

Effects of Cashew Nut Shell Liquid as a Plasticizer on Cure Characteristics, Processability, and Mechanical Properties of 50 : 50 NR/EPDM Blends: A Comparison with Paraffin Oil

Wanvimon Arayapranee,¹ Garry L. Rempel²

¹Department of Chemical and Material Engineering, Rangsit University, Phatum Thani 12000, Thailand

²Department of Chemical Engineering, University of Waterloo, Ontario, Canada N2L 3G1

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ABSTRACT: 50 : 50 natural rubber (NR) and ethylene-propylene–diene monomer rubber (EPDM) blends were prepared with different contents of cashew nut shell liquid (CNSL), a natural product obtained from the shells of the cashew nut, as a plasticizer. For comparison, a commercial paraffin oil plasticizer was also used. The effect of plasticizer content on the cure characteristics, processability, and mechanical properties such as tensile strength, elongation at break, and Young's modulus before and after ageing was investigated. Scanning electron microscopy (SEM) was used to observe the blend morphology. The results indicated that the CNSL plasticizer resulted in lower Mooney viscosity and lower cure time of the 50 : 50 NR/EPDM blends. The incorporation of CNSL into 50 : 50 NR/EPDM blends

improved tensile strength and elongation at break but decreased Young's modulus. On addition of CNSL the resistance of the blends to heat and weathering ageing improved. Scanning electron micrographs revealed that the morphology of the blend plasticized with CNSL is finer and more homogeneous compared with the blend plasticized with paraffin oil. Overall results indicate that CNSL can be used as a cheaper plasticizer to replace paraffin oil in NR/EPDM blends with improved processability and mechanical properties. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2696–2702, 2007

Key words: natural rubber; ethylene–propylene–diene monomer rubber; cashew nut shell liquid; plasticizer

INTRODUCTION

Blending of two elastomers is a useful method to improve certain material properties because while it combines the attractive properties of both the constituents of the blend, it is relatively free of the economical and technical uncertainties associated with synthesis of new polymeric materials. Ethylene–propylene–diene monomer rubber (EPDM) is obtained by polymerizing ethylene and propylene with a small amount of a nonconjugated diene, which normally imparts good ageing characteristics, good weathering oxidation, and chemical resistance. Usually, the blending of EPDM with natural rubber (NR) and high diene rubbers has given rise to compounds with good ozone and weathering and chemical resistance.^{1–7} NR is a natural biosynthesis polymer that has an attractive range of properties, possessing excellent physical properties and good processing characteristics, but is

found somewhat lacking with respect to heat and UV resistance. Often, NR is added to EPDM to improve the compounds with respect to good ozone, weathering and chemical resistance, and elastic properties. Although blending looks promising, most of the polymer blends are immiscible and incompatible, thus resulting in poor mechanical properties because of the unsaturation of their constituents, resulting in widely differing cure rates. Thus, several attempts have been made to improve the poor compatibility of EPDM with high diene rubbers by introducing an additive into the blend matrix. For instance, Go and Ha⁸ blended EPDM and butadiene rubber (BR) by adding a mixture of aliphatic and aromatic hydrocarbon (AAHC) resins, effectively enhancing the compatibility between EPDM and BR, resulting in good mechanical properties such as high tear strength and fatigue resistance of the vulcanized EPDM/BR blends. Paraffin oil is widely used in the compounding of diene rubbers to improve the processability of the compounds and to impart the desired physico-mechanical properties of their vulcanizates. Cashew nut shell liquid (CNSL) represents one of the major and cheapest sources of a naturally occurring mixture of monofunctional and difunctional phenol derivatives, and each of them has a C₁₅ hydrocarbon radical side chain such

Correspondence to: G. L. Rempel (grempe@cape.uwaterloo.ca).

