Physicochemical, Thermomechanical, and Swelling Properties of Radiation Vulcanised Natural Rubber Latex Film: Effect of Diospyros peregrina Fruit Extracts

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A range of radiation vulcanised natural rubber latex (RVNRL) films were prepared using various concentrations of aqueous extracts of mature Diospyros peregrina fruit, which acted as a cross-linking agent. The surface of the RVNRL films exhibited an aggregated morphology of the rubber hydrocarbon with increasing roughness due to increasing fruit extract contents in the latex. An improvement in tensile strength, tensile modulus, and storage modulus of RVNRL films was observed with the addition of fruit extracts compared to the control film due to their cross-linking effect. The glass transition (T_g) temperature of all the RVNRL films was found to be at around −61.5°C. The films were also observed to be thermally stable up to 325°C, while the maximum decomposition temperature appeared at around 375°C. The incorporation of fruit extracts further revealed a significant influence on increasing the crystallinity, gel content, and physical cross-link density of the RVNRL films.

1. Introduction

Virgin natural polymers like rubber latex, an elastic macromolecular polymer (polysoprene), have inherently low mechanical and thermal stability properties. Natural rubber is highly sensitive to thermal decomposition and autoxidation and, therefore, undergoes thermal aging when exposed to heat, air, and ozone resulting in poor mechanical, thermal, and swelling properties. In order to improve their mechanical properties the rubber molecules are being processed with different types of antioxidants and particulate fillers, such as silica [1, 2], clays [3], carbon black [4], and carbon nanotubes [5, 6] to expand their applications in various fields. Radiation vulcanisation is also being employed to improve the mechanical properties of natural rubber [5, 7, 8]. Some nonwater soluble amino acids, such as cystine, asparagines, and alanine, were also used as antioxidant in radiation vulcanised natural rubber latex (RVNRL) films and showed good antiaging effect on RVNRL films with tensile strength retentions ranging from 70% to 80% after accelerated aging at 100°C for 24 h compared to RVNRL film containing no antioxidant (tensile strength retention ~35%) [9]. They also reported Keratin from chicken feather as a potential antioxidant (tensile strength retention ~60%) for RVNRL film. Tris(nonylated phenyl)phosphite (TNP) [10–12], polyfuran, polythiophene [13], polyamines [3, 14], and pyridazine derivatives [15] were also reported to be effective antioxidants to prolong the life of natural and synthetic rubber films.

Košíková et al. [16] investigated sulphur free lignin (10–30 phr) as a natural filler in natural rubber which significantly improved the tensile properties of the films. For
example, tensile strength of ~3.99 MPa was reported for the rubber film containing 10 parts per hundred rubber (phr) lignins compared to the control rubber film with no lignin content (~1.87 MPa). In another study, carbon black filled natural rubber containing lignin was suggested to have positive stabilising effect after thermooxidative aging of rubber films at 80°C, which was comparable to the conventional synthetic antioxidant (N-phenyl-N’-isopropyl-p-phenylenediamine (IPPDL)) [17]. Rodrigues et al. [18] investigated the Cashew Nut Shell Liquid (CNSL) as a natural antioxidant in cis-1,4-polyisoprene rubber and showed that addition of 5% CNSL had the highest antioxidant activity over the thermal oxidation at 140°C of polyisoprene rubber.

The Diospyros peregrina fruit belongs to the Ebenaceae family locally called River ebony, Gaub, and/or Indian persimmon. The extremely slimy pulp comes out of the fruit as gum exudates which mainly contained triterpenes, alkenes, flavonoids, and tannins [19–22] and had already showed its antioxidant [23], antidiabetic [24, 25], antidiarrhoea, and antidisentery properties [26]. The aqueous extracts of Diospyros peregrina fruit have been used in the radiation vulcanised (from 0 to 20 kGy) natural rubber latex films as a natural antioxidant to evaluate the mechanical properties according to ISO 37-1977(E) method [32] or universal n-BA. The RVNRL films were leached with distilled water for 24 h at room temperature and air-dried until transparent films were achieved [31].

Table 1: Formulations and sample codes for the RVNRL films investigated in this study.

