Utilization of waste expanded polystyrene: Blends with silica-filled natural rubber

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ABSTRACT

Expanded polystyrene (EPS) constitutes a considerable part of thermoplastic waste in the environment in terms of volume. In this study, this waste material has been utilized for blending with silica-reinforced natural rubber (NR). The NR/EPS (35/5) blends were prepared by melt mixing in a Brabender Plasticorder. Since NR and EPS are incompatible and immiscible a method has been devised to improve compatibility. For this, EPS and NR were initially grafted with maleic anhydride (MA) using dicumyl peroxide (DCP) to give a graft copolymer. Grafting was confirmed by Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy. This grafted blend was subsequently blended with more of NR during mill compounding. Morphological studies using Scanning Electron Microscopy (SEM) showed better dispersion of EPS in the compatibilized blend compared to the noncompatibilized blend. By this technique, the tensile strength, elongation at break, modulus, tear strength, compression set and hardness of the blend were found to be either at par with or better than that of virgin silica filled NR compound. It is also noted that the thermal properties of the blends are equivalent with that of virgin NR. The study establishes the potential of this method for utilising waste EPS.

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1. Introduction

The significance of polymer recycling has greatly increased over the years. Expanded polystyrene is a major constituent of plastic wastes. Recycling of EPS involves various technological challenges stemming mainly from its low bulk density (15–50 kg/m^3) [1]. Owing to its light weight, buoyancy, thermal insulation, dimensional stability, chemical resistance, electrical properties, hygienic appearance, low cost etc., EPS is used for a large number of applications. Today, global consumption of EPS exceeds 3 million tons with an increase of approximately 6% a year [2,3]. After use, EPS usually ends up in landfills or is incinerated. Its nuisance value in the environment is high because of its large volume. Added to this are the high transportation costs associated with shipping low bulk density waste EPS. [4]. In response to the high cost of disposal and growing public opposition to land filling, a number of recycling strategies for EPS has been devised. If the waste EPS can be used in other polymers by cost effective methods then the economics of recycling can be favourable.

Any reduction in the amount of waste EPS will have a salutary impact on the environment in terms of reduction in volume of waste. Moreover, in view of the rising price of NR, replacement of NR even by a small percentage of a waste material can have considerable impact on the economic viability of NR processing.

Hence, blending EPS with NR has been done in this study to gainfully utilize waste EPS. Although there is hardly any information in the literature about NR–EPS blends, there are some detailed references about studies on thermoplastic elastomers based on NR–PS blends [5,6].

The properties of a blend are dependent on phase behaviour, blend ratio and cross linking levels [7,8]. Immiscible blends are preferable over miscible blends because in miscible blends only an average of the individual properties is obtained [9]. However, very often many of the immiscible blends exhibit poor mechanical properties as well as unstable morphology. Even though both NR and EPS are nonpolar materials, they exhibit poor adhesion between the interfaces. Therefore, compatibilization of the blend is necessary to improve its properties to usable levels.

Addition of compatibilizers or interfacial agents to polymer blends affects the flow behaviour because of the interactions between the blend components via the blend compatibilization. This results in improved interfacial adhesion and physical properties [10–12]. Grafting reactions could induce significant changes in the polymer chain relating to chemical composition, polymer chain structure and molecular mass. These parameters are responsible for the interactions between polymers [10]. MA grafting of polymers has been increasingly used as a means of compatibilization. The effect of the addition of different compatibilizers such as bromobutyl rubber (BIIR) and maleic anhydride on the elastic behaviour of natural rubber/butyl rubber (NR/IIR) blend has been studied by Hamza et al. [13]. Grafting of natural rubber and nitrile rubber

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on low density polyethylene has been performed successfully using acrylic acid and maleic anhydride [14]. The grafted compounds were found to be superior compared to nongrafted compounds in mechanical properties, chemical resistance, aging, and so on [15]. The incorporation of MA-functionalized polypropylene (PP-g-MA) as a compatibilizer agent in PP/rubber blends has been studied with the aim of improving the dispersion and interaction of rubber within the PP matrix [16,17]. With different rubber types, it has been observed that maleic anhydride grafted styrene–ethylene–butadiene–styrene (MA-g-SEBS) rubber is most effective for toughening of PET [18,19]. The grafting performance by MA on SBS was reported by Lasalle et al. [20].

The present study uses MA compatibilized NR/EPS blends for subsequent blending with more of NR followed by vulcanisation by conventional methods. It has been shown during earlier studies that cardanol separated from cashew nut shell liquid (CNSL) is a good substitute for petroleum based NR plasticisers [21]. Hence this study uses cardanol as plasticiser as an additional step to conserve fossil fuel based substances and utilizes a cheap agrobyproduct.