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as anacardic acids, cardols, cardanols, and methylcardols.⁹ CNSL, a most abundant natural phenolic liquid with a long aliphatic side chain, and its derivatives have been used as antioxidants, plasticizers, and processing aids for rubber compounds and modifiers for plastic materials derivatives.¹⁰ CNSL, cardanol, and cardol are all used to provide oxidative resistance to sulfur-cured natural rubber products. Cardanol, CNSL, or sulfured CNSL is added to rubber gum stock or nitrile rubber to improve the processability, mechanical properties, and resistance to crack and cut properties of the vulcanizates. Kukreja et al.¹¹ studied the effects of additives with various oils such as paraffin oil, vegetable oil, castor oil, and CNSL on the physical, mechanical, and adhesion properties of carbon black or rubber compounds. They reported that all vegetable oils provided enhanced properties relative to those of paraffin oil, which is used as a normal additive as a plasticizer for regular carbon black/rubber compounds. The modification of filled and unfilled NR compounds with a phosphorylated derivative of CNSL, leads to the improvement of physico-mechanical properties.¹²⁻¹⁶

The use of CNSL, obtained as a byproduct during the process of removing the cashew kernel from the nut, as a partial or full replacement additive in rubber compounds may be of immense interest in the days of dwindling petroleum deposits. Hence, it can be used as a plasticizer that may help in the reduction of the cost of the rubber blends. In the present study, CNSL was introduced into 50:50 NR/EPDM blends and the effects of additive loading compared with those of the commercial additive, paraffin oil, was investigated, using cure characteristics and mechanical properties as performance indicators. The mechanical properties of the blends are usually described in terms of tensile strength, elongation at break, and Young's modulus. The properties were correlated with the morphology of the blends studied by Scanning Electron Microscopy (SEM). Heat ageing and weatherability of the blends were also assessed.

EXPERIMENTAL

Material

All mixing ingredients, the commercial grade as used in the rubber industry, were used as received. Natural rubber (STR XL) was supplied by Yala Latex Industry (Yala, Thailand). EPDM (DuPont's Nordel[®] IP 4570) of 4.9 wt % ethylenedene norbornene diene content and of 50 wt % ethylene content had a Mooney viscosity (ML_{1+4} at 125°C) of 70 was obtained from Dupont Dow Elastomers (Wilmington, DE). The CNSL, a viscous reddish brown liquid, is traditionally obtained as a byproduct during the isolation of the kernel by roasting the raw nuts. The CNSL used in this study was obtained from Patcharee Cashew Nut Co., Ltd.

(Cholburi, Thailand). Paraffin oil was supplied by Gumy Mooning Petrochemicals Co., Ltd. (Shanghai, China). Other chemicals, such as stearic acid, zinc oxide (ZnO), sulfur (S), mercaptobenzothiazole sulfoamide (MBTS), and tetramethyl thiuram disulfide (TMTD) were obtained from Lucky Four Co., Ltd. (Bangkok, Thailand).

Preparation of NR/EPDM blends

Formulations of the blends are provided in Table I. NR/EPDM (50:50 wt %) blends were prepared in an internal mixer using conventional mixing procedures involving two stages. In the first stage, the blends were prepared in a dispersion kneader machine with a fill factor of 0.7, at a chamber temperature of 75°C and a rotor speed of 40 rpm. NR was initially masticated in the mixer for 3 min and blended with the EPDM component, followed by the other ingredients in this order: plasticizer (paraffin oil or CNSL), activators (zinc oxide and stearic acid) and accelerators (MBTS and TMTD). In the second stage, complete vulcanized compounds were prepared by the addition of sulfur using a laboratory-sized two-roll mill at 70°C for 3 min.

Cure characteristics

Cure characteristics were studied using a rheometer (TECH-PRO) according to ISO 3414 for 30 min at 150°C. The Mooney viscosity (ML_{1+4} at 100°C) was determined by using a Mooney viscometer (TECH-PRO). The testing procedure was conducted according to the method described in ISO 289-1.

Vulcanization process

All blends were compression molded at 150°C with a force of 17.5 MPa using a hydraulic hot press according to their respective cure time, t_{90} , determined with a TECH-PRO instrument.

Mechanical properties

Tensile properties were determined on an Instron Testing Instrument (Model 1011, Norwood, MA) using C-type Dumbbell-specimens, according to ASTM D 412.