<table>
<thead>
<tr>
<th>Sample codes used in this study</th>
<th>Latex (phr)</th>
<th>Fruit extract (phr)</th>
<th>n-BA (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>95</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>NR-10</td>
<td>85</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>NR-15</td>
<td>80</td>
<td>15</td>
<td>5</td>
</tr>
</tbody>
</table>

The surface roughness of RVNRL films was conducted on a Dumbell-shaped test specimens according to ISO 37-1977(E) method [32] on a universal tensile testing machine (Hounsfield-H50KS, UK).

2.2. Morphological Characterisation. The surface morphology of the RVNRL films was characterised using an SEM (Philips XL30, FEI) at an accelerating voltage of 10 kV and a working distance of 10 mm. A sputtered platinum coating was used to avoid any charging effect on the film during the characterisation.

2.3. Surface Roughness Analysis. The surface roughness of RVNRL films was conducted on a Surftest (SV-600, Mitutoyo) using a diamond stylus tip (5 μm tip radius, 0.05 μm resolution, and 0.2 mm s⁻¹ travel speed). Data were collected from 4.8 mm measurement distance and from at least ten different positions of each film.

2.4. Tensile Test. The tensile test (tensile strength, modulus at 500% elongation and elongation at break) of RVNRL films was conducted using dumbbell-shaped test specimens according to ISO 37-1977(E) method [32] on a universal tensile testing machine (Hounsfield-H50KS, UK).

2.5. Dynamic Mechanical Analysis (DMA). DMA were conducted using a Q800 from TA Instruments (USA) in multifrequency strain mode to investigate the tensile storage modulus (E’) and tan delta of RVNRL films with increasing temperature. The specimens were prepared by cutting strips from films with a width of 5 mm and length of 25 mm and heated from −70°C to 60°C at rate of 10°C min⁻¹ using 15 mm gap distance, 0.1% strain, 0.01 N preload force, 125% force track, and 1 Hz frequency.

2.6. Differential Scanning Calorimetry (DSC) Analysis. The glass transition temperature (Tg) of RVNRL films was investigated using a DSC instrument (Q2000, TA instruments, UK). The samples (7 mg) were heated from −85°C to 50°C at a heating rate of 10°C min⁻¹ under nitrogen gas flow (50 mL min⁻¹).

2.7. Thermogravimetric Analysis (TGA). TG analysis of RVNRL films was performed on a TA Q500 from 25°C to 600°C with a heating rate of 10°C min⁻¹ under 60 mL min⁻¹ nitrogen gas flow. TA Universal analysis 2000 software was
Table 2: Tensile properties of RVNRL films prepared from irradiated NR latex with varying proportion of fruit extracts.

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa) (±standard deviation)</th>
<th>Modulus at 500% elongation (MPa) (±standard deviation)</th>
<th>Elongation at break (%) (±standard deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>28.85 ± 0.58</td>
<td>2.84 ± 0.09</td>
<td>1036 ± 9</td>
</tr>
<tr>
<td>NR-10</td>
<td>31.56 ± 0.50</td>
<td>3.20 ± 0.04</td>
<td>1000 ± 7</td>
</tr>
<tr>
<td>NR-15</td>
<td>32.68 ± 0.43</td>
<td>3.31 ± 0.07</td>
<td>996 ± 11</td>
</tr>
</tbody>
</table>

2.8. X-Ray Diffraction (XRD) Analysis. The crystallinity of the RVNRL films was observed using a D500 diffractometer (SIEMENS) using a Cu-Kα radiation source (λ = 0.154) at 30 kV and 15 mA and the data obtained from 10° to 40° 2θ using a scan step time of 2 sec and step size of 0.04°.

2.9. Swelling Properties. The swelling ratio (SR) of the rubber films was measured from the 10 mm round shape test specimens (at least five pieces) according to British standard (BS 1673: Part 4, 1953) by measuring the mass of the sample before and after immersing in toluene (purchased from Merck, Germany) for 72 h until equilibrium swelling at room temperature [32]:

\[
SR = \frac{W_s - W_d}{W_d},
\]

where \( W_d \) and \( W_s \) are the weight of dry and swollen sample in toluene, respectively.