2. Experimental details

2.1. Materials

EPS used in this study was purchased from S-tech Thermocool Industry, Cherthala, Kerala with a density value of 15 Kg/m^3. Waste EPS was not selected for the study because of the need to get a clean material for the initial studies. Natural rubber (ISNR-5) was obtained from Rubber Research Institute of India; Kottayam, Kerala. Other rubber chemicals were of commercial grade. Cardanol was separated from commercial grade CNSL (purchased from Vijayalaksmi Cashew Exports, Kollam, India) by distillation under reduced pressure. Maleic anhydride was obtained from Sdfine-chem Ltd., Mumbai, and DCP was supplied by Merck, India.

2.2. Compatibilization

Blends of NR and EPS were first prepared by melt mixing. Melt mixing was carried out in a Brabender Plasticorder at 140 °C maintaining the rotor speed at 50 rpm. About 5 g EPS was allowed to soften in the Brabender Plasticorder initially. Then varying quantities (weight %) of MA (0, 0.5, 1, 1.5, 2) was added at a constant DCP concentration (.125%), followed by 35 g of NR. Total mixing time in all cases was fixed as 8 min. Thus five batches of 35/5 blends of NR/EPS were prepared. Blend with 0% MA is referred to as nongrafted and others, grafted blends.

2.3. Compounding and curing

The mixing of the ingredients was done on a two-roll mill (16 × 33cm^2) according to ASTM D 3184-11at a friction ratio of 1:1.22 [22]. The temperature of the rolls was maintained at 70 ± 5 °C. At first 60 g NR was masticated for a while and then it was blended with the graft copolymer of NR and EPS already prepared in Brabender Plasticorder so that a final 95/5 NR/EPS blend was obtained. Then the compounding ingredients were added in the following order: zinc oxide (ZnO), stearic acid, precipitated silica, cardanol, diethylene glycol (DEG), styrenated phenol (SP), N-cyclohexyl-2-benzothiazolesulfenamide (CBS), tetramethylthiuramdisulfide (TMTD) and sulphur. The final formulation used is given below in Table 1.

A compound consisting of pure NR (without EPS, MA and DCP) and other ingredients was also prepared known as the silica filled NR. Final cured compound containing grafted blend is referred to

Table 1
Formulation for NR compounding.

Ingredients	Quantity (phr)
Natural rubber	95
EPS	5
ZnO	5
Stearic acid	2
Precipitated silica	15
Cardanol	1.5
DEG	1
SP	1
CBS	0.6
TMTD	0.1
Sulphur	2.5

as compatibilized blend and that containing non-grafted blend is referred to as non-compatibilized blend. Both are silica filled compounds. The compounds were cured in a hydraulic press at 150 °C after estimating the cure time in a Rubber Processing Analyser (RPA 2000 Alpha Technologies, USA), as per ASTM D 2084-07 [23] .

3. Characterization

3.1. Fourier Transform Infrared Spectroscopy

The blends obtained from Brabender Plasticorder were Soxhlet extracted for 48hours. After extraction of the nonreacted MA by water, the nongrafted sample was solution cast using toluene as solvent. The solvent was evaporated in a hot air oven at 60 °C for 30 min before recording the IR spectra. The grafted sample was found to only swell in toluene. It was directly used for IR study after drying. The FTIR spectra were recorded using a Thermo Nicolet FTIR Spectrometer Model Avtar 370 instrument. The scanning range was from 400 to 4000 cm^{-1}.

3.2. Cure characteristics

Cure characteristics of the mixes were determined at 150 °C, as per ASTM standard D 2084-07 [23]. The cure time (t_{90}), scorch time (t_2), minimum torque (M_L) and maximum torque (M_H) were obtained from the rheograph. Cure rate index (CRI) is a measure of the speed with which the cure reaction is taking place and is calculated using the equation:

$$CRI = 100/(t_{90} - t_2)$$

3.3. Mechanical properties

The tensile tests were done on dumb-bell shaped specimens punched out from vulcanized sheets of 2 mm thickness. The measurements were carried out on a Universal Testing Machine (10 kN), Shimadzu Autograph AG-I series with a grip separation of 40 mm as per ASTM D 412-06ae2 [24]. The experiments were conducted at room temperature. These tests provided the tensile strength, elongation-at-break and Young's modulus values of the NR and NR–EPS blends. Tear strength was determined by ASTM D 624-00(2007) [25]. The testing speed for tensile and tear properties was 500 mm/min.

3.4. Miscellaneous properties

For compression set test, cylindrical test specimens (12.5 mm diameter and 6.0 mm thickness) were moulded and the tests were done according to ASTM D 395-03(2008) Test method B [26].

