Investigation of the preparation and physical properties of a novel semi-interpenetrating polymer network based on epoxised NR and PVA using maleic acid as the crosslinking agent

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ABSTRACT

Natural rubber (NR) and its derivatives as renewable and biodegradable materials have attracted considerable attention because of the serious pollution problems caused by synthetic materials and a shortage of resources. A new semi-interpenetrating polymer network (semi-IPN) based on epoxidised natural rubber and polyvinyl alcohol containing maleic acid as a crosslinking reagent was synthesized and characterized by FTIR, XRD, SEM, swelling ratio in both distilled water and toluene, and mechanical properties. The curing time and dose of maleic acid were varied from 10 to 60 min, and from 10 to 60% (w/w), respectively. An IR spectroscopic study indicated the presence of an ester linkage at 1730 cm^{-1} in maleic acid crosslinked with PVA in semi-IPN films. In addition, the crystalline content of PVA dramatically decreased after adding maleic acid in the semi-IPN, as observed from its XRD. The semi-IPNs exhibit good mechanical properties, thermal stability, characteristics of a polyvinyl alcohol–maleic acid polymer network. An SEM of the semi-IPNs containing maleic acid showed no phase separation, when compared with the sample prepared in the absence of maleic acid.

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1. Introduction

Medical products made from elastomer materials especially natural rubber (NR) latex have found extensive applications such as in tubings, surgical gloves, catheters, balloons and other products [1–4]. The advantages of NR products are their elasticity, flexibility and resistance against splitting [5]. But their disadvantages are their low resistance to thermal degradation due to its structure containing unsaturated units, their poor resistance to ozone, their resistance to organic solvents and being biologically incompatible to humans. It will be essential to modify NR polymers in order to improve their properties [5–8]. Three main approaches can be used to modify the properties of NR polymers. These include changes to its chemical microstructure, addition of different material reagents and blending with other polymers [9–14]. Blending with other polymers is an interesting method because it can be an easy, cheap and economical method and can produce new materials with novel properties [12–14]. The blending of two or more polymers often yields a polymer with novel properties that cannot be achieved from any of the individual components. In previous work, NR has been blended with many polymers such as polypropylene (PP), polyethylene (PE), polyvinyl alcohol (PVA), nitrile rubber (NBR), ethylene–propylene copolymer (EPM), ethylene–propylene–diene terpolymer (EPDM) and epoxidized natural rubber (ENR) [9,13,14]. In addition, the semi-interpenetrating polymer network is one polymer blend obtained through a chemical reaction with a curing reagent. There have been literature reviews [15–22] on the properties of semi-IPN polymers based on NR mixed with different polymers such as polystyrene, polyamide and methyl methacrylate. The advantages of IPNs are more solvent resistance compared to the individual polymers and their ability to creep and flow compared to the individual polymers. For example, Mathew and Thomas [23] studied the mechanical, thermal, viscoelastic and transport properties of a series of semi and full interpenetrating polymer networks produced from NR and polystyrene (PS). The results showed that the izod impact strength of the IPNs depended on the effect of the crosslinking level of PS and blend ratio. Jayasuriya and Hourston [24] studied the IPN from NR and poly(methyl methacrylate). They found that the blends when observed by DMTA were phase-separated. The glass transition temperature of the NR component in the IPN sample was shifted to a higher temperature compared to the NR alone when tested under the same conditions. This indicated a limited amount of mixing of the components in these samples. Incorpo-
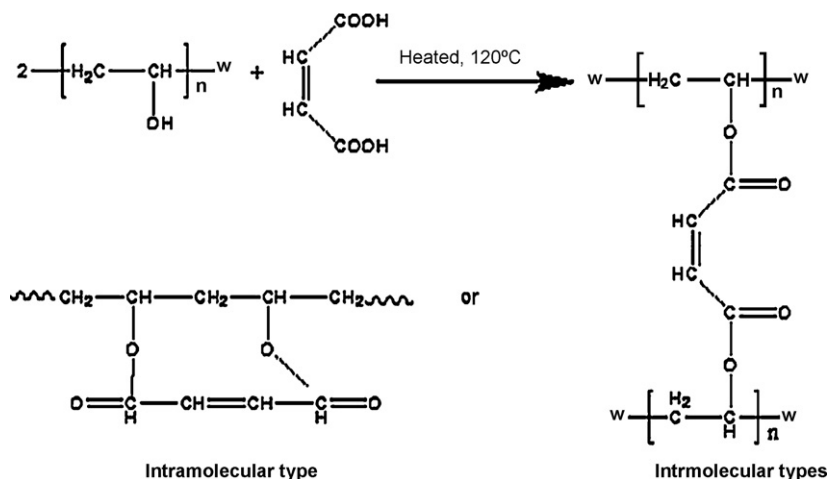
Fig. 1. Schematic representation of the possible reactions between PVA and maleic acids.

