

Properties of HVA-2 Vulcanized High Density Polyethylene/Natural Rubber/Thermoplastic Tapioca Starch Blends

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ABSTRACT: Blending of high density polyethylene (HDPE), natural rubber (NR), and thermoplastic tapioca starch (TPS) has been studied. Two series of blends having 5 wt %, 10 wt %, 20 wt %, and 30 wt % TPS were prepared: (a) unvulcanized blends and (b) *N, N'*-*m*-phenylenebismaleimide (HVA-2) vulcanized HDPE/NR/TPS blends. The composition of HDPE/NR was fixed at blend ratio of 70/30. Tensile strength, Young's modulus, and elongation at break exhibited significant improvement when HDPE/NR/TPS blends were subject to HVA-2 crosslinker. Tensile strength increased to 1.4 MPa, 2.3 MPa, 3.4 MPa, and 5.1 MPa from 15 MPa, 12 MPa, 9.7 MPa, and 7.87 MPa of unvulcanized counterparts. SEM micrographs showed fine TPS dispersion and well embedded in vulcanized HDPE/NR matrix. Comparison were also made based on the results of gel content, thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). The improvement in tensile properties, thermal stability, and blends modulus can be correlated to the crosslink formation within the NR phase. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

High density polyethylene (HDPE) is one of the dominant synthetic plastic with interesting physical properties and high thermal stability. Blending HDPE with natural rubber (NR) generally enhances the physical properties of the blends since the low modulus of elastomer is considered to be an impact modifier in tough HDPE matrix.^{1,2} Incorporation of starch into thermoplastic natural rubber (TPNR) system contributes toward the producing of biodegradable materials with inexpensive and widely abundant availability of starch from various plant sources. Thermoplastic starch (TPS) can be prepared by plasticization of native starch at high temperature and high shear conditions.^{3–7} However, some drawbacks such as strong polar surface and tendency of starch to absorb water become the critical factors in determining the mechanical performance of the blends. Incorporating TPS particle usually leads to weak mechanical property, as a result of incompatibility of hydrophobic and hydrophilic components. Several works have been carried out to study the effect of partial replacement of TPS in thermoplastics system or blend with NR.^{8–14} It has been reported that the blends with TPS cause marked decrement in tensile properties. This can be attributed to TPS-based plastics which exhibit weak water resistance and its tendency not to disperse in the blend systems.

To overcome the incompatibility and produce a blend which can meet the desired properties, this study was focused on the NR vulcanization using dynamic vulcanization method. Dynamic vulcanization process is a promising method in improving the mechanical properties of TPNR blends. It involves the NR particles being crosslinked in the molten unvulcanized thermoplastic and leading to significant alteration in the mechanical properties of the resulting blends. This work was intended to crosslink intra- and intermolecular bonds in NR polymer chains, and thus increases the stability and strength of the NR phase. Besides sulfur or sulfur derivative, dynamic vulcanization process also can be performed by utilization of bismaleimide such as HVA-2. The structure of the HVA-2 has been shown in Figure 1. Adding free radical source such as dicumyl peroxide (DCP) is reported to accelerate the crosslinking of NR phase and thus enhance the crosslink density of the blends.¹⁵ Another study also reported that the effective crosslinking can also be achieved by irradiating the blends with electron beam.¹⁶ However at high enough temperature, HVA-2 is able to vulcanize NR without the presence of free radical initiator.^{17,18}

In this work, HVA-2 as a crosslinking agent in forming intra- and intermolecular linkages from the linear NR polymer chains was investigated. The purpose of this work is to evaluate the

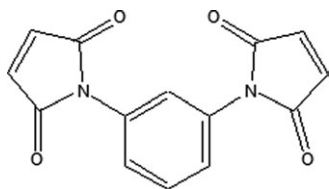


Figure 1. *N, N'*-*m*-phenylenebismaleimide.

crosslinking in the NR phase in order to compensate the deterioration of properties caused by incorporation of TPS. The potential effects of HVA-2 on HDPE/NR/TPS blends properties have been carried out by tensile measurement and thermogravimetric analysis. Gel contents and blends morphology which were correlated to the tensile properties has also been studied in this present work.

EXPERIMENTAL

Materials and Methods

HDPE granulates with density 0.96 g/cm^3 was supplied by Titan Chemicals, Malaysia. NR grade SMR L was obtained from Lembaga Getah, Malaysia. Tapioca starch used was a food grade and obtained from Thye Huat Chan Sdn Bhd., Malaysia. HVA-2 (Aldrich Chemical Company, St. Louis, USA) was used as a crosslinking agent. Reagent grade glycerol was obtained from Merck, Darmstadt, Germany and used as received.

Preparation of Thermoplastic Tapioca Starch

Tapioca starch was dried at 80°C in vacuum oven for 24 h. Tapioca starch was first pre-mixed with 35 wt % of glycerol using a kitchen blender (3000 rpm, 2 min) until a homogenous mixture was obtained.⁵ The amount of plasticizers used plays an important part in destroying the starch granules and at the same time are able to maintain the overall TPS performance. Then, the mixture was stored overnight in a desiccator. Later the mixture was processed using heated two-roll mill at 150°C for 10 min.

Preparations of HDPE/NR/TPS Blends

The blends were prepared by varying TPS portion from 5% to 30% with respects to the total weight and the ratio between HDPE/NR was fixed at 70/30, which is based on the preliminary study. TPNR with a blend ratio of HDPE/NR 70:30 exhibited adequate value for tensile strength and elongation at break. An increase in NR composition up to 40% and 50% of blend ratio show significant decrease in tensile strength. The mixing was carried out in a Haake Rheomix 600 mixer equipped with roller rotors and processed at 150°C and 55 rpm. The HDPE was first charged into the mixing chamber for 3 min and followed by NR. Then, the mixing time was continued for 4 min before mixed with HVA-2 and TPS and process continued until plateau torque was reached. The whole process proceeded for 12 min. Later, the blend was converted into 1-mm thick sheet using a hydraulic hot pressing Gotech Testing Machine. The hot press procedures involved preheating at 150°C for 6 min and followed by 2 min compressing at the same temperature, subsequent cooling at 70 kg/m^2 pressure for 4 min. The percentage of HVA-2 content was fixed to 0.5% relative NR content, which is found to be optimum concentration on NR vulcanizes.¹⁸

Tensile Properties

Measurements of the tensile properties were performed by using an Instron Universal Testing Machine (model 3366), with cross-head speed of 50 mm/min. Dumbbell sample (1 mm thick) with 50 mm gauge length were tested according to ASTM D 638. The mean value, out of five samples was reported with standard deviation.