Hardness (Shore A) was measured using Shore A Durometer Hardness Tester in accordance with ASTM D 2240-05(2010) [27].

3.5. Morphological studies

Studies on morphology of the tensile fractured surfaces of silica filled NR, non-compatibilized NR/EPS and compatibilized NR/EPS (1% MA) blends were carried out using a JOEL Model JS M840A scanning electron microscope.

3.6. Thermogravimetric analysis (TGA)

The thermogravimetric analyses of the samples were carried out under nitrogen atmosphere at a heating rate of 10 °C/min in a TGA Q-50 thermal analyser (TA Instruments). A constant sample weight (5 mg) was used in all cases. Thermograms (TG) were recorded from room temperature to 800 °C. The temperature at which the rate of mass loss is maximum was determined from the differential thermogravimetry (DTG) curves and called the decomposition temperature (Td).

3.7. Differential scanning calorimetry (DSC)

The glass-transition temperature (T_g) was measured using a TA Instruments Q 100 DSC under nitrogen atmosphere. A constant weight of each sample was sealed in an aluminium pan with a perforated lid and placed in differential scanning calorimetry cell and heated. Then the samples were quenched to −80 °C. The DSC scans were made from −80 to 150 °C at a heating rate of 10 °C/min.

4. Results and discussion

4.1. Fourier Transform Infrared Spectroscopy

A representative infrared spectrum of the non-grafted and grafted NR/EPS blends with 1% MA is shown in Fig. 1. An intense characteristic band at 1778 cm^{-1} and a weak absorption band at 1854 cm^{-1} are observed. These bands can be assigned to grafted anhydride rings. They are due to symmetric (strong) and assymetric (weak) carbonyl (C=O) stretching vibrations of succinic anhydride rings grafted on PS (polystyrene) and NR [28–30]. This proves the presence of grafted anhydride groups on the NR and PS chains. The small shoulder at 1718 cm^{-1} (the carbonyl stretching frequency of the acid group) in the spectrum of the grafted
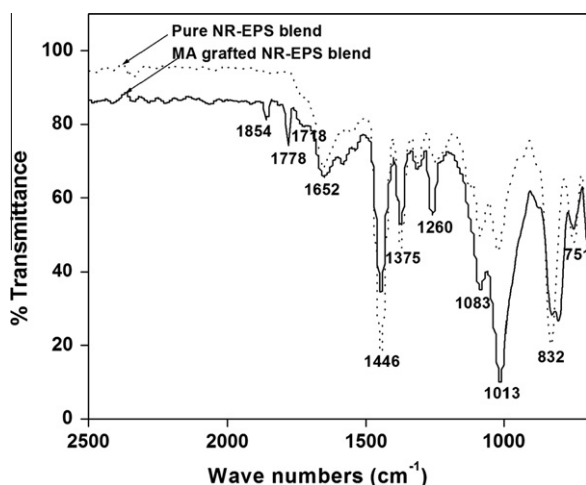
blend arises from the acid peak resulting from maleic anhydride modification. Therefore, the possible functionalization reactions of EPS and NR with MA can be shown as in Fig. 2. In general, the anhydride modification may result in anhydride or acid forms depending upon the addition or removal of water. Normal carbonyl group stretching frequency is 1760 cm^{-1} [31]. According to literature, the acid peak is indicated by 1714 cm^{-1} whereas the anhydride shows the absorption peaks at wavenumbers of 1789 cm^{-1} (strong) and 1864 cm^{-1} (weak) [32]. We can also notice the peaks corresponding to absorbances at 1652 and 832 cm^{-1} due to the stretching of the C=C bond of the NR. The peak at 3026 cm^{-1} and 2868 cm^{-1} (not shown here) were assigned to the aromatic C—H stretching of polystyrene. These peaks corresponding to C—H stretching are slightly shifted and the intensities are reduced on addition of MA. The signals at 1375 cm^{-1} and 1446 cm^{-1} can be attributed to the aliphatic C—H stretching in natural rubber [33]. The band at 1260 cm^{-1} corresponds to the C—O—C stretching in the ester moiety. These peaks suggest that the mechanism of grafting involves both the (a) anhydride linkage and (b) opened ring
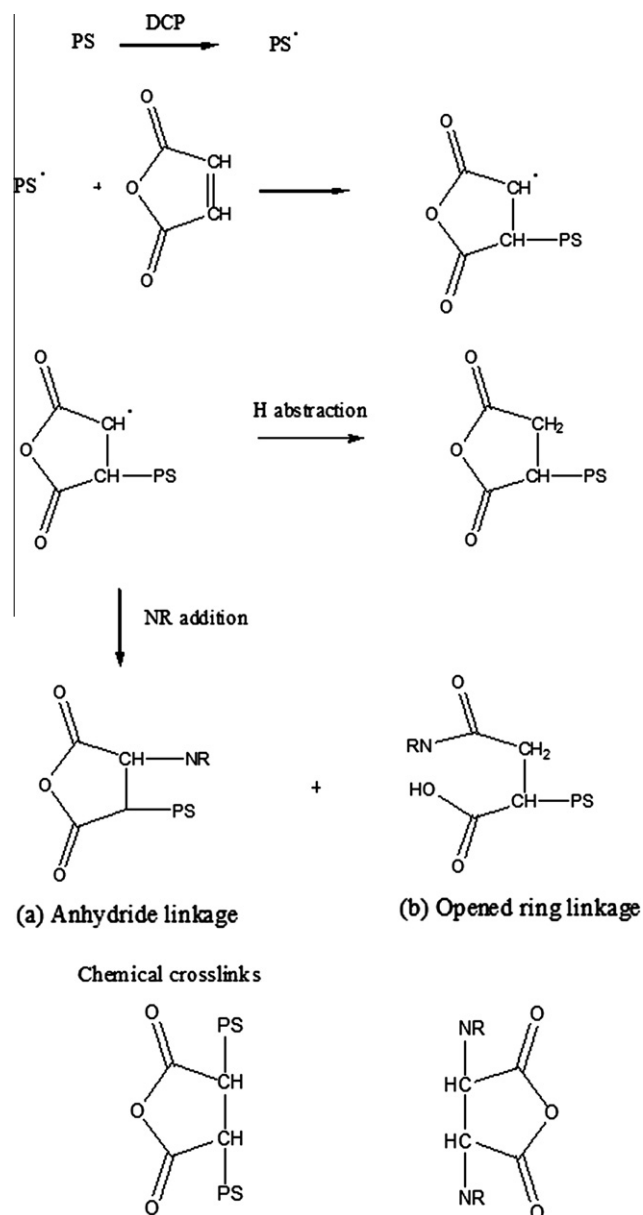