The swollen samples were then dried in an oven at 50°C for 48 h and then further vacuum dried at the same temperature for 24 h to remove the residual solvent. The gel
content of the specimens was calculated using the following equation:

\[
\text{Gel content} = \frac{W_d - W_{ds}}{W_d},
\]  

where \( W_d \) and \( W_{ds} \) are the weight of dry RVNRL films before and after being swollen in toluene, respectively.

2.10. Cross-Link Density Measurement. The physical cross-link density \((V_e)\) of the RVNRL films was calculated using the Flory-Rehner equation using the volume fraction \((V_R)\) of the swollen rubber network in the solvent at equilibrium state according to following equation [33]:

\[
V_e = \frac{\ln (1 - V_R) + V_R + X_1 V_R^2}{V_1 \left(V_1^{1/3} - V_R/2\right)},
\]

\[
V_R = \frac{W_d/\rho_d}{W_d/\rho_d + W_{sol}/\rho_{sol}},
\]

where \( V_1 \) and \( X_1 \) are the molar volume and interaction parameter of solvent (for toluene, \( V_1 = 87.5 \text{ mol}\cdot\text{cm}^{-3} \) and \( X_1 = 0.39 \) [3], \( W_d \) and \( \rho_d \) are the weight and density of dry rubber (for vulcanised rubber, \( \rho_d = 0.9203 \text{ g}\cdot\text{cm}^{-3} \) [15], and \( W_{sol} \) and \( \rho_{sol} \) are the weight and density of solvent (for toluene, \( \rho_{sol} = 0.865 \text{ g}\cdot\text{cm}^{-3} \)).

3. Results and Discussion

The use of aqueous extract of *Diospyros peregrina* as a natural antioxidant has already made them promising candidate to improve the mechanical properties of natural rubber after thermal aging because of their excellent antioxidant and gum-like properties. Here we investigated whether this natural gummy fruit extract can be used to improve the thermomechanical, crystallization, and swelling properties of RVNRL films by increasing their cross-link density.

3.1. Morphological and Surface Roughness Properties. The surface morphology of RVNRL films with varying fruit extract contents was analysed via SEM and is presented in Figure 1. Images obtained revealed the dispersion of rubber particulates within the film (Figure 1(a)). However, with the addition of fruit extracts the rubber particulates were observed to be aggregated as can be seen in Figures
3.2. Mechanical Properties. Tensile properties (tensile strength, modulus at 500% elongation and elongation at break) of the RVNRL films with varying fruit extract contents are tabulated in Table 2. Tensile strength and modulus at 500% elongation were found increasing with the addition of fruit extracts in the blend. For example, NR-15 film showed around 13.2% and 16.5% increase in tensile strength and modulus properties compared to NR film (tensile strength ∼28.85 MPa and modulus ∼2.84 MPa). This was attributed to the influence of fruit extracts on increasing the cross-link density in RVNRL films during the radiation vulcanization [23] which was evaluated and this is discussed later in this paper. However, the elongation at break was observed decreasing with the addition of fruit extract, which was (NR-15), which is in well agreement with the SEM images and again the aggregation of rubber particulates within the films was suggested.
3.3. Thermomechanical Properties. Figure 3(a) revealed the temperature dependency of storage modulus of RVNRL films with different fruit extract contents. The storage modulus of the RVNRL films showed an increasing trend with the addition of fruit extracts in the RVNRL films in the entire temperature region investigated in this study and this was again suggested to be due to the cross-linking effect of the fruit extract on the rubber hydrocarbon [34]. The variation of tan delta curves of NR, NR-10, and NR-15 films as a function of temperature is presented in Figure 3(b). It is observed from the tan delta curves that with the addition of fruit extracts the tan delta peaks ($T_g$ values) of NR-10 and NR-15 films were seen to shift slightly to the left by 3°C, that is, to the lower temperature regions as compared to the tan delta peak of NR (appeared at $-57^\circ$C). The height of the tan delta peaks was also seen to decrease with the addition of fruit extracts in the RVNRL films compared to NR film. This was probably due to the presence of lower amount of rubber polymer in the NR-10 and NR-15 that were taking part in the thermal transition.