ration of PMMA into the NR phase increased the strength of the IPN sample. Jia et al. [25] reported the preparation of polyether-based polyurethane/poly(methyl methacrylate-co-ethyleneglycol dimethacrylate) interpenetrating polymer networks [PU/P(MMA-co-EGDMA)-IPNs] for adhesives to adhere to vulcanized natural rubber (NR) and soft poly(vinyl chloride) (PVC). The structures and morphology of these IPN adhesives in bulk and near the adhesive/substrate interfaces were described. However, the synthesis of the semi-interpenetrating polymer network based on epoxised NR (ENR) and poly(vinyl alcohol) (PVA) using maleic acid as the crosslinking agent have not been found in the literature reviews. ENR is a derivative of NR modified by epoxidation of its cis-1,4-polyisoprene units. ENR has a higher glass transition temperature than the unmodified cis-1,4-polyisoprene units, and has an increased polarity of the system while retaining the inherent high strength of NR [14]. In one paper, ENR PVA was produced by blending poly(vinyl alcohol) and latex using an aqueous solution blend method and maleic acid as the curing reagent. PVA is a polymer that is easily prepared, it has good biodegradability, and has been used for many applications such as medical devices, membranes and gloves [17], home textiles, coating materials and for food packaging and other products due to its excellent high chemical resistance, good mechanical behavior and ability to form films [27]. Since ENR contains epoxy groups that can be converted to hydroxyl groups, it is potentially partially miscible with PVA due to the formation of hydrogen bonding. Maleic acid or (Z)-butenedioic acid or cis-butenedioic acid is an organic dicarboxylic acid [26] molecule consisting of an ethylene group flanked by two carboxylic acid groups. Possible reactions between PVA and maleic acid are presented in Fig. 1.

To the best of our knowledge, this is the first study of its kind wherein the semi-interpenetrating polymer network has been based on biodegradable polymers prepared from natural rubber and poly(vinyl alcohol). In this present work, the preparation of a semi-IPN from ENR/PVA sheet used maleic acid as a crosslinker. The aim was to increase the surface hydrophylicity of NR for use as a new hydrophilic surface. From swelling studies of the crosslinked semi-IPN NR/PVA and ENR/PVA sheet, we have evaluated the optimum content of maleic acid as well as the best curing times. Crosslinking of the semi-IPN ENR/PVA sheet with addition of maleic acid was examined with the help of ATR-FTIR spectroscopy. In order to determine the mechanical properties of the semi-IPN ENR/PVA sheet we used a tensometer. The morphological analysis of the semi-IPN semi-IPN ENR/PVA sheet was studied through scanning electron microscopy.

2. Materials and methods

2.1. Materials

High ammonia NR (HA-NR) (Chalong Latex Industry Co. Ltd.), hydrogen peroxide (Riede-de Haen Co. Ltd., Germany), formic acid (Riede-de Haen Co. Ltd., Germany), poly(vinyl alcohol) (PVA, commercials grades) with 87% hydrolysis, Terric 16A-16 (Lucky four), maleic acid (MA, Fluka Co. Ltd., Switzerland). 200 g of HA-NR latex containing 20% dry rubber content (DRC) was blended with 10 g of 10% Terric acid as a non-ionic surfactant at ambient temperature while stirring for 1 h. The sample mixture was neutralized, then acidified with 12 g of formic acid (Fluka Co. Ltd., Switzerland). After that, 80 ml of hydrogen peroxide (BHD, Analar) was added at 30 °C within 10–15 min. The epoxidation process was carried out at 70 °C for 5 h and the resulting ENR latex possessing a 20% of epoxided content was used in this paper.

2.2. Preparation of semi-IPN based on ENR and PVA

The PVA solution (20% w/v) was prepared in Millipore water by heating it on a water bath at 70 °C while being continuously stirred. The 50 g of PVA solution was blended with 50 g of epoxided natural rubber latex at ambient temperature while using a mechanical stirrer. Then, the desired quantity of maleic acid (dose varied from 10 to 60% (w/w) with respect to the weight of PVA) was mixed with the mixture solution at ambient temperature with the help of a mechanical stirrer. The mixture was poured in the form of a sheet on a glass surface. The sheet with a 0.55-mm thickness was dried at ambient temperature and subsequently cured in an oven for different curing times (e.g., 60 min) at 120 °C.