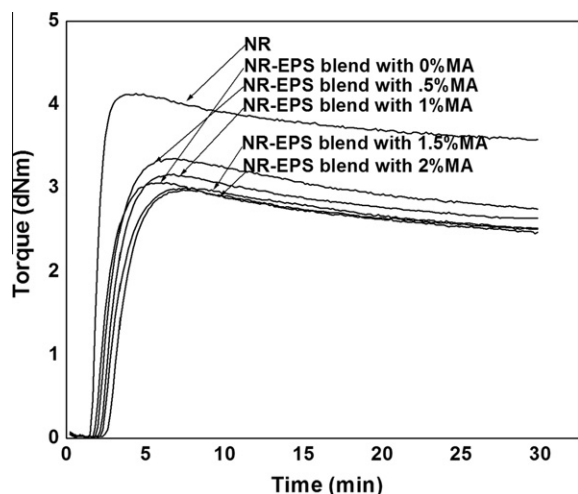Fig. 2. Possible functionalization reactions of EPS and NR with MA.

Fig. 1. Infrared spectra of non-grafted NR–EPS blend and grafted NR–EPS blend with maleic anhydride (1%).

Fig. 3. Rheographs of mixes at 150 °C.

Fig. 4. Stress–strain curves for NR and NR/EPS blends with various MA concentrations.

linkage [14,34]. Some possible chemical crosslinks are also shown in Fig. 2 although a good many other reactions arising from the presence of one/two NR/PS chains cannot be ruled out in the grafted product with the anhydride ring intact or opened by cleavage of the ester linkage.

4.2. Cure characteristics

The rheographs of silica filled NR and NR–EPS blends with varying MA concentrations at 150 °C are shown in Fig. 3. The highest torque is exhibited by pure silica filled NR and the torque decreases for the blends. The low torque value for the blends is associated with the low viscosity of the PS phase compared to NR. Unattached PS chains can also reduce the cohesion of the rubber matrix by hindering the sulphur crosslinks although at some stage the grafted copolymer may attain somewhat higher torques because of the interlinking of different polymer chains. The latter effect is presumably of low magnitude considering that NR exhibits a still higher value of torque.

The processing characteristics of silica filled NR and silica filled NR/EPS blends are given in Table 2. The cure time and scorch time are higher for blends than for NR and increase with increasing MA content. The grafted compounds display significantly longer scorch and cure times compared to NR, as shown in Table 2 due to (1) the presence of acid groups from the ring opening of succinic anhydride groups (2) the presence of PS chains and (3) the possible interlinking of polymer chains. The acid groups can deactivate the accelerators and the zinc complex. Therefore, the vulcanization reaction is retarded [35]. The decreased CRI values for the blends compared to pure NR also suggest a deceleration of the crosslinking reaction.