TABLE I
Formulation for 50 : 50 NR/EPDM Blends

Ingredient	Parts per hundred of rubber
NR (STR XL)	50
EPDM	50
Plasticizer	Variable (2-10)
ZnO	2.0
Stearic acid	2.0
TMTD	0.15
MBTS	1
Sulfur	2

Accelerated thermal ageing test

Tensile specimens were aged at 100°C for 72 h in an air-circulating ageing oven. Tensile properties of the aged samples were determined according to ASTM D573 (1994).

Weatherability

Weathering resistance (ASTM G 154-00a) was measured at 60°C, using a Q-UV Accelerated Weathering Tester (Cleveland, OH) coupled with a UV lamp set at a wavelength of 315 nm. Tensile properties of the samples were tested after exposure to UV and moisture for 14 days.

Scanning electron microscopy

Scanning electron microscopic studies of the compounds' tensile fracture surfaces were carried out on gold-coated samples using a Joel Microscope (model JSM 5600 LV, Tokyo, Japan) at a magnification of 5000.

RESULTS AND DISCUSSION

Cure characteristics and processability of NR/EPDM blends

Each of the two plasticizers (CNSL and paraffin oil) was incorporated at a loading ranging from 2 to 10 phr (parts per hundred of total rubber by weight) in 50:50 NR/EPDM blends to study the effect of plasticizer loading on the cure properties of the blends. Figure 1 shows the optimum cure times (t_{90}) for both plasticizers at a given loading; the blends with CNSL exhibited a shorter t_{90} than the blends with paraffin oil. The optimum cure time decreased with increasing CNSL concentration for 50:50 NR/EPDM blends, sug-

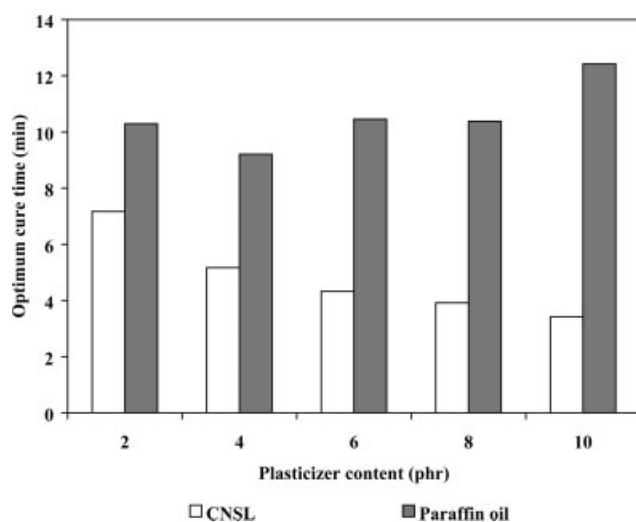


Figure 1 Relationship between plasticizer content and optimum cure time of 50 : 50 NR/EPDM blends plasticized with CNSL and paraffin oil.

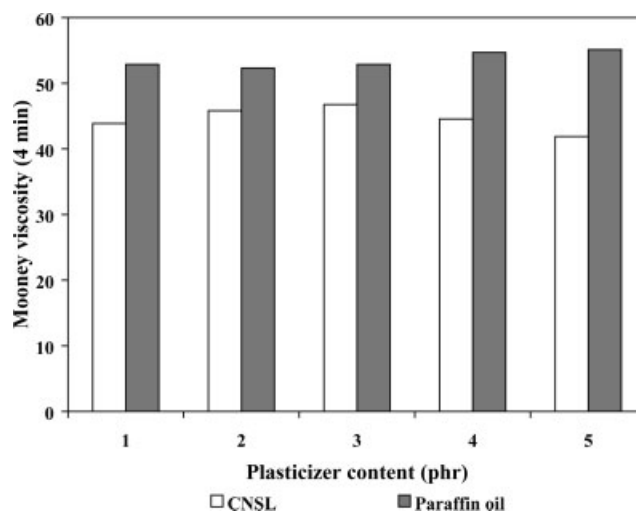


Figure 2 Relationship between plasticizer content and Mooney viscosity (ML_{1+4} at 100°C) of 50 : 50 NR/EPDM blends plasticized with CNSL and paraffin oil.