2.3. Analysis of semi-IPN

The semi-IPN sample was characterized by attenuated total reflection mode Fourier Transform Infrared Spectroscopy (ATR-FTIR) Equimox 55, Bruker spectrophotometer, scanned 100 times at 4000–650 cm^{-1}). X-ray diffractometry was performed on an X'Pert MPD, Philips X-ray diffractometer under the following conditions: Nickel filtered Cu Kα radiation ($\lambda = 0.15406$ nm) at a current of 25 mA and a voltage of 35 kV. The scanning rate was 4°/min in the angle range of 3–28° and 5–50° (2θ). Semi-IPN samples of specific dimensions (2.5 cm × 2.5 cm) and with an average thickness of 0.5 mm were weighed and immersed in Millipore water for a period of 5 days at 32 °C. The samples were then dried in an oven at 50 °C
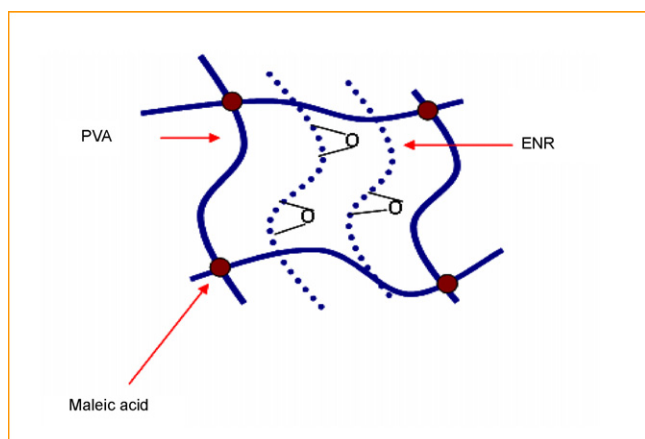
Fig. 2. Model of the semi-interpenetrating polymer networks (IPNs) based on ENR and PVA by maleic acid as a crosslinking reagent.

for 24 h and weighed until a constant weight was achieved. The degree of swelling ratio was estimated from Eq. (1)

$$\text{Swelling ratio} = \frac{W_2 - W_1}{W_1} \tag{1}$$

where W_1 is the original weight of the sample and W_2 is the weight of swollen sample.

A scanning electron microscope (JMS-5800 LV, JEOL, and SEM) was used to investigate the morphologies of cross-sections of the samples at an accelerating voltage of 6 kV. Semi-IPN sample sheets containing different amounts of maleic acid were fractured in liquid nitrogen and the cross-sections were mounted on SEM stubs with double-sided adhesive tape, and then coated with platinum under a 12 Pa *vacuum*. The thermogravimetric (TG) analysis was performed on a Pwein Elmer Thermobalance. The mass of each sample was about 6.00–7.00 mg. The carrier gas was N_2 with a flow rate of 45 mL/min. The temperature was raised from 50 to 800 °C at a heating rate of 10 °C/min. The tensile strength and elongation at the break of the semi-IPN product was measured according to ASTM D412-98a at a crosshead speed of 500 mm/min with a load cell of 100 N. Modulus of the semi-interpenetrating sample were measured according to JIS K6251 using the tensile tester (model Strograph E-L, according to TOYO-SEIKI) at a crosshead speed of 500 mm/min with the load cell of 500 N.
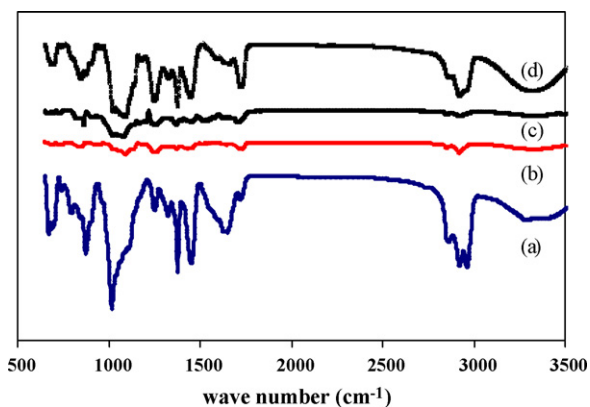

Fig. 3. FTIR spectra of (a) ENR alone, (b) PVA, (c) semi-IPN ENR/PVA in the presence of maleic acid 40%, and (d) ENR/PVA.
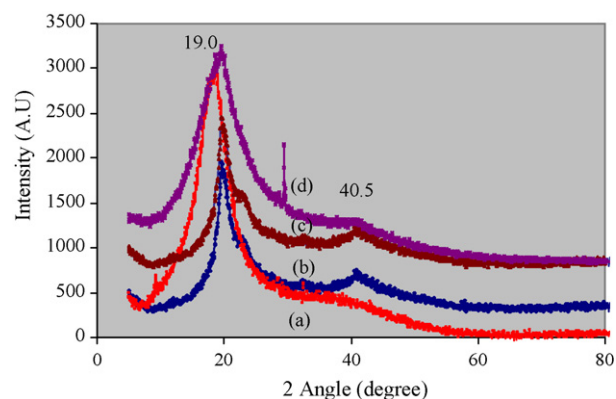

Fig. 4. XRD spectra of (a) PVA, (b) ENR, (c) ENR/PVA and (d) semi-IPN ENR/PVA in the presence of 40% maleic acid.