4.3. Mechanical properties

Fig. 4 shows typical stress–strain curves for the NR and NR/EPS blends with various MA concentrations. The properties of silica
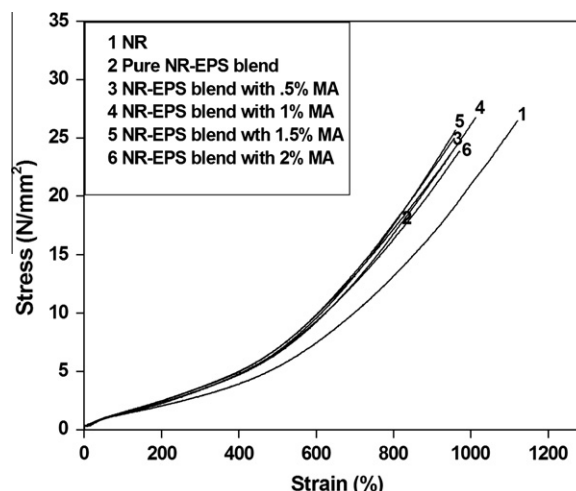
Table 3
Properties of 15 phr silica filled NR and silica filled NR/EPS blend with 1% MA.

Properties	Silica filled NR	Silica filled NR/EPS blend with 1phr MA
Tensile strength (N/mm^2)	26.445	26.714
Elongation at break (%)	1120.08	1022.26
Modulus at 300% (N/mm^2)	2.884	3.647
Tear strength (N/mm)	46.232	59.136
Compression set (%)	60.833	62.116
Hardness (Shore A)	47	53

filled pure NR and silica filled NR/EPS blend with 1% MA are given in Table 3. Corresponding values for all the blends are provided in the form of graphs. Fig. 5 shows the tensile properties of non-compatibilized and various compatibilized blends. The incorporation of EPS directly to NR showed a reduction in tensile strength and elongation at break. The elongation for blends is less than that of pure NR due to some loss of elasticity. But, for the compatibilized blends the above properties are enhanced. The tensile properties reflect an improved degree of silica dispersion in the vulcanizates as demonstrated by the morphology of the blends observed by SEM (Fig. 8). Thus the addition of 1% MA in the blend increases the tensile strength (Fig. 5a) of the blend not containing MA by about 14% and the elongation at break by 8% (Fig. 5b). These are comparable with that of NR alone. The probable reasons for this have already been cited under the discussion on FTIR. The addition of the compatibiliser also enhances the favourable interactions at the interface. The interfacial tension reduces thereby improving adhesion between the components as well as between the filler and the polymer matrix which enhances the tensile strength of the blends [12,15]. Moreover, it has been reported that silica filled NR shows better properties on MA grafting [36]. The modulus at 300%

Table 2
Processing characteristics of silica filled NR and silica filled NR/EPS blends.

Cure characteristics	NR	NR/EPS (0% MA)	NR/EPS (0.5% MA)	NR/EPS (1% MA)	NR/EPS (1.5% MA)	NR/EPS (2% MA)
Min torque, MH (dNm)	0.010	0.006	−0.010	0.010	0.020	0.013
Max torque, ML (dNm)	4.129	3.056	3.350	3.161	3.001	2.974
Scorch time, t_2 (min)	1.560	1.550	2.050	2.190	2.280	2.480
Cure time, t_{90} (min)	3.370	3.460	4.130	4.210	4.500	4.590
Cure rate index (min^{-1})	55.248	52.356	48.077	49.505	45.045	47.393

Fig. 5. Tensile properties of compatibilized and non-compatibilized blends.