Gel Content

The gel content of the samples was determined by using soxhlet extraction technique. The samples were first extracted with hot water (10 h) to remove TPS phase and then they were extracted with hot xylene for 4 h and 8 h. The samples were placed in folded 120 mesh stainless steel cloth cages. The samples and cages were weighed before extraction. The extracted samples were then dried at 80°C until there was no further weight loss. The gel content was calculated from the following equation:

$$\text{Gelcontent} = 100 - \% \text{ extract} \quad (1)$$

$$\% \text{ Extract} = \frac{\text{weight before extraction} - \text{weight after extraction}}{\text{weight before extraction}} \times 100 \quad (2)$$

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) of unvulcanized and HVA-2 vulcanized blends were measured using a Perkin Elmer System 2000 to characterize the possible reaction between TPS and PE-g-MA. The transmittance spectra regions were obtained between 4000 cm^{-1} and 800 cm^{-1} with a 4 cm^{-1} resolution.

Scanning Electron Microscopy

Fracture surface of the samples were observed by a Leo Supra-35VP field emission scanning electron microscopy (SEM) at an acceleration voltage of 20 kV. The fracture surfaces of the specimen were mounted on aluminum stubs and sputter coated with thin layer of gold to avoid electrostatic charge during examination.

Differential Scanning Calorimetry

Thermal analysis of HDPE/NR and HDPE/NR/TPS blends were performed using a Mettler Toledo differential scanning calorimetry (DSC) TS800GCL under nitrogen atmosphere at scan rate $10^\circ\text{C}/\text{min}$. The samples were heated from ambient temperature to 190°C and held at this temperature for 3 min to eliminate thermal history and destroy the polyethylene nuclei. Then, samples were slowly cooled at $10^\circ\text{C}/\text{min}$ to room temperature before the crystallized samples were subsequently heated to 230°C at the same heating rate. The melting temperature (T_m) and the heat of fusion (ΔH_{exp}) were determined from the endothermic peak integration during the second heating.

Thermogravimetric Analyses

The thermogravimetric analyses (TGA) of the blends were operated using a Perkin Elmer Pyris 6 machine. The thermal stability of the HDPE/NR/TPS blends was tested at a heating rate of $10^\circ\text{C}/\text{min}$ from ambient temperature to 600°C under nitrogen environment.

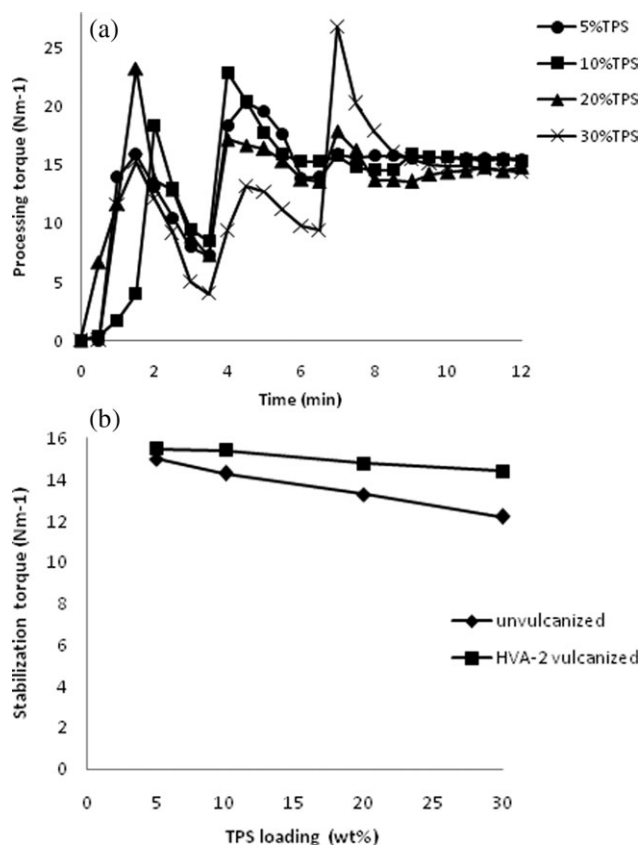


Figure 2. (a) The processing torque of HVA-2 vulcanized HDPE/NR/TPS blends. (b) The effect of HVA-2 as crosslinker on the stabilization torque of HDPE/NR/TPS blends as a function of TPS content.

Dynamic Mechanical Thermal Analysis

A Mettler Toledo DMA861 was used to examine the dynamic mechanical properties of HDPE/NR/TPS blends. Specimen dimensions approximately 10.5 mm × 6.5 mm × 1 mm were tested in a tensile mode at a frequency of 1 Hz and the oscillation amplitude was 20 μm. The analysis was run at 10°C/min and started from -65°C to 120°C for the chosen blends. The peak temperature of the tan δ versus temperature curve was taken as T_g .

RESULTS AND DISCUSSION

Processing Characteristics

The melt processing characteristics of HVA-2 vulcanized HDPE/NR/TPS blends have been studied by monitoring the shape and intensity from the processing torque–time curve. Figure 2(a) shows the processing torque of the melt mixed HVA-2 vulcanized HDPE/NR system with different TPS contents. In the melt processing graph, the first and second peaks correspond to the shear torque before melting of HDPE and NR, respectively. The third peak appearing at around 7 min corresponds to the introduction of TPS. The different peaks were obtained for all cases which were related to different amount of each component that was charged into the mixing chamber.

The stabilization torque for mixing HDPE/NR with different TPS contents, as recorded at the end of mixing can be seen in

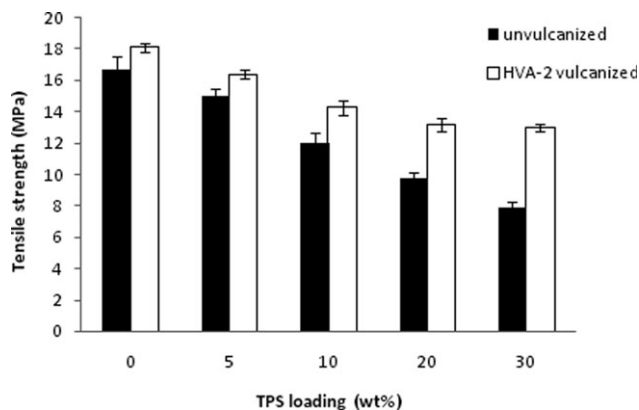


Figure 3. Tensile strength for unvulcanized and HVA-2 vulcanized HDPE/NR/TPS blends.

Figure 2(b). With the dynamic crosslinking occurring in NR phase, the changes in stabilization torque are affected only by TPS content. Therefore, a comparison can be generally made to distinguish the effect of dynamic crosslinking for both HVA-2 vulcanized and unvulcanized blends. It clearly shows that the stabilization torque decreases as the TPS content increases. This can be attributed to the blends plasticized by glycerol in TPS and this plasticization effect was found to be stronger for the unvulcanized blends. Whereas, stabilization torque of HVA-2 vulcanized blends which is reflected on the melt blends viscosity tends to be linear, although TPS concentration has increased up to 30%. The increment in orthography can be correlated to the crosslinking formation in the NR phase.