3. Result and discussion

The model of this semi-interpenetrating polymer networks (IPNs) contain poly(vinyl alcohol) represented as solid lines and epoxide natural rubber represented by dot lines that are separately crosslinked into two interpenetrated networks with no chemical bonds between them as shown in Fig. 2. The poly(vinyl alcohol) reaction with the maleic acid is represented at the red spot.

3.1. FTIR results

The semi-interpenetrating polymer network of NR-poly(vinyl alcohol) containing maleic acid was prepared by the solution-latex method. The influence of the maleic acid content on the properties of the rubber blend was studied. The presence of a large number of hydroxyl groups in PVA resulting from the semi-interpenetration between NR and poly(vinyl alcohol) and strong hydrogen bonding (perhaps both the intermolecular and intramolecular types), will affect the solubility of PVA in water. The FT-IR spectrum of PVA
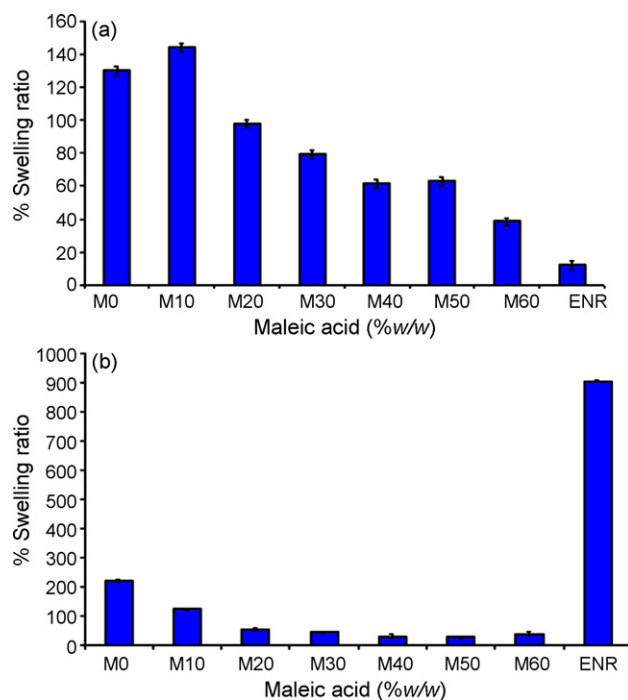