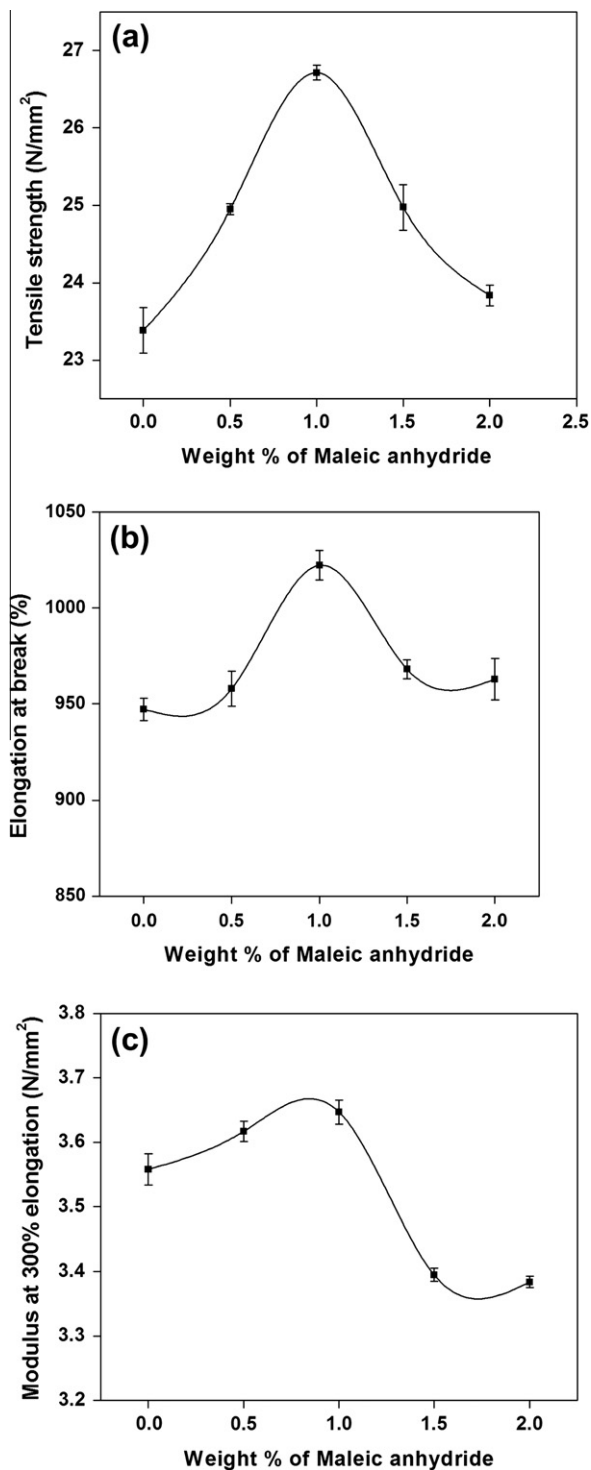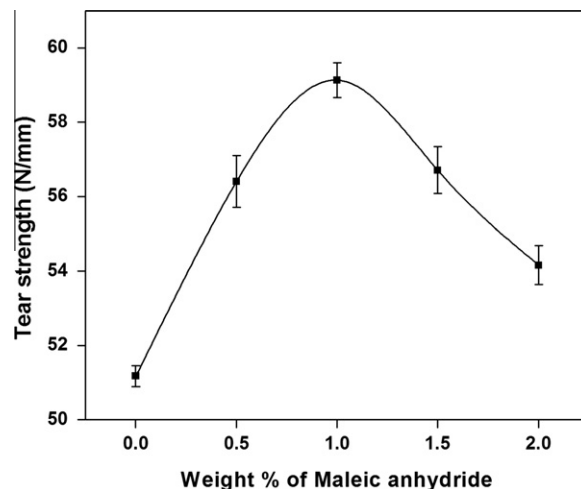Fig. 6. Tear strength of compatibilized and non-compatibilized blends.

Fig. 7. Compression set & hardness of compatibilized and non-compatibilized blends.

elongation (Fig. 5c) of the blends shows an improvement compared to NR. The blends show a maximum of 26.45% improvement in the modulus at 300% over that of NR. The tensile properties for the blends reach a maximum at an optimum concentration of ca.1%. It is observed that tensile properties of the blends at higher MA concentrations decrease. This may be due to an excess of MA at the interface which creates an energetically unbalanced design [12]. This will affect the interfacial adhesion between the components. A higher loading of MA can cause some adverse reactions such as homopolymerisation, resulting in the decrease of mechanical

properties [37]. However, if the loading of MA is less than 1%, sufficient free radicals would not be present for the grafting reaction.

It is interesting to note that at the optimum MA concentration, the tensile strength of the compatibilized blend is equal to that of NR even when the blend contains 5% EPS. The succinic anhydride groups grafted onto NR and EPS molecules enhance the polarity of the blend and an interaction between the succinic anhydride groups and the hydroxyl groups on silica surface is quite likely [36]. Similar interactions between the hydroxyl and maleic anhydride groups have previously been proposed such as in the cases of PP-g-MA versus nano-silica [38] and maleated NR versus paper sludge filler [39]. The polar interactions due to hydrogen bonds between the hydroxyl groups on the silica surface and the carboxyl groups of the grafted molecules or the hydroxyl group of the succinic acid improve the compatibility between rubber and silica and reduce filler aggregation. As a consequence there is an increase in the degree of filler dispersion.

