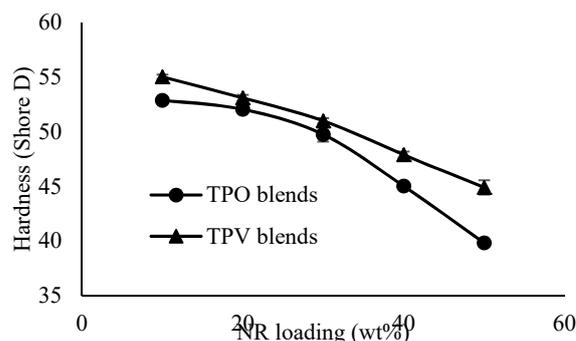Fig. 3 Stress-strain curves for TPV blends at different NR loadings

Fig. 4 Hardness of TPO and TPV blends at different NR loadings

Hardness, which is given by Fig. 4, is gradually decreased with increase in NR loading for both TPO and TPV blends. TPV blends show slightly high hardness compared to the respective TPO blends. This is associated with the crosslinking of NR and/or HDPE phases or the formation of adhesions between two phases.

Fig. 5 shows the variation of tear strength against NR loading for both blends. Tear strength linearly decreases with increase of NR loading. TPVs compared to TPOs show higher

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tear strengths due to enhancement of the phase adhesion between NR and LDPE effectively or crosslinking of phases with DCP at a loading of 0.5 phr.
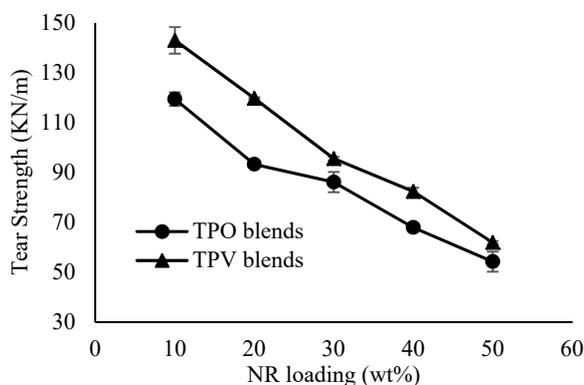

Fig. 5 Tear strengths of TPO and TPV blends at different NR loadings

TABLE I
THERMAL PROPERTIES OF TPO AND TPV BLENDS

Composition NR/HDPE	Degree of Crystallinity %		Melting Temperature (ºC)		Glass Transition Temperature (T_g)	
	TPO	TPV	TPO	TPV	TPO	TPV
10/90	56.1	51.7	130.6	133.3	-65.3	-62.2
20/80	54.6	45.1	129.5	135.4	-65.0	-62.6
30/70	53.8	34.3	130.7	133.9	-63.9	-62.5
40/60	24.2	25.4	130.8	135.0	-63.8	-62.4
50/50	24.1	21.1	130.7	133.7	-63.5	-62.4

B. Thermal Properties

T_g and T_m of NR and HDPE were recorded at 130°C and -63°C, respectively. When NR is blended with HDPE in TPOs, T_g lowered to -65°C to at 10 wt% NR loading (Table I). T_g of TPV blends increased by 1°C, confirming that the NR phase in TPV blend is crosslinked due to addition of 0.5 phr of DCP.

T_m of TPO blends were not varied with the NR loading and lie within the range 130-131°C and similar to T_m of virgin HDPE. However, T_m of TPVs shows increment around 2°C, confirming the HDPE phase was also crosslinked. .
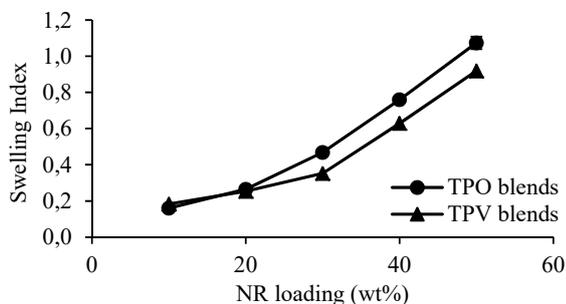
C. Sol-Gel Analysis

Fig. 6 Swelling indices of TPO and TPV blends at different NR loadings

Swelling index and gel content of both TPO and TPV blends at different NR loadings are shown in Figs. 6 and 7,

respectively. Both blends show an increase with the increase in NR loading. NR is amorphous and toluene could easily diffuse to the blends when NR loading is high. However, up to 20 wt% of NR loading, no significant change of swelling was shown, and it could be due to difficulty in diffusing toluene in to small NR dispersed phase through HDPE matrix. Due to formation of crosslinks in NR and HDPE phases or between phases, solvent diffusion to the blend is decreased and therefore TPV blends show lower swelling index than TPO blends.