gesting that the CNSL functioned as a lubricant for the blends, which allows easier slippage of the macromolecules. The CNSL consists of differing polarities; one part of the chain end was polar in nature, whereas the paraffin chain end of the CNSL is nonpolar. In polymer blending, this mixture of polarity provided a true solvating effect in wetting out the two component polymers, thus leading to a decrease in cure time with an increase in the content of CNSL. A similar reduction in the cure time has been reported in NR with 10 phr of phosphorylated CNSL, wherein the long chain aliphatic unsaturated segment of the prepolymer is understood to take part in the cure reaction with NR, which prevents the crosslinking between NR at nearby unsaturated sites.¹⁶ However, with paraffin oil, a contrasting trend was observed. As seen in Figure 1, the curing time increased with increasing paraffin oil content. The increasing trend observed may be explained by the poor polarity of the paraffin oil containing a long-chain hydrocarbon. The dispersion of the paraffin plasticizer in the two component polymers was poor indicating a longer cure time.

The effect of plasticizer loading on the Mooney viscosity of the blends is shown in Figure 2. It can be seen that for both plasticizers, the change of viscosity with plasticizer loading was small. However, at a similar plasticizer loading, blends plasticized with paraffin oil exhibited a higher Mooney viscosity than that of the blends in which CNSL was used. Since CNSL consists of styrenic phenols and unsaturated long chains, CNSL takes part in dual interactions: one part of the chain end, which is polar in nature, can interact with the EDPM phase, whereas the nonpolar paraffin chain end can interact with the NR phase, leading to an enhancement in the mobility of the rubber chains via the coupling action of the CNSL. Therefore, the

CNSL used could act as coupling agent between EPDM and NR phases, accounting for a lowering of viscosity with respect to a paraffin oil blend. In the case of paraffin oil blends, the higher viscosity indicated that they could be processed less easily than the CNSL blends. The lack of different polarities in paraffin oil results in low interactions between the two polymer components, which causes inhomogeneous mixing and phase separation.

Mechanical properties before heat and weathering

In polymer blend studies, mechanical properties are important parameters in characterization. Variation in the tensile properties of the blends such as tensile strength, elongation at break, and modulus at 100% elongation with concentration of the plasticizer are provided in Figures 3–5 respectively. It can be seen in Figure 3 that, at a given loading, the blends plasticized with CNSL had the higher strength values compared with the blends plasticized with paraffin oil. Since paraffin oil is nonpolar, low values for the tensile strength result. CNSL seemed to act as a coupling agent in the NR/EPDM blends because of its capacity for interactions with both NR and EPDM, thereby improving the strength of the rubber blends. For CNSL, the tensile strength increased by increasing CNSL loading up to 6 phr; then, it remained unchanged at higher loading of CNSL. The presence of polarity in CNSL is believed to play a significant role in promoting a good interaction and compatibility with the NR/EPDM matrices, thus resulting in the better performance in ultimate tensile strength at high loading. However, for blends plasticized with paraffin oil, the tensile strength showed no significant change

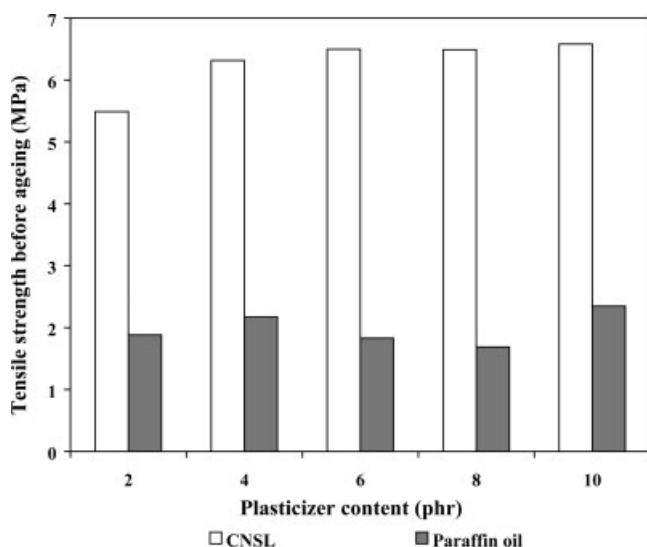


Figure 3 The effect of plasticizer content on tensile strength of 50 : 50 NR/EPDM blends plasticized with CNSL and paraffin oil.