Tensile Properties

Tensile strength, Young’s modulus, and elongation at break of 0–30% TPS content in unvulcanized and HVA-2 vulcanized HDPE/NR/TPS blends are compared in Figures 3–5. For both unvulcanized and vulcanized blends, with increasing in TPS content, the tensile strength was found to decrease as shown in Figure 3. This is due to the poor interfacial adhesion and inability of TPS to support stress transfer from HDPE/NR matrix phase. Effective stress transfer between phases was the major factor that determined the tensile properties of the blends. However, an interesting increase in tensile strength in vulcanized

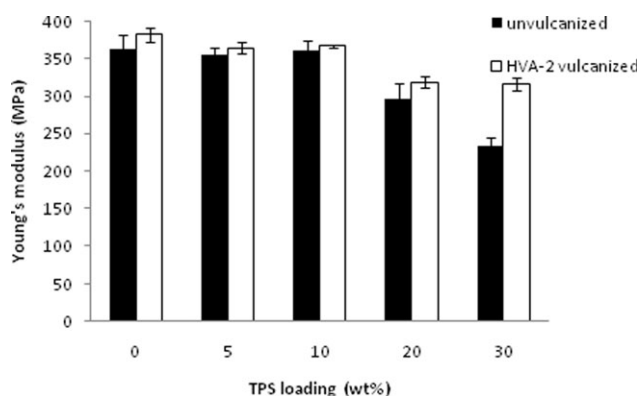


Figure 4. Young’s modulus for unvulcanized and HVA-2 vulcanized HDPE/NR/TPS blends.

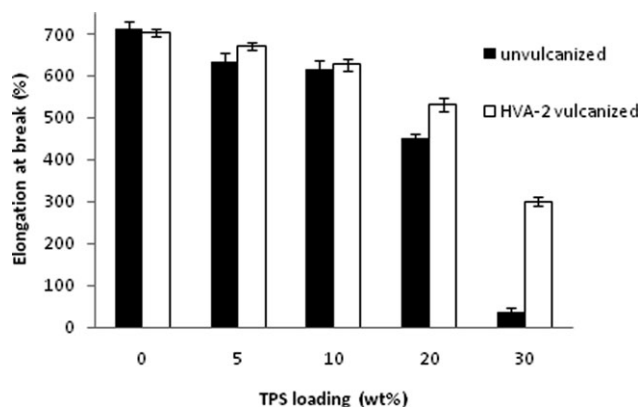


Figure 5. Elongation at break for unvulcanized and HVA-2 vulcanized HDPE/NR/TPS blends.

HDPE/NR/TPS blends was observed in all studied blends. For HVA-2 vulcanized blends, tensile strength increased by 1.4 MPa for both HDPE/NR and the blend with 5% TPS content. At 10%, 20%, and 30% TPS content, the tensile strength increased by 2.3 MPa, 3.4 MPa, and 5.1 MPa, respectively, when compared to unvulcanized counterparts. For all unvulcanized blends, tensile strength decreased marginally with increase in TPS. Whereas, the tensile strength of vulcanized blends decreased slightly for the concentration of TPS until 10% and remained unaffected with further increase of TPS up to 30%. As mentioned earlier, the addition of HVA-2 can promote the intra- and intermolecular linkages in NR phase and from the observations of tensile strength it is clear that HVA-2 crosslink system can be used to improve the blends properties. In other words, HVA-2 vulcanization system has been applied in these blends as a way to compensate the strength deterioration caused by incorporation of TPS.

Figure 4 shows the change in Young's modulus before and after vulcanization using HVA-2 as a function of different TPS content. Adding TPS in HDPE/NR blends can lead to decrease in Young's modulus especially at higher TPS content due to the effect of incorporation soft TPS materials and the presence of glycerol in TPS. At the lower concentration of TPS ($\leq 10\%$), Young's modulus is seen to be almost the same for unvulcanized blends and after HVA-2 vulcanization. The noticeable decrease can be observed at further TPS content up to 30% for both blends. The clear influence of HVA-2 vulcanization can be seen at 20% and 30% TPS content where the value of Young's modulus is maintained at around 319 MPa, while it is found to decrease markedly to 297 MPa and 233 MPa for unvulcanized blends, respectively. The increment in Young's modulus is normally observed when NR phase have been vulcanized indicating the rise of the blends stiffness. HVA-2 is responsible in forming crosslink structure and increase the dimensional stability of NR phase. Considering the fact that blends of HDPE/NR/TPS consists of low modulus component such as NR and TPS, increasing the crosslink of NR phase can improve the blends modulus considerably. On the other hand, the vulcanized NR phase can also prevent the polymer chain to slip and thereby resulting in more rigid polymer blend.

The effect of HVA-2 vulcanization on elongation at break of HDPE/NR/TPS blends is shown in Figure 5. The elongation at

break of both blends decrease with increasing TPS content and HVA-2 vulcanized HDPE/NR/TPS blends show better flexibility. Generally, the elongation at break of thermoplastic elastomer (TPE) shows similar behavior to the tensile strength trends. It exhibits increase in tensile strength value in concordance with the increase in elongation at break. This phenomenon can be explained by strain-induced crystallization. It can be seen that elongation at break of both blends are not much affected by increasing of TPS for the concentration up to 10%. But the elongation at break of unvulcanized blends appears to markedly decrease on further TPS content, indicating a weak interfacial interaction between TPS and HDPE/NR. Meanwhile for HVA-2 vulcanized HDPE/NR/TPS blends, all tested blends show higher elongation at break. At the 20% and 30% TPS content, the elongation at break of vulcanized blends show 15.1% and 88.2% improvement when compared to unvulcanized counterparts. This indicates that better compatibility between the components and HVA-2 vulcanization implies better adhesion between NR and HDPE/NR matrix.