Fig. 5. % Swelling ratio of semi-IPN ENR/PVA with different maleic acid contents in (a) water and (b) toluene.
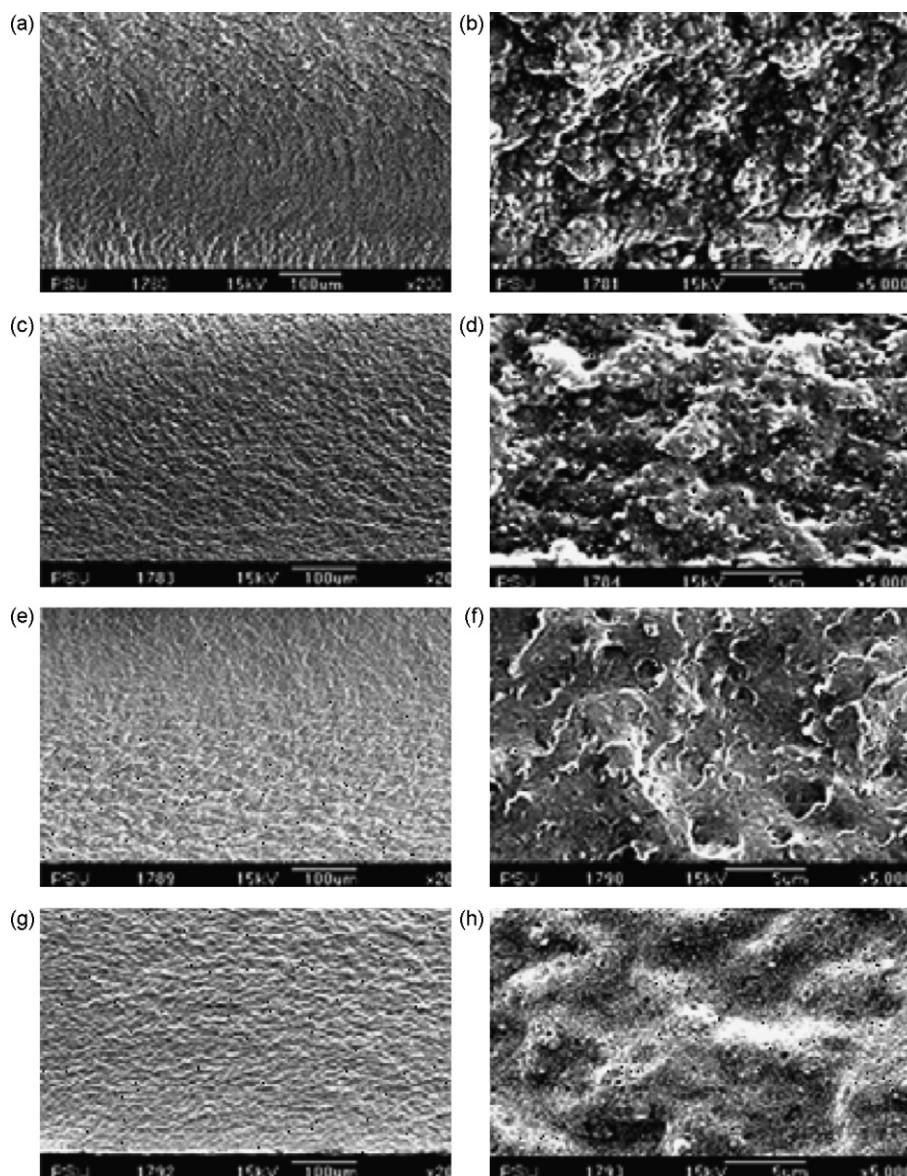
Fig. 6. Scanning electron micrographs of semi-IPN NR/PVA with (a) 0% (w/w), (b) 0% (w/w) (expanded region), (c) 10% (w/w), (d) 10% (w/w) (expanded region) (e) 20% (w/w), (f) 20% (w/w) (expanded region), (g) 40% (w/w) and (h) 40% (w/w) (expanded region) maleic acid.

alone, ENR alone, the ENR/PVA blend and semi-IPN samples are shown in Fig. 3. Maleic acid treatment of PVA produces intermediate heat stability. It is possible that in this temperature zone the total energy input is inadequate to break the double bond structure (–C=C–) of the heat-treated samples but it is sufficient to start the degradation of the–C–O– bond of the maleic acid treated PVA in the semi-IPN samples as shown in Fig. 3. The ester linkage of the semi-interpenetrating sample is confirmed by FTIR. The absorption bands of the *cis*-1,4-polyisoprene in ENR is found at 2860 cm^1 (C–H stretching), 1665 cm^1 (C=C stretching), 1453 cm^1 (–CH$_2$– deformation), 1378 cm^1 and (methyl C–H deformation) [2,3].

The absorptions at 876 and 1252 cm^{-1} can be attributed to the epoxy group, and the weak absorption at 1735 cm^{-1} can be assigned to the carbonyl group of the ester. The main peaks of PVA alone shown at 1327 and 843, and 1087 cm^{-1} are attributed to C–H bending and C–O stretching, respectively. The changes of the characteristic spectra peaks reflect the chemical interactions when two or more substances are blended. In the typical spectrum of the semi-IPN sample sheet, the characteristic peak at 1729 cm^{-1}

was shifted to 1730 cm^{-1}. This document indicates that there are hydrogen bonded interactions between the hydroxyl groups, carbonyl groups of PVA and carbonyl groups of maleic acid and the epoxy groups of ENR that helped them to be compatible.

3.2. XRD results

The XRD scans of the semi-interpenetrating polymer network between epoxidzed NR and PVA, ENR and PVA are shown in Fig. 4. The observed PVA alone spectrum reveals a semi-crystalline feature. It is vital to note that there are two halos cited at 19.5° and 40.5°. The first one has a clear crystalline peak at a scattering angle $2\theta = 19.5°$ that corresponds to a (1 0 1) spacing. The second halo has a low intensity and broad shape and corresponds to noncrystalline zones within the crystalline polymer matrix. After adding maleic acid in the semi-interpenetrating sample sheet, the intensity of the diffraction peak at 19° for PVA becomes gradually broader when compared to the PVA alone and the ENR/PVA blend without maleic acid, due to crosslinking between PVA and maleic acid. In

addition, the intensity of the peak at 40.5° in the semi-IPN sample with 40% (w/w) of maleic acid decreased compared to the ENR/PVA blend without maleic acid and poly(vinyl alcohol) alone. It demonstrates that the existence of maleic acid decreased the crystallinity of PVA. This phenomenon is due to the significant hydrogen bonding interactions among PVA, ENR and maleic acid molecules as well as formation of covalent bonds between PVA and maleic acid. In other word, the addition of maleic acid in the semi-interpenetrating sample improves the compatibility between PVA and ENR. The broad peak of the hydrated crystalline structure of ENR shows the same tendency as that observed for the peak at 19°.