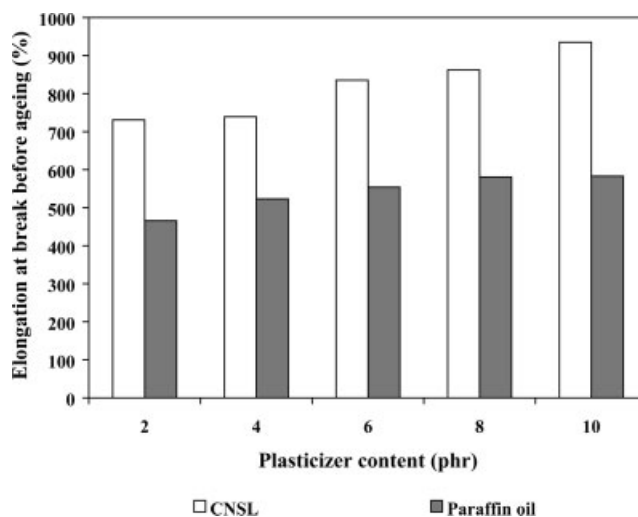


Figure 4 The effect of plasticizer content on elongation at break of 50 : 50 NR/EPDM blends plasticized with CNSL and paraffin oil.

with an increase in loading. This may be due to the lack of the interaction between the rubber phases, as mentioned above.

The effect of plasticizer loading on elongation at break of the blends is illustrated in Figure 4. For both plasticizers, the elongation at break of the blends increased with increase in plasticizer loading. As more plasticizer was introduced into the blend, the elasticity of the rubber chains was increased, resulting in comparatively softer blends with lower stiffness and greater flexibility. It can be seen that the elongation at break of blends plasticized with CNSL was higher than the blends plasticized with paraffin oil at the same plasticizer content. This is probably due to the presence of the differing polarities in CNSL, in

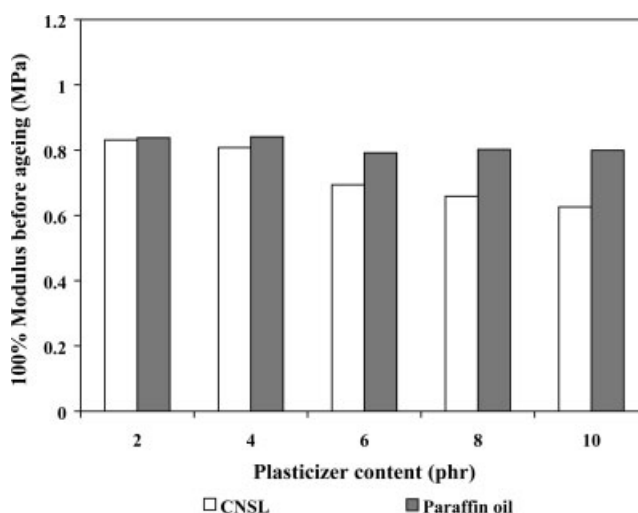


Figure 5 The effect of plasticizer content on 100% modulus of 50 : 50 NR/EPDM blends plasticized with CNSL and paraffin oil.

comparison with paraffin oil, which supported the softening effect of CNSL in the blends. This can again be explained in terms of the interactions between the two polymer components via the CNSL plasticizer then leading to enhanced elasticity of the macromolecules.

The variations in Young's modulus as a function of plasticizer loading are presented in Figure 5. Young's modulus is an indication of the relative stiffness of the material. The modulus at 100% elongation showed a decrease with an increase in plasticizer content of CNSL, whereas paraffin oil showed a small decrease in this property. This can again be explained in terms of the incorporation of the plasticizer resulting in an increase in elasticity of the rubber chains thus leading to lower stiffness at higher plasticizer loading. However, at the same loading, NR/EPDM blends plasticized with CNSL possessed lower modulus than those of paraffin oil. This is in agreement with the finding of Kukreja et al.¹¹ in that the properties of carbon black/rubber compounds containing CNSL were superior to those of the corresponding compounds containing paraffin oil.