Fig. 6 shows the tear strength of compatibilized and non-compatibilized blends. There is considerable improvement (~28%) at 1% MA compared to silica-filled NR (not containing MA or PS). As the filler agglomeration is less for compatibilized blends, the filler particles can be properly wetted by macromolecules and hence adhesion between the filler and matrix improves. Thus, the energy required to propagate a crack increases, resulting in higher tear
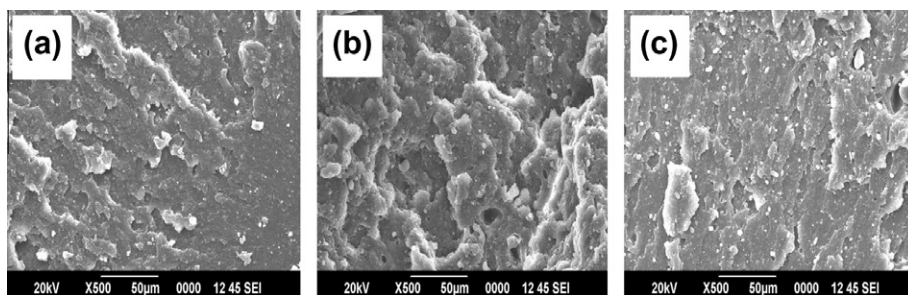
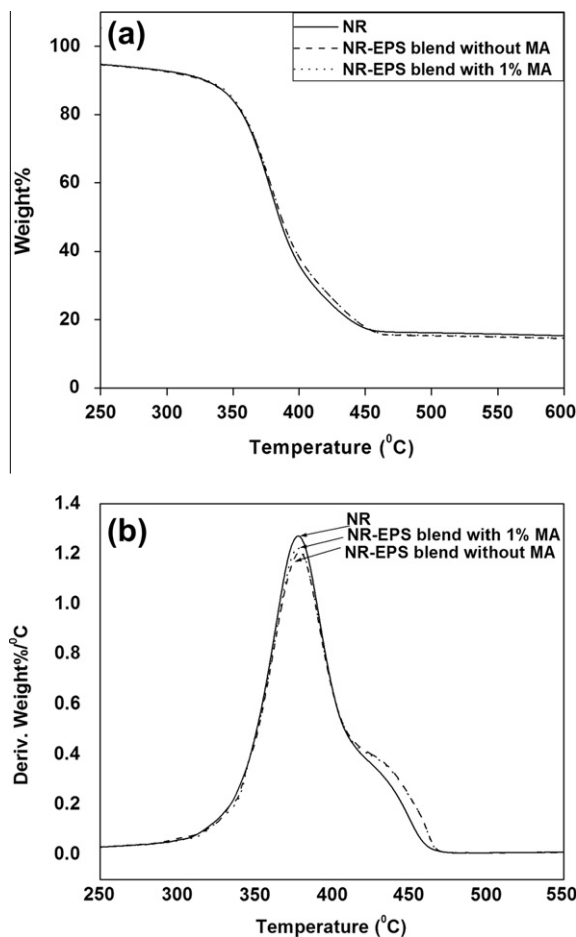**Fig. 8.** SEM of tensile fractured surfaces of (a) NR, (b) non-compatibilized NR–EPS blend and (c) compatibilized NR–EPS (1% MA).

Fig. 9. TG (a) DTG (b) curves of NR, non-compatibilized NR–EPS blend (0%) and compatibilized NR–EPS (1% MA).

Fig. 10. DSC curves of NR, non-compatibilized blend and compatibilized blend (1% MA).

Table 4
TGA data for NR, non-compatilised NR/EPS blend and compatibilized NR/EPS blend.

Property	NR	Non-compatibilized NR–EPS blend	compatibilized NR–EPS blend
Onset degradation temperature (°C)	314.37	319.02	321.19
Maximum degradation temperature (°C)	378	378	378
End set degradation temperature (°C)	460.75	466.14	467.7
Temperature (°C) at 5% degradation	240.05	236.1	238.4
Temperature (°C) at 50% degradation	384.84	386.5	386.51
Residue (%)	14.77	13.98	14.17

strength [40]. The values show a decreasing tendency as the MA concentration further goes up.