Gel Content

Figure 6(a, b) shows the portion of the blends remained after extracted with water and xylene at 100°C and 140°C,

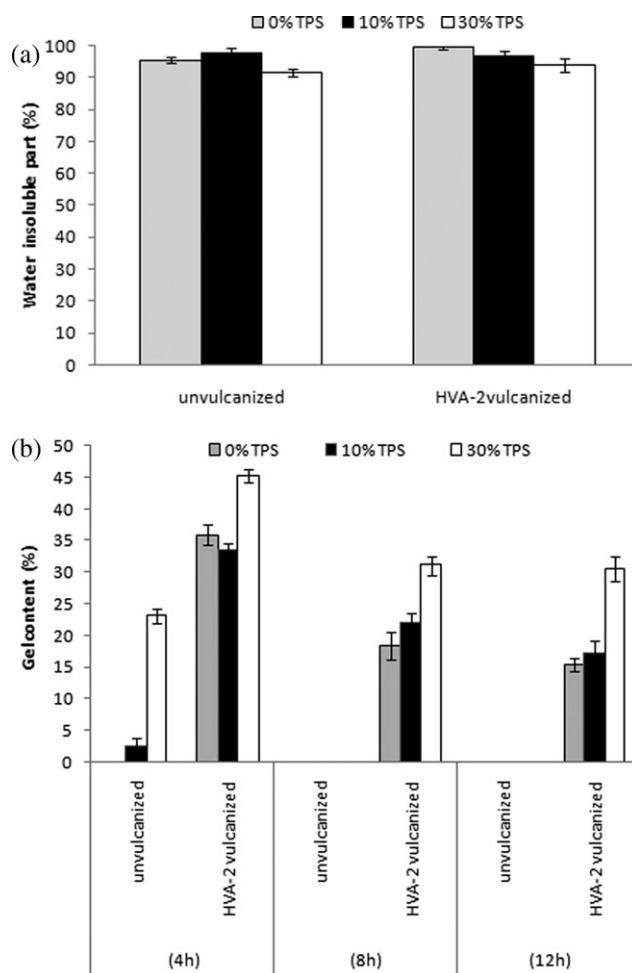


Figure 6. (a) Water insoluble part of HDPE/NR and HDPE/NR/TPS blends. (b) Effect of HVA-2 vulcanization on the gel content of the HDPE/NR/TPS blends.

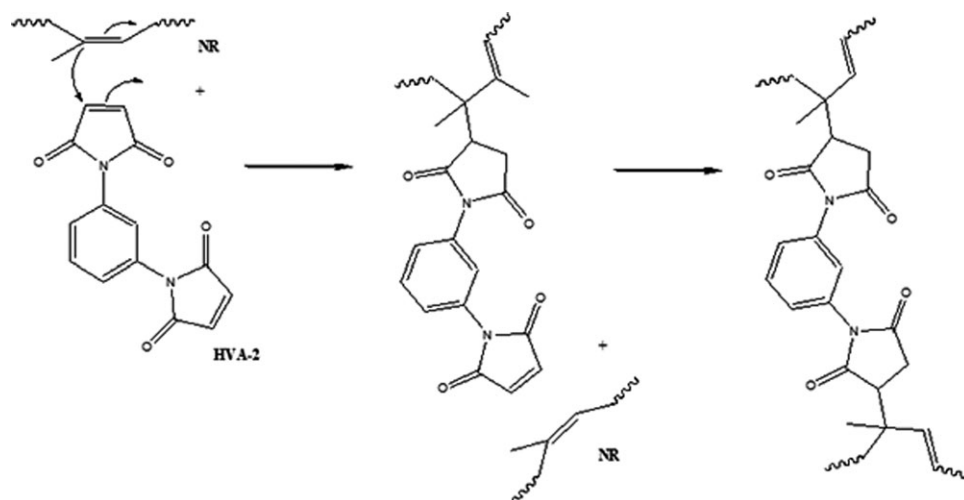


Figure 7. The possible crosslink reaction between HVA-2 and NR (adapted from Coran¹⁵).

respectively. Comparative study is carried out for both unvulcanized and vulcanized blends after water (12 h) and xylene (4 h and 8 h) extraction. Water was used for TPS extraction, whereas xylene as a extracting solvent for HDPE and uncrosslinked NR. This method is generally used to determined the gel content which is related to the crosslink density. The degree of crosslink density is responsible for the blend characteristics and has major influence on the tensile properties. After extraction with water (10 h), almost more than 90% of the blends are still remaining. This shows that water is not effective in extracting TPS phase completely, which probably is due to TPS particle being entrapped in the continuous matrix phase.

For the samples extracted in xylene for 4 h, the unvulcanized HDPE/NR blend was observed to have completely dissolved, whereas almost 36% of HVA-2 vulcanized HDPE/NR blends still remain undissolved. At 10% and 30% TPS content, the gel content of HVA-2 vulcanized blends are found to be increase 92.2% and 49% when compared to the unvulcanized blends, respectively. Furthermore, as the extraction time was increased to 8 h, all the unvulcanized blends are being dissolved in hot xylene. It is difference with HVA-2 vulcanized blends, where almost 18.4%, 22%, and 31.1% of the blends are still remaining, with respect 0%, 10%, and 30% TPS content. Since all the unvulcanized samples are being dissolved, we propose that the suitable time for extraction HVA-2 vulcanized HDPE/NR/TPS is around 8 h. As can be seen at 30% TPS content, the gel content of HVA-2 vulcanized blends are observed to be higher than NR component. This could be due to the vulcanizing fraction which may hinder complete leaching of the TPS particles. The results obtained can be justified that the stable crosslink structure have been formed after the blends were subjected with the HVA-2 crosslinker. Xylene extraction at 12 h was used as a comparison and its can be seen that the prolonged extraction time has not much affected the crosslink portion of vulcanized blends. The possible crosslink mechanism between HVA-2 and NR are given in Figure 7. The formation of crosslink structure implies that the blends are resistant to the chemical penetration and cannot be easily removed.

Structural Analysis

FTIR test were carried out on unvulcanized HDPE/NR blends and the blends with 10% TPS loading and compared with the HVA-2 vulcanized counterpart. Figure 8(a) shows only minimal variations of HVA-2 vulcanized spectra from unvulcanized blends. The presence of HVA-2 additive could not be detected and the interaction is expected to occur only between HVA-2 crosslinker and NR phase. This interaction can be seen in Figure 7 and there was no newly formed functional groups observed in HVA-2 vulcanized spectra. Xylene extraction of the vulcanized blends was further studied by using FTIR. FTIR spectra for HDPE/NR, HDPE/NR-10% TPS, and HDPE/NR-30% TPS blends before and after xylene extraction (12 h) are presented in Figure 8(b). The peaks that interest us were broad peak at 3200–3400 cm^{-1} , 2916 cm^{-1} , 2847 cm^{-1} , 1472 cm^{-1} , 1462 cm^{-1} , 1112 cm^{-1} , 1043 cm^{-1} , 730 cm^{-1} , and 719 cm^{-1} . The band range occurring at 3200–3400 cm^{-1} corresponds to the hydroxyl groups which are mainly from the TPS phase. The peak at 2916 cm^{-1} and 2847 cm^{-1} is representing the C–H asymmetry and symmetry stretching vibrations of CH_2 groups.¹⁹ This peak was found to be of strong intensity in HVA-2 vulcanized blends and much weaker after xylene extraction. Other distinct peaks that featured HDPE are at 1472 cm^{-1} and 1462 cm^{-1} , which correspond to the C–H bending vibrations of crystal and amorphous region of HDPE.²⁰ In relation to these peaks, the doublet peak at 730 cm^{-1} and 719 cm^{-1} was also being used to refer the crystallinity region of HDPE.²¹ Both of these doublet peaks were found to be strong peak for HVA-2 vulcanized spectra, but almost absent after xylene extraction, indicating most of the HDPE part has been already extracted out from the blends. Additionally, xylene extraction spectra for both blends with 10% and 30% TPS also exhibited the absorption peak that associated with TPS phase. The absorption peak at 1043 cm^{-1} is the vibration stretching in C–O–C and 1112 cm^{-1} peak is attributed to the vibration stretching of C–O in C–O–H groups in TPS.²² As the blends underwent xylene extraction, the presence of these peaks has confirmed that some of the TPS particle was still entrapped in vulcanized NR phase.