3.3. Swelling ratio results

The swelling of any polymeric film in a solvent depends upon the diffusion coefficient of the solvent, the relaxation rate of the amorphous regions of the polymer chain and its degree of crystallinity. Polymer gels may be classified into two different categories, i.e., physical gel and chemical gel. In a physical gel the junction points of the network arise owing to physical bonding like Van Der Waals interactions, hydrogen bonding, the presences of crystallites, etc.; hence, in a good solvent such networks exhibit a large extent of volume change owing to the facile penetration of the solvent [4]. The PVA selected for the present study possesses a degree of hydrolysis of 98%. The swelling ratio of a semi-interpenetrating sample could be used practically to approximate the crosslinking density in the sample. The swelling ratio of the maleic acid crosslinked semi-IPN based on the ENR/PVA having different maleic acid contents and ENR alone and all cured at 120 °C for 60 min was studied in water and toluene after keeping the samples immersed
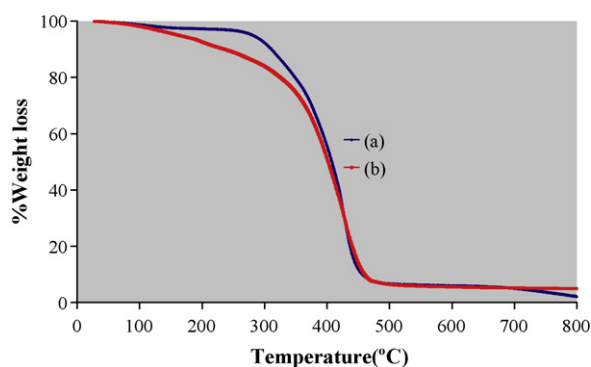

Fig. 7. TGA of (a) ENR/PVA and (b) semi-IPN ENR/PVA in the presence of 40% maleic acid.

in solvents for 5 days. The semi-IPN based on the ENR and PVA had a lower swelling ratio after being cured with maleic acid (Fig. 5(a) and (b)), when compared with the uncured measurement. This indicates that the chemical reaction that occurred between the semi-IPN based on the ENR/PVA network with maleic acid. Fig. 5(a) determined the swelling ratio in water that varied with the maleic acid content of the ENR/PVA. The swelling ratio of the sample in water decreased as the amount of maleic acid in the sample increased. The toluene resistance of the semi-IPN ENR/PVA system also increased with increasing amounts of maleic acid in the sample after curing (Fig. 5(b)). The swelling ratio of semi-IPN ENR/PVA with 10% (w/w) maleic acid was 230%. When the maleic acid content of the sample was increased from 10 to 50% (w/w), the swelling ratio of the semi-IPN ENR/PVA was 30% (Fig. 5(b)).
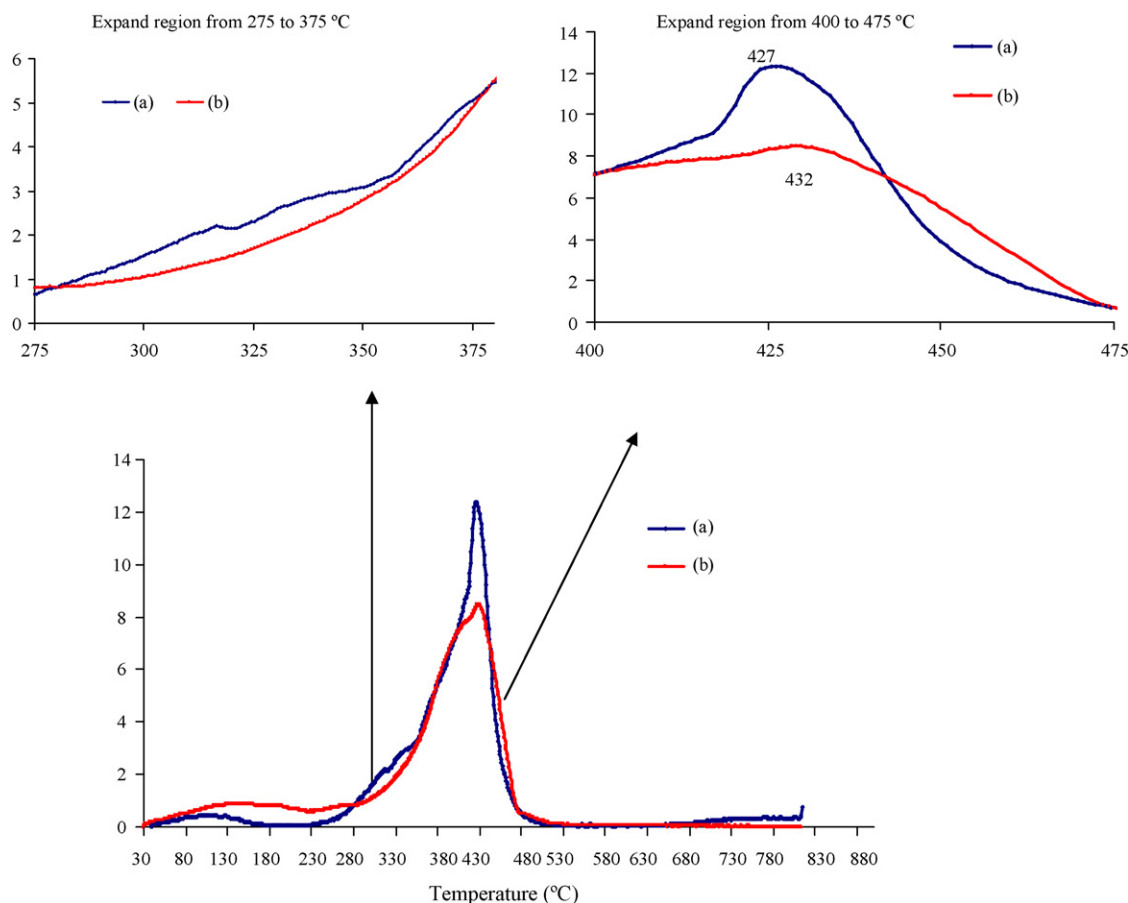