3.4. Thermal Properties. From the DSC analysis it can be seen that the glass transition temperature ($T_g$) of NR appeared at around $-61.5^\circ$C (see Figure 4) which is in well agreement with the literature values [4, 35] and with the addition of fruit extracts in the blend $T_g$ values found to shift to the lower temperature region very slightly and this was in well agreement with the $T_g$ value measured via DMA using tan delta curves. Though a decrease in $T_g$ ($P > 0.05$) and increase in mechanical and thermomechanical properties ($P < 0.05$) apparently showed a discrepancy when fruit extracts were added as a cross-linking agent within the natural rubber latex, however, this was presumably due to the plasticizing effect of the natural filler used in this study.

Thermogravimetry (TG) curves of the radiation vulcanised NR, NR-10, and NR-15 films are presented in Figure 5(a). The TG analysis revealed that all the RVNRL films were thermally stable up to $325^\circ$C (90% retention of residual weight), indicating that the processing temperature for these blends should be kept below $325^\circ$C. However, at higher temperature (around $400^\circ$C) the residual weight of the films was found to be decreased with the addition of fruit extracts which suggested the thermal instability of the additive used at the higher temperature.

The major thermal decomposition profiles of NR, NR-10, and NR-15 films were characterised from their derivative thermogravimetry (DTG) curves (presented in Figure 5(b)), which showed the maximum decomposition temperature ($T_{\text{max}}$) for all the RVNRL films at $365^\circ$C. The thermal degradation of all the major functional groups in the RVNRL films occurred in the range 300–425°C through solid state transformations and loss of low molecular mass fragments.

3.5. Crystallisation Properties. The XRD traces of RVNRL films with varying filler contents are depicted in Figure 6. The diffraction patterns of all the RVNRL films revealed the natural rubber’s characteristics peaks at around 19$^\circ$ two theta [30]. An increase in the intensity of the XRD traces was observed with the addition of fruit extract, which was attributed to the induced crystallisation of the fruit extracts on the rubber polymer.

3.6. Swelling Properties and Cross-Link Density. The effect on the swelling ratio (SR) of radiation vulcanised rubber films with varying fruit extract contents obtained at 15 kGy absorbed dose is shown in Figure 7. Swelling ratio decreased from 14.9 to 7.0 with the addition of 15 phr fruit extracts to the blends. However, the gel content of the RVNRL films was seen to increase with the fruit extract contents in the RVNRL blends.

The physical cross-link density of the rubber hydrocarbon in RVNRL films with the addition of fruit extracts is presented in Figure 8. The cross-linking densities were observed increasing significantly to $5.2 \times 10^{-5}$ mol·g$^{-1}$ in case of NR-15 films compared to the control NR film ($1.5 \times 10^{-5}$ mol·g$^{-1}$). This was attributed to the effect of fruit extracts through the aggregation of rubber particulates within the vulcanised rubber films.

The RVNRL films produced in this study showed that the incorporation of Diospyros peregrina fruit extracts provides improvements in mechanical, thermomechanical, crystallisation, swelling, and cross-linking density properties of the radiation vulcanised rubber films when compared to the control NR film which could minimise the use of synthetic filler as well as toxic antioxidant in the natural rubber-based materials.

4. Conclusion

Aqueous extracts of Diospyros peregrina as natural cross-linking agent were successfully blended with rubber latex in various contents (0, 10, and 15 phr) before being irradiated.
at 15 K Gy absorbed dose to obtain the RVNRL films. An aggregated morphology of the rubber particulates was seen with the incorporation of fruit extracts within the RVNRL films, which played an influential role in imparting some surface roughness on the films. The addition of fruit extracts within the rubber latex did not exhibit any significant change in their glass transition and thermal decomposition properties. However, an improvement in tensile strength, tensile modulus, and storage modulus properties of the rubber films demonstrated the cross-linking effect of the Diospyros peregrina fruit extracts in rubber particulates. The presence of 15 phr fruit extract had a significant effect on increasing physical cross-linking density of the rubber films which influenced significantly decrease in swelling ratio and increase in the gel content and crystallisation properties of the RVNRL films.

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References


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