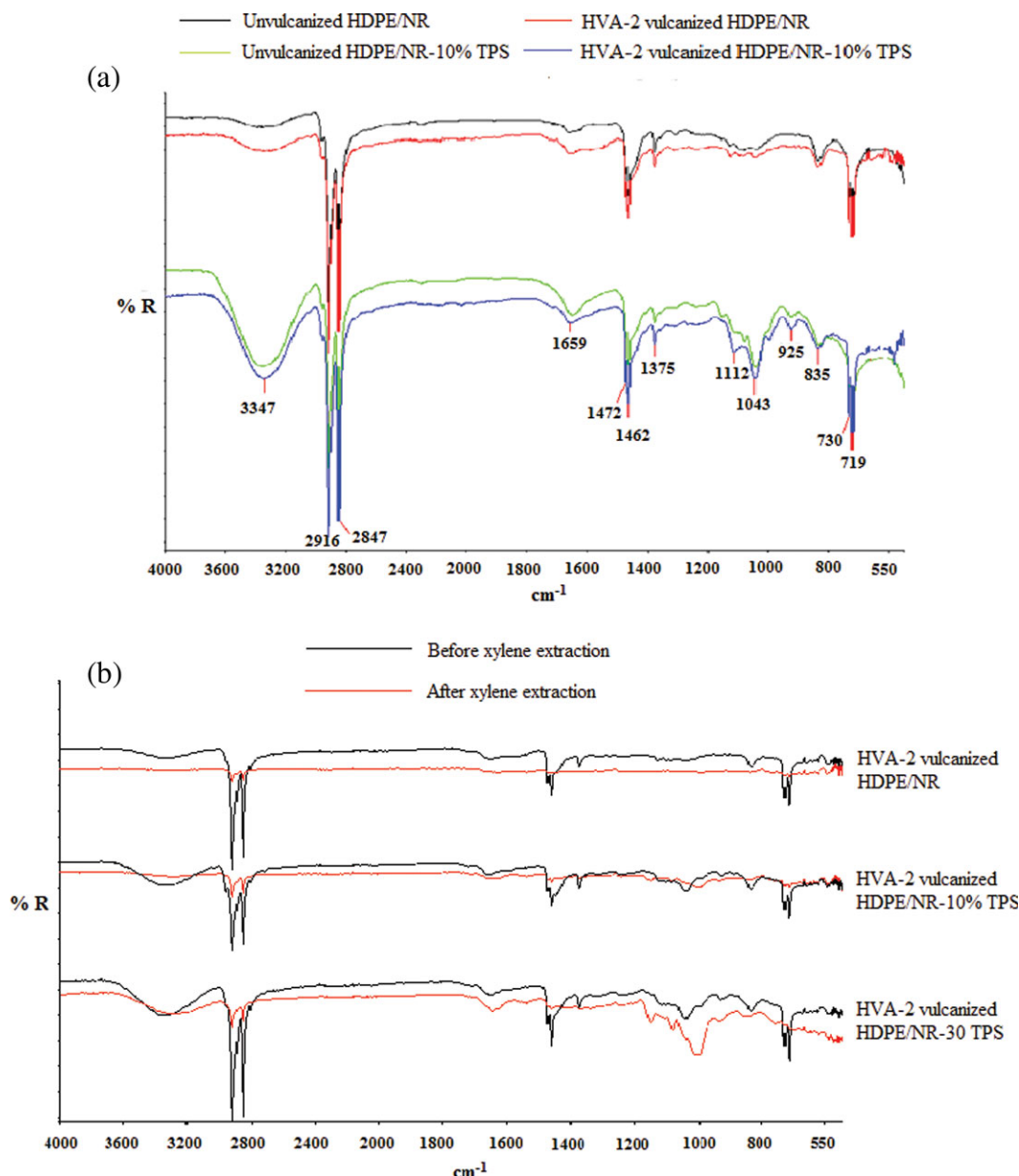


Figure 8. (a) HDPE/NR and HDPE/NR-10% TPS spectra for unvulcanized and vulcanized blends. (b) HVA-2 vulcanized HDPE/NR and HDPE/NR/TPS spectra before and after xylene extraction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Blends Morphology

SEM micrographs of unvulcanized and HVA-2 vulcanized HDPE/NR/TPS blends are shown in Figure 9. SEM micrographs of unvulcanized and vulcanized HDPE/NR matrix have also been carried out in order to have an insight of the fracture behavior and to compare the HDPE/NR/TPS morphology. Fracture surface of vulcanized blend [Figure 9(b)] is coarser when compared to unvulcanized blends [Figure 9(a)] which is associated with better fracture resistance to the external force applied on the blends. For the unvulcanized HDPE/NR/TPS blends [Figure 9(c)], SEM micrographs show some apparent voids indicating poor degree of interfacial interaction between TPS and HDPE/NR matrix. This is due to compatibility problem between hydrophilic TPS and hydrophobic HDPE/NR. TPS parti-

cle does not tend to disperse homogeneously in HDPE/NR matrix and its size range from 10 μm to 30 μm . In the Figure 9(e), TPS particle size increased up to 100 μm , indicating poor dispersion and a higher degree of phase separation. It also clearly shows the crack fracture broken near to the interphase TPS-HDPE/NR and TPS particle appears clean from the adhering polymer.