Fig. 8. DTG of (a) ENR/PVA and (b) semi-IPN ENR/PVA in the presence of 40% maleic acid.

3.4. SEM results

The phase morphology of PVA and cured semi-IPN ENR/PVA containing various amounts of maleic acid was studied through scanning electron microscopy. The cross-sectional view of the samples is shown in Fig. 6. The morphology of the ENR/PVA blend exhibited many microphase separations because there was no crosslinking in the PVA molecules due to the absence of maleic acid. When maleic acid was present in the ENR/PVA matrix the morphology showed less microphase separations. The low microphase separation morphology was not observed in samples of the semi-INP in the presence of maleic acid due to crosslinking between the PVA molecules by maleic acid. This indicates that the NR molecules did penetrate into the crossliked PVA molecule.

3.5. TGA analysis results

The objective of this TGA is to investigate the variation and to understand the thermal behavior and the modifications to polymer structure. The TGA and DGA measurements of ENR/PVA and PVA/PVA in the presence of maleic acids are shown in Figs. 7 and 8, respectively. From the thermogravimetric analysis and observations of the temperature maximum, a better heat stability for the maleic acid crosslinked PVA was observed. Three temperature regions can be identified over which most of the weight change occurs in the ENR/PVA blend. The first weight loss occurs between 90 and 120 °C which corresponds to the removal of water. The second weight loss occurs between 300 and 400 °C and corresponds to the side chain decomposition of PVA and the main chain of the ENR molecule. The third degradation between 400 and 550 °C corresponds to the decomposition of the PVA main chain and the residual ENR molecules. In the case of the semi-IPN sample containing 40% maleic acid, four weight losses were observed. An improvement in the thermal stability of the ENR/PVA can be seen when maleic acid is present, as observed by the temperature maximum. A fourth weight loss was observed in the semi-IPN sample. The weight loss at 100–120 °C (first region) is due to the moisture vaporization and at 130–180 °C (second region) is due to the decomposition of residual maleic acid (the melting point of maleic acid is 130–139 °C). The first part of the third region that occurs over a range of temperature from 200 to 450 °C is caused by thermooxidative degradation of the semi-IPN sample molecule and the second part or fourth region occurred over a range of temperatures from 450 to 550 °C. The temperature maximum peak is shifted to higher temperatures by about 5 °C compared with the ENR/PVA blend as shown in Fig. 8 at the expanded region. The lower thermal degradation of PVA in the semi-IPN sample showed two regions including the first region from 275 to 375 °C and another region from 400 to 475 °C when compared to the ENR/PVA blend without maleic acid. These results implied that the thermal stability of the semi-IPN sample was higher than for the ENR/PVA blend without maleic acid due to chemical bonding between the PVA molecule and maleic acid. Peng and Kong [28] studied the thermal degradation of PVA using TGA. They found that the degradation behavior of PVA possessed two steps including the peak degradation temperature (T_p) of the first degradation step at 350 °C and the T_p of the second degradation step at 470 °C.