Mechanical properties after heat and weathering

Figures 6–8 show the influence of heat and weathering ageing on the tensile properties of the blends plasticized with CNSL and paraffin oil as a function of plasticizer. All of the blends after ageing showed a lower tensile strength and elongation at break but a higher Young's modulus than the blends before ageing (Figs. 3–5). Regardless of their composition and nature, all of the blends showed a reduction in tensile strength and elongation at break, as compared with those

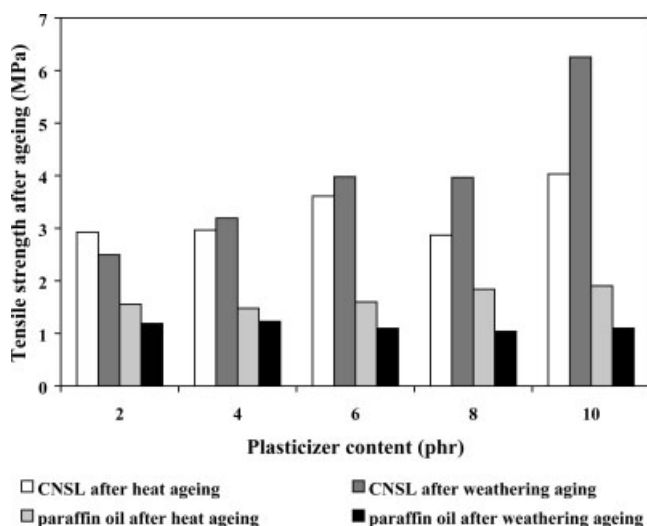


Figure 6 The effect of plasticizer content on tensile strength after ageing of 50 : 50 NR/EPDM blends plasticized with CNSL and paraffin oil.

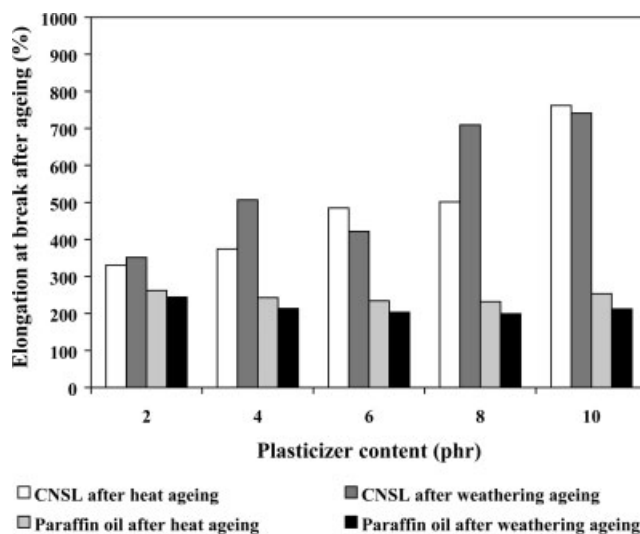


Figure 7 The effect of plasticizer content on elongation at break after ageing of 50 : 50 NR/EPDM blends plasticized with CNSL and paraffin oil.

before ageing, indicating a deterioration of their properties with accelerated ageing. The accelerated ageing of rubbers that contain unsaturated bonds normally results in a reduction in their strength properties. Figure 6 shows the tensile strength of the blends plasticized with CNSL and paraffin oil after accelerated ageing. The superiority of CNSL blends over the paraffin oil blends with respect to tensile strength was obvious. It should be noted that NR/EPDM blends plasticized with CNSL showed a higher aged tensile strength than paraffin oil because of the presence of differing polarities in CNSL. The retention in tensile strength of the blends increased with an increase in the content of CNSL. This is in agreement with the

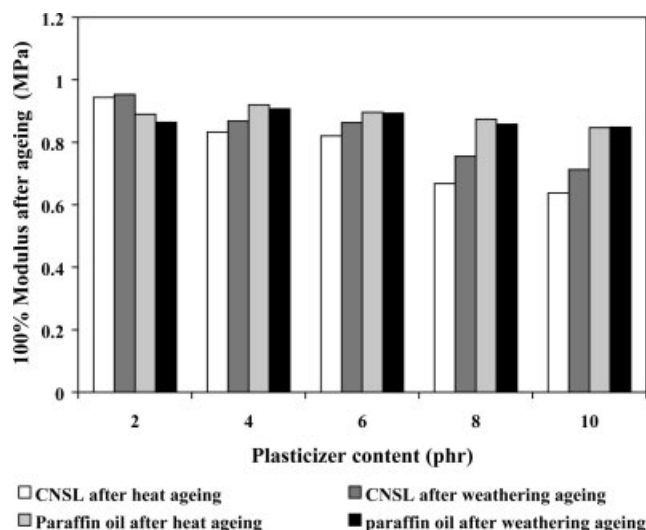


Figure 8 The effect of plasticizer content on 100% modulus after ageing of 50 : 50 NR/EPDM blends plasticized with CNSL and paraffin oil.