When subjected to the vulcanization, the fine TPS particles for both 10 wt % and 30 wt % TPS content are observed in Figure 9(d, f). As can be seen in these figures, the smaller TPS particles, at around 10 μm are homogeneously dispersed throughout the HDPE/NR matrix. In contrast, TPS phase in unvulcanized blends are observed as a co-continuous agglomerate phase [Figure 9(e)], whereas vulcanized blend display a discrete morphology with TPS and is well embedded in HDPE/NR matrix

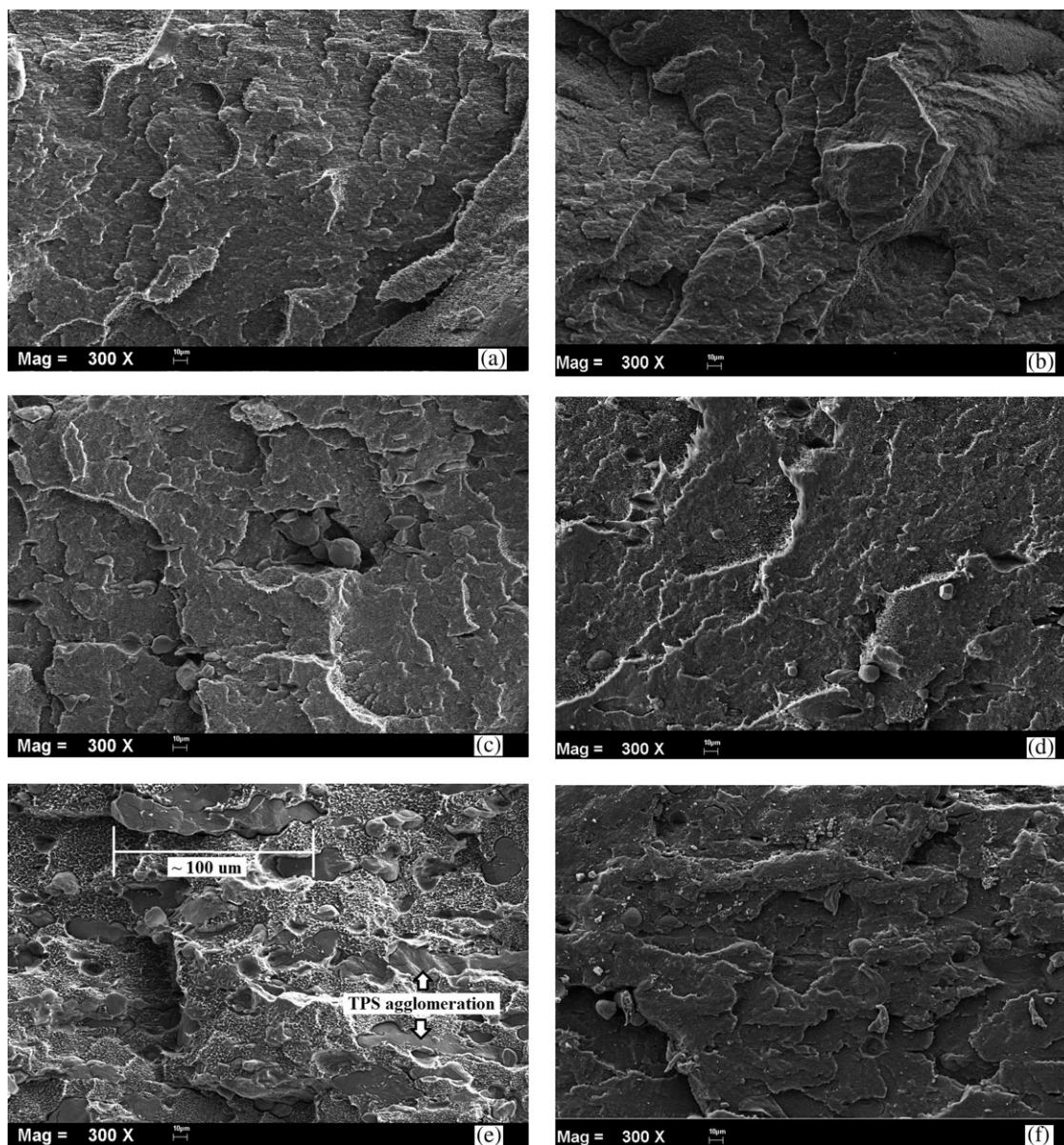


Figure 9. SEM micrographs of (a) unvulcanized HDPE/NR, (b) HVA-2 vulcanized HDPE/NR, (c) unvulcanized 10% TPS-HDPE/NR, (d) HVA-2 vulcanized 10% TPS-HDPE/NR, (e) unvulcanized 30% TPS-HDPE/NR, and (f) HVA-2 vulcanized 30% TPS-HDPE/NR.

[Figure 9(f)]. This is due to the fact that good interfacial adhesion between TPS and HDPE/NR exists, and it contributes to break-down of the TPS particle into the smaller sized dispersed phase.

Differential Scanning Calorimetry

Thermal behavior of unvulcanized and HVA-2 vulcanized HDPE/NR blends and the blends with 10% and 30% TPS for HVA-2 vulcanized were analyzed using DSC. Table I presents crystallization temperature (T_c), melting temperature (T_m), heat of fusion ΔH_m , the degree of crystallization (X_c), and weight fraction of HDPE (W_f) in the blends. DSC thermograms show single exothermic and endothermic peaks which are reflected to the crystal formation and melting of HDPE, since NR and starch usually do not have melting shape and start to decompose before melting temperature. Unvulcanized HDPE/NR melts at temperature peak 135.7°C and shows noticeable decrease

when the blends were subjected to the HVA-2 crosslinker. However, the melting temperature and crystallization temperature of HDPE were not much influenced by incorporation of TPS. Only slight decrease observed in T_c and T_m for HVA-2 vulcanized blends at 10% and 30% TPS but the degree of crystallization was affected much by TPS loading.

Crystallinity of the blends was calculated based on the following equation:

$$\text{Degree of Crystallinity, } X_c (\%) = \frac{\Delta H_{\text{exp}}}{\Delta H_m \times W_f} \times 100 \quad (3)$$

where, ΔH_{exp} is the experimental data of heat fusion, ΔH_m is the heat of fusion of the 100% crystalline HDPE, and W_f is the weight fraction of HDPE in the blend. The enthalpy of the fully