3.6. Mechanical property results

The tensile strength of semi-IPN samples is a vital factor for its adhesive and biomedical applications. Thus, it was important to establish if the tensile strength of the semi-IPN sample was improved by the addition of maleic acid.

The tensile strength of the semi-IPN NR/PVA samples as a function of curing times and maleic acid contents are presented in
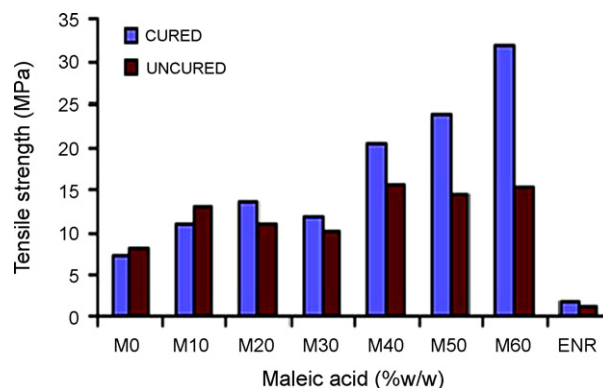

Fig. 9. Tensile strength of semi-IPN based on ENR/PVA with maleic acid contents.

Fig. 9. The data indicate that the tensile strength of the semi-IPN based on the NR/PVA blend increased with increasing curing time (Fig. 9). This might be used as evidence for the existence of chemical crosslinks between maleic acid and PVA. However, it was also clear that the tensile strength of semi-IPN was slightly increased with curing times. This can be explained by a certain amount of crosslinking of PVA being generated by activation of the double bonds of maleic acid during curing. It should be emphasized that the tensile strength values of the cured semi-IPN based on the NR/PVA was high when compared to NR alone. The mechanical properties of the semi-ENR/PVA are shown in Fig. 9. Following curing, the tensile strength of semi-IPN based on ENR/PVA was increased with an increased maleic acid content. It was a surprise to find that the tensile strength of the semi-IPN based on its ENR/PVA reached 32 MPa when the maleic acid concentration reached 60% (w/w). This result could be explained by the finding from the swelling measurement that the highest crosslikiking density of the semi-IPN sample from poly(vinyl alcohol) and maleic acid occurred in the presence of 60% maleic and this produced the highest tensile strength value.

Fig. 10 shows the elongation at the break of the semi-IPN based on its ENR/PVA with different maleic acid contents. The elongation at the break of the semi-IPN sample decreased with increasing maleic acid content. The elongation at the break of the samples with 10 and 50% (w/w) maleic acid before vulcanization was 600 and 100%, respectively. After the vulcanization process, the elongation at the break of these samples was only slightly reduced, compared to the sample without the vulcanization process, due to the high density of crosslinking in the sample.
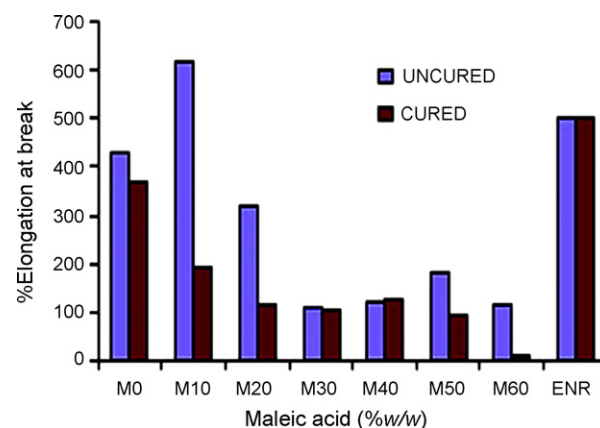

Fig. 10. Elongation at breaking of the semi-IPN based on ENR/PVA with different maleic acid contents.

4. Conclusions

The preparation of semi-IPN between NR and PVA or ENR and PVA using maleic acid as the crosslinking agent was carried out successfully. The highest tensile strength of the semi-IPN based on its ENR and PVA with 60% maleic acid was 32 MPa. The lowest swelling ratio of semi-IPN based on ENR and PVA in both water and toluene was found in the uncured condition. A chemical reaction between PVA and maleic acid was confirmed by ATR-FTIR. The crosslinking properties of the semi-IPN films increased as a function of the maleic acid content and curing reaction times. In addition, the crystalline content of PVA dramatically decreased after adding maleic acid in the semi-IPN, as observed from its XRD. The semi-IPN samples show good mechanical properties and thermal stability. The SEM's of the semi-IPNs containing maleic acid showed that no phase separation occurs, when compared with the sample in the absence of maleic acid.

Acknowledgements

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