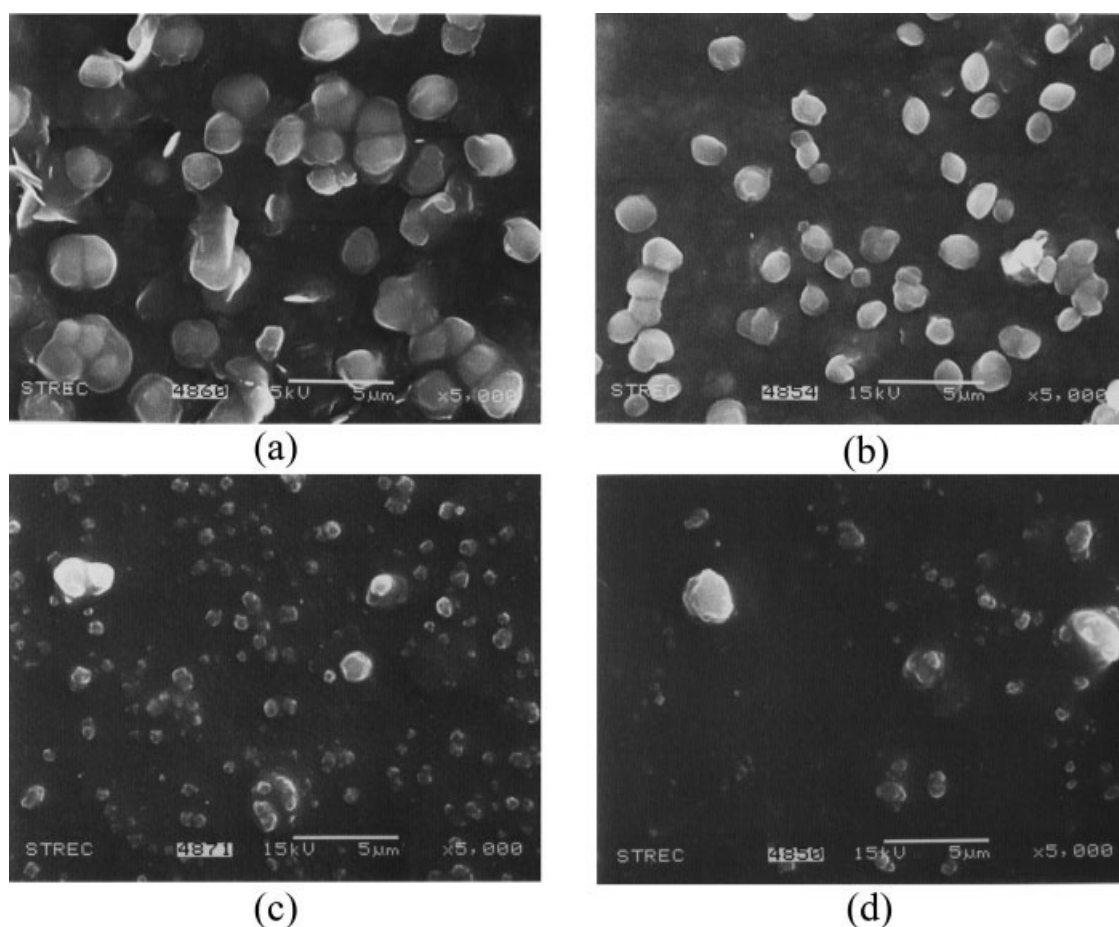


Figure 9 SEM micrographs of 50 : 50 NR/EPDM blends after tensile fracture (a) plasticized with 4 phr paraffin oil, (b) plasticized with 10 phr paraffin oil, (c) plasticized with 4 phr CNSL, and (d) plasticized with 10 phr ($\times 5000$).

findings of Menon et al.¹⁵ in that the retention in tensile strength of the modification of NR vulcanizates with phosphorylated cashew nut shell liquid prepolymer after heat ageing were superior to those of the corresponding vulcanizates with unmodified and oil-modified NR vulcanizates. However, in the case of paraffin oil, with an increase in plasticizer content in NR/EPDM blends, the retention in tensile strength showed no significant change with increased loading.