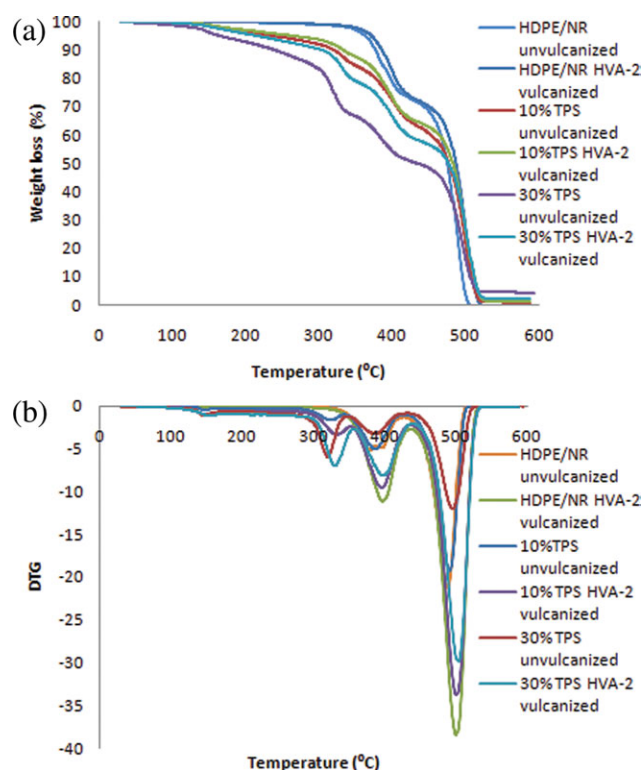


Figure 10. (a) Thermogravimetric analysis of unvulcanized and HVA-2 vulcanized HDPE/NR/TPS blends. (b) DTG of unvulcanized and HVA-2 vulcanized HDPE/NR/TPS blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crystalline HDPE was reported to be equal to 292 J/g.²³ As seen from the Table I, X_c value tends to decrease with the incorporation of TPS, indicating that TPS particle could interfere in the mobility of the polymer and reduce its possibility to form crystals. In case of HVA-2 vulcanized blends, the degree of crystallinity was found to be affected by network structure in NR phase, and further decreased significantly with the incorporation of TPS. The X_c of unvulcanized HDPE/NR blend was 60.6%, while for those HVA-2 vulcanized HDPE/NR HDPE/NR-10%TPS and HDPE/NR-30% TPS blends were 34.9%, 17.4%, and 12.8%, respectively. Although the crosslink process was taking place in the amorphous NR, it has been reported that the network structure formed near the surface of the chain fold would affect the nearby crystallinity.²⁴ The crosslinked structure has low mobility and will cause the disturbance in crystalline formation of HDPE chains.

Thermogravimetric Analysis

The TGA experimental results of unvulcanized and vulcanized HDPE/NR and HDPE/NR/TPS blends are shown in Figure 10(a). The thermograms show that both unvulcanized and vulcanized blends experience major thermal degradation in three steps. The first significant weight loss occurred at about 290°C–350°C and it can be attributed to the thermal degradation of tapioca starch.²⁵ The next stage starts from 360°C to 430°C, for all studied blends which are related to the decomposition temperature of NR phase. A further weight loss at temperature above 450°C can be ascribed to thermal decomposition of

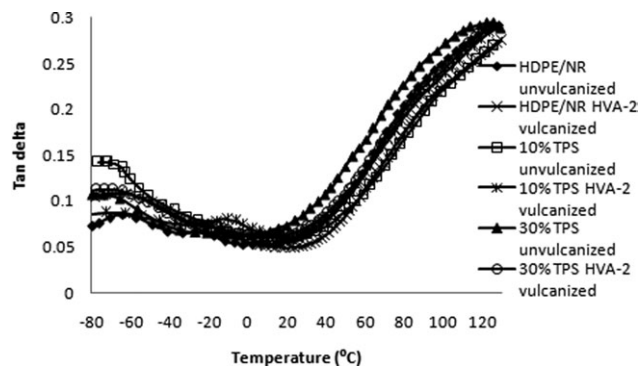


Figure 11. Changes in $\tan \delta$ with temperature for unvulcanized and HVA-2 vulcanized HDPE/NR and HDPE/NR-TPS blends.

HDPE and a nearly complete decomposition is observed to occur at 520°C. Lower degradation temperature of both unvulcanized and vulcanized HDPE/NR/TPS blends indicated that their thermal stability is less than HDPE/NR blends. Low thermal stability of TPS and poor interaction at the interface between TPS and HDPE/NR matrix might lead to this behavior.

The DTG peak measurement as observed from the Figure 10(b) represents the temperature where the degradation rate is at its maximum. DTG thermograms can be used as a relative comparison for the thermal stability of HDPE/NR/TPS blends. Cross-link structure in NR vulcanized could affect the activation

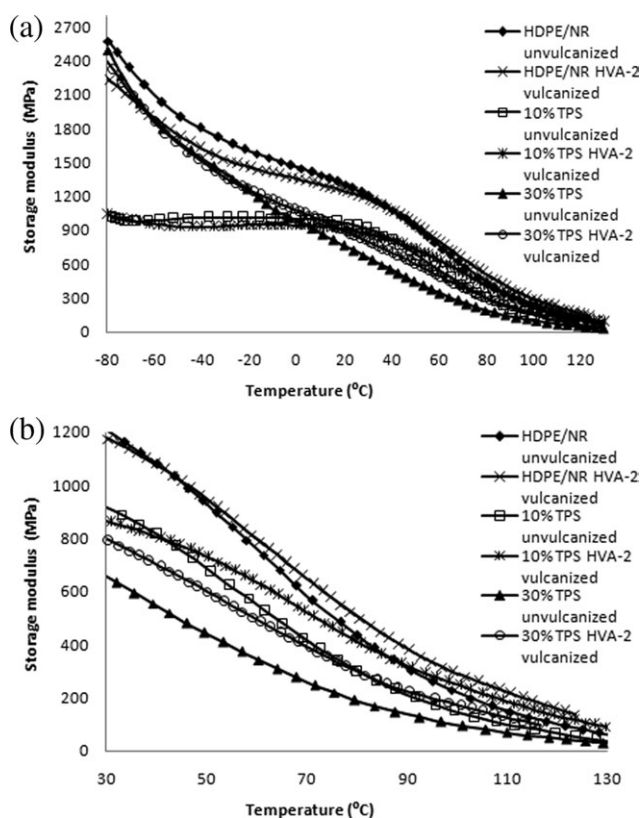


Figure 12. (a) Changes in storage modulus with temperature for unvulcanized and HVA-2 vulcanized HDPE/NR and HDPE/NR-TPS blends. (b) Storage modulus at the higher temperature region.

Table I. DSC Analysis of Unvulcanized HDPE/NR and HVA-2 Vulcanized HDPE/NR and HDPE/NR/TPS Blends

	T_c peak (°C)	T_m peak (°C)	ΔH_m (Jg ⁻¹)	X_c (%)	W_f
HDPE/NR unvulcanized	116.3	135.7	124.2	60.6	0.70
HDPE/NR HVA-2 vulcanized	115.2	131.3	71.4	34.9	0.70
10% TPS HVA-2 vulcanized	114.7	131.9	32.1	17.4	0.63
30% TPS HVA-2 vulcanized	115.1	131.2	18.3	12.8	0.49

energy needed for thermal decomposition of the blends.^{26–28} DTG thermograms of vulcanized blends show the decomposition point for 10% and 30% TPS content higher than those of unvulcanized counterparts. The second and third degradation peaks of compatibilized blends also show a similar trend, which is around 10°C higher than unvulcanized blends. This behavior occurs due to the crosslink structure in NR phase which can improve the barrier for diffusion of oxygen into materials, and thus can slow the rate of degradation.