4.4. Miscellaneous properties

Fig. 7 shows the hardness (Shore A) and compression set of non-compatibilized and compatibilized NR/EPS blends. A significant improvement in surface hardness is observed for the blends due to the higher hardness of PS. There is less compression set for the uncompatibilized blends over that of pure silica-filled NR. This effect further improves in the presence of MA. The overall improvement in properties suggests that MA can be used as a reactive compatibiliser in NR/PS blends.
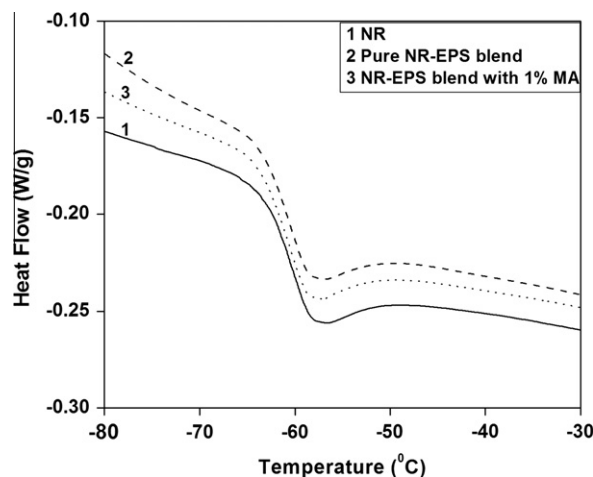
4.5. Morphological studies

The scanning electron micrographs of the tensile fractured surfaces of silica filled NR, non-compatibilized and compatibilized (1% MA) NR/EPS blends are presented in Fig. 8. The dispersed objects present in silica-filled NR (Fig. 8a) can be silica particles. Other micrographs also contain similar objects as all the compounds are silica filled. In the case of non-compatibilized (Fig. 8b) and compatibilized (Fig. 8c) NR/EPS blends some additional particles are present due to the EPS phase. Here the minor phase is EPS with a lower viscosity compared to NR and it is dispersed in the NR matrix as small spherical particles [41]. There is a surface roughness in the morphology of the non-compatibilized blend. But a fine and more uniform phase distribution is exhibited by the MA compatibilized

blend sample. For the compatibilized blend the fine dispersion of EPS phase in the NR matrix alters the crack path giving resistance to crack propagation. In compatibilized blend a more uniform distribution, size reduction and less pull out of the minor phase are found [12]. The unidirectional ripples present in the SEM of compatibilized blend are an indication of compatibility between the components [42]. The SEM analyses is in conformity with the improvement in mechanical properties of the compatibilized NR/EPS blends.

4.6. Thermogravimetric analysis

Fig. 9 shows the TG (Fig. 9a)/DTG (Fig. 9b) curves of NR, non-compatibilized NR–EPS blend and compatibilized NR–EPS (1% MA). Vulcanised NR and pure PS have almost the same thermal stability [43]. They both degrade in the temperature range of 300–400 °C.

The curves indicates that the decomposition ranges from approximately 300–450 °C with a mass loss of about 85%, which can be assigned to the thermal decomposition of natural rubber into monomers, dimers, trimers, etc. in inert atmosphere. A small shoulder can be observed in the DTG curves at approximately 410 °C attributable to cross linked and cyclised networks which degrade at higher temperature [44]. The temperature of the maximum mass loss rate and the peak temperature of the DTG curves in Fig. 9b are around 378 °C for the three cases. The temperature at which 50% decomposition occurs is generally considered as an index of thermal stability. Our results have shown that this temperature for NR is 385 °C and for blends it is 386.5 °C indicating an increase in thermal stability upon the addition of PS to NR. Table 4 shows the TGA data for NR, non-compatibilized NR–EPS blend and compatibilized NR–EPS blend (1% MA). The results suggest that blends have thermal stability either higher or comparable to NR.

4.7. Differential scanning calorimetry

Fig. 10 shows DSC curves measured from NR, non-compatibilized blend and compatibilized blend. Many of the important technical properties of elastomers such as resilience and abrasion resilience can be correlated to T_g [45]. DSC provides information concerning the glass transition, a second order event which manifests itself in a DSC curve as a step change corresponding to the change in the heat capacity of the system. The DSC curves exhibit changes in baseline in the temperature of approximately −61 °C, which are attributable to the glass transition temperature of natural rubber. There are no significant differences among the T_g values of NR and NR–EPS blends.

5. Conclusion

In this work, non-degradable and not easily recyclable waste EPS has been substituted for 5% NR by a compounding process. Most properties of the blend show remarkable improvement on compatibilisation with MA. For an optimum MA concentration of 1%, the tensile strength is comparable with that of silica filled NR. Properties like modulus at 300% elongation and compression set were the best for compatibilized blends. Tear strength shows an impressive 25% improvement in the case of compatibilized blends. Greater degrees of dispersion of PS have been confirmed by SEM in the case of compatibilized blends. The inclusion of PS does not lead to any deterioration of thermal properties. The overall data suggest that 5% waste expanded polystyrene can be incorporated into NR compounds as a waste management measure with some improvement in mechanical properties as bonus. This is also economically significant for NR processors as the method holds promise for higher percentages of EPS.

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