Gel content of the blends give related to their crosslink densities or phases adhesions. Up to 30wt% loading of NR, gel content remains same for both blends, but decreases drastically thereafter since NR dissolves in toluene. Crosslinked NR is swollen in toluene and therefore TPV blends compared to TPO blends showed higher gel content at higher NR loadings.
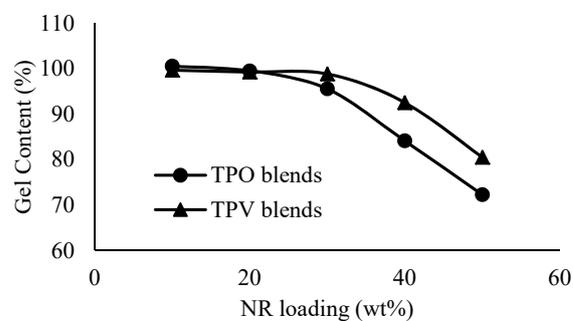

Fig. 7 Gel content of TPO and TPV blends at different NR loadings

D. Water Absorption

Water absorption of TPV and TPO blends having NR loading from 30 wt% is shown in Table II. Up to 20 wt% of NR loading, water absorption is not measurable. Since water absorption of NR is higher than that of HDPE due to its loose packing of molecules, water absorption increases with increase in NR loading. Diffusion of water to the blend is interrupted by the formation of crosslinked structures and hence TPV blends showed lower absorptions compared to TPO blends.

TABLE II
WATER ABSORPTION OF TPO AND TPV BLENDS

Composition	TPO Blends (%)	TPV Blends (%)
10/90	0.12	0.05
20/80	0.17	0.09
30/70	0.17	0.17
40/60	0.26	0.25
50/50	0.35	0.33

E. UV Resistance

Variation of tensile strength of TPO and TPV blends after exposure to UV radiation is shown in Fig. 8. Tensile strengths of both blends reduced after to exposure to UV radiation and show similar strengths at every loading. The percentage of reduction of tensile strength, which is shown in Table III, is

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higher in TPV than TPO. This explains that whether HDPE and NR is crosslinked or not, both degrades under UV radiation. This reduction is significant for both blends and reveals the necessity of an antidegradant. Further, NR and HDPE products with UV absorbers are commonly used in outdoor applications such as bridge bearings, tires, roofing materials, water tanks, etc. Hence, NR/HDPE blends could also be developed with superior anti-aging properties.

TABLE III
PERCENTAGE REDUCTION TENSILE STRENGTH OF TPO AND TPV BLENDS

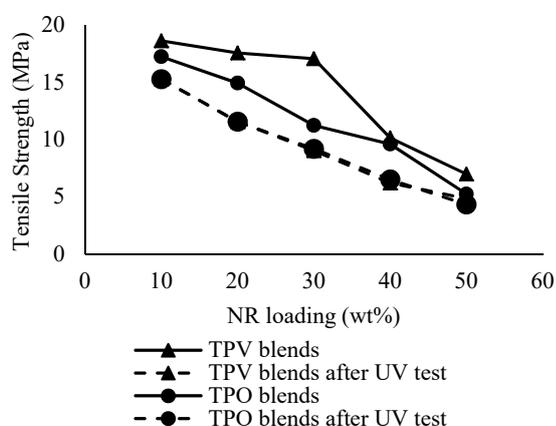| Composition	TPO Blends (%)	TPV Blends (%)
10/90	11	18
20/80	23	34
30/70	19	46
40/60	32	39
50/50	34	36

Fig. 8 Tensile Strength variation after exposure to UV radiation

IV. CONCLUSIONS

Tensile strength, hardness and tear strength of TPV blends show higher values than those of TPO blends, while water absorption and swelling index shows lower values, suggesting that TPV blends are more suitable for roofing applications than TPO blends. Increase of gel content of TPV blends than TPO blends reveals that the formation of crosslinks within and/or between the two phases. Tensile and tear properties and hardness of both blends decrease with increase in NR loading, showing best properties at 10 wt% loading of NR. However, impact strength of the blends show the maximum at 20 wt% loading of NR. Impact strength, as being an energy absorbing property, is more important for a roofing material in order to resist from impact loads. Therefore, the most suitable blend composition is identified as 20/80 (NR/HPDE). Drop of tensile strength when exposure to UV radiation reveals the necessity of a suitable antidegradant. UV resistance and other properties required for a roofing material could be achieved when suitable additives are incorporated to TPV blends.

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