The effect of plasticizer loading on elongation at break of blends after ageing is given in Figure 7. It can be seen that the elongation at break was higher in blends plasticized with CNSL compared with blends plasticized with paraffin oil. Elongation at break for CNSL plasticizer generally increased with an increase in plasticizer loading whereas elongation at break for paraffin oil is little affected with an increase in loading. This can again be explained in terms of the incorporation of CNSL plasticizer helping to maintain the elasticity of the rubber chains after ageing, providing more flexibility at higher plasticizer loading.

The effect of heat and weathering ageing on Young's modulus is illustrated in Figure 8. Young's modulus for all of the blends plasticized with both

CNSL and paraffin oil at a given loading shifted to a higher value after ageing. These increases are generally attributed to increases in the stiffness of the rubber matrix brought about by a reduction in the number of double bonds. On comparing these results, it is observed that the blends plasticized with paraffin oil mostly showed a higher 100% Young modulus than the blends plasticized with CNSL. For blends plasticized with CNSL, as mentioned earlier, the effect of CNSL helped to reduce the stiffness of the polymer matrix; thus Young modulus generally decreased with an increase of CNSL loading. However, Young modulus slightly decreased with increasing paraffin oil loading. This may be possibly due to the poor polarity of paraffin oil compared with CNSL.

Morphology

The fracture surface of the tensile pieces of the blends was examined by SEM. The SEM photographs are provided in Figure 9(a–d). EPDM domains were formed outside of the continuous phase (NR), thus forming an incompatible blend providing poor mechanical properties for blends plasticized with paraf-

fin oil [Fig. 9(a,b)]. However, a finer phase morphology was observed and the component elastomers were found to provide homogeneous blends when EPDM and NR were plasticized with CNSL [Fig. 9(c,d)]. For 4 phr CNSL content [Fig. 9(c)], small EPDM domains were observed in the blends. The fracture surfaces became finer and more homogeneous with 10 phr CNSL content [Fig. 9(d)]. This indicates that the CNSL was also an effective compatibilizer that improved the morphology of the NR/EPDM blends. It is also likely that interaction between phases may be created in the presence of CNSL, which may produce a finer phase morphology resulting in better mechanical properties.

CONCLUSIONS

It can be concluded that EPDM/NR blends plasticized with CNSL improve the cure characteristics as well as mechanical properties such as tensile strength and elongation at break of the blends. The cure time for the blends decreased with an increase in CNSL content whereas the Mooney viscosity of the blends did not change significantly. The increase in tensile strength and elongation at break and decrease in modulus with an increase in CNSL content is due to the presence of the interaction of the CNSL between the two rubber phases. For blends plasticized with paraffin oil, the tensile properties showed a small change (increase or decrease) with an increase in content of paraffin due to the lack of polarity in this oil, resulting in the absence of interaction of paraffin oil between two rubber phases, thus leading to poor mechanical properties. The addition of CNSL to blends based on EPDM and NR can improve the resistance of their blends to heat and weather. Blends plasticized with CNSL showed finer morphologies than the blends plasticized with paraffin oil. SEM on a fracture surface showed weak interaction between the rubber phases and poor compatibility with paraffin oil plasticized NR/EPDM blends. This explains why tensile strength and elongation at break showed no significant

improvement with paraffin oil plasticized NR/EPDM blends. From the overall mechanical properties, it appears that CNSL has superior plasticizing ability compared to paraffin oil. Thus, one may consider the use of CNSL as a plasticizer in NR/EPDM blends to aid in processing, reduction in cure time of the blends, improvement in tensile strength, and enhancement of resistance to heat and weather, for economic and ecological reasons.

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