Dynamic Mechanical Thermal Analysis

Figure 11 illustrated the broad tangent δ peak which can be estimated as the glass transition temperature (T_g) of the blends. The tangent peak relaxation of HDPE/NR blends occur at temperature -64°C which is associated with the glass transition temperature of NR phase. It can be seen from the graph that T_g relaxation for the vulcanized HDPE/NR blend are broader than unvulcanized blend. This might be due to the crosslink structure in NR phase which exhibits more resistance to increase in free volume of the NR chains. Unlike HDPE/NR blend, the blends containing 10% TPS and 30% TPS for both blends did not show clear glass transition peak for NR phase, which might be due to the overlapping by the relaxation peak of glycerol in TPS. The glass transition temperature for the pure glycerol is located at -75°C ²⁹ and the broad relaxation occurring at around -80°C to -50°C were identified as the relaxation for plasticizer rich phase in TPS. Another broad relaxation occurred at around $70\text{--}120^\circ\text{C}$ for HDPE/NR and HDPE/NR-TPS blends which are associated with the chain segment mobility in the crystalline HDPE phase.³⁰

The variations of storage modulus which is reflected to the degree of the crosslink in the NR phase are graphically illustrated in Figure 12(a, b). HDPE/NR blend exhibited higher values of the storage modulus. The addition of TPS that has decreased the storage modulus of the blends especially at the elevated temperature is due to the plasticization effect of the glycerol present in the blends. Comparisons were made at the higher temperature region to study the difference in storage modulus when the samples were subject to the HVA-2 crosslinker [Figure 12(b)]. As can be seen in the curve, the slopes for vulcanized blends are shifting to higher temperature side indicating an increment in the blends stiffness.

CONCLUSIONS

This study demonstrated that dynamic vulcanization of HDPE/NR/TPS by using HVA-2 crosslinker was an effective method in improving the properties of the blends. The tensile properties increased with the addition of HVA-2 as a crosslinker. In all the

tested samples, HVA-2 vulcanized blends displayed significant enhancement in tensile properties and better thermal stability. This observation can be attributed to the crosslink formation in NR phase. SEM studies of fracture surfaces showed that the vulcanized system has better dispersion of TPS particle and is well embedded in HDPE/NR matrix.

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REFERENCES

1. Yan, L.; Zhang, Y.; Zhang, Y. *Polym. Test.* **2004**, *23*, 83.
2. Karger-Kocsis, J.; Kalló, A.; Szafner, A.; Bodor, G.; Senyei, Z. S. *Polymer* **1979**, *20*, 37.
3. van Soest, J. J. G.; Benes, K.; de Wit, D.; Vliegthart, J. F. G. *Polymer* **1996**, *37*, 3543.
4. Carvalho, A. J. F.; Zambon, M. D.; Curvelo, A. A.; Gandini, A. *Carbohydr. Polym.* **2005**, *62*, 387.
5. Abdul Majid, R.; Ismail, H.; Mat Taib, R. *Polym. Plast. Technol. Eng.* **2010**, *49*, 1142.
6. Shi, R.; Zhang, Z.; Liu, Q.; Han, Y.; Zhang, L.; Chen, D.; Tian, W. *Carbohydr. Polym.* **2007**, *69*, 748.
7. Teixeira, E. M.; da Róz, A. L.; Carvalho, A. J. F.; Curvelo, A. A. S. *Carbohydr. Polym.* **2007**, *69*, 619.
8. Yang, Z.; Bhattacharya, M.; Vaidyat, U. R. *Polymer* **1996**, *37*, 2137.
9. Mani, R.; Bhattacharya, M. *Eur. Polym. J.* **1998**, *34*, 1467.
10. Averous, L.; Moroa, L.; Dole, P.; Fringant, C. *Polymer* **2000**, *41*, 4157.
11. Ramis, X.; Cadenatoa, A.; Sallaa, J. M.; Moranchoa, J. M.; Vallés, A.; Contat, L.; Ribes, A. *Polym. Degrad. Stab.* **2004**, *86*, 483.
12. Wu, Y.; Qi, Q.; Liang, G.; Zhang, L. *Carbohydr. Polym.* **2006**, *65*, 109.
13. Liu, H.; Xie, F.; Yu, L.; Chen, L.; Li, L. *Prog. Polym. Sci.* **2009**, *34*, 1348.
14. Mondragon, M.; Hernandez, E. M.; Rivera-Armenta, J. L.; Rodriguez-Gonzalez, F.J. *Carbohydr. Polym.* **2009**, *77*, 80.
15. Awang, M.; Ismail, H. *Polym. Test.* **2008**, *27*, 321.
16. Zurina, M.; Ismail, H.; Ratnam, C. T. *Polym. Test.* **2008**, *27*, 480.

17. Coran, A.Y. In: Encyclopedia of Polymer Science and Engineering, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, **1989**; p 688–691.
18. Hassan, A.; Wahit, M. U.; Chee, C. Y. *Polym. Test.* **2003**, *22*, 281.
19. Giancola, G.; Richard, L.; Lehman, R. L.; Idol, J. D. *Powder Technol.* **2012**, *218*, 18.
20. Page's, P.; Carrasco, F.; Saurina, J.; Colom, X. *J. Appl. Polym. Sci.* **1996**, *60*, 153.
21. Colom, X.; Canavate, J.; Page's, P.; Saurina, J.; Carrasco, F. *J. Reinf. Plast. Compos.* **2000**, *19*, 818.
22. Fang, J. M.; Fowler, P. A.; Tomkinson, J.; Hill, C. A. S. *Carbohydr. Polym.* **2002**, *47*, 245.
23. Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New Jersey, USA, **1989**; p. V-23.
24. Dahlan, H. M.; Khairul Zaman, M. D.; Ibrahim, A. *Radiat. Phys. Chem.* **2002**, *64*, 429.
25. Vallejosa, M. E.; Curvelo, A. A. S.; Teixeira, E. M.; Mendes, F. M.; Carvalho, A. J. F.; Felissia, F. E.; Area, M. C. *Ind. Crops Prod.* **2011**, *33*, 739.
26. Mathew, A. P.; Packirisamy, S.; Thomas, S. *Polym. Degrad. Stab.* **2001**, *72*, 423.
27. Wang, Q.; Wang, F.; Cheng, K. *Radiat. Phys. Chem.* **2009**, *78*, 1001.
28. Soo-Jin, P.; Ki-Sook, C. *J. Colloid Interface Sci.* **2003**, *267*, 86.
29. Mathew, A. P.; Dufresne, A. *Biomacromolecules* **2002**, *3*, 609.
30. Huang, Y.; Jiang, S.; Wu, L.; Hua, Y. *Polym. Test.* **2004**, *23*, 9.