

Effect of Molecular Weight and Testing Rate on Peel and Shear Strength of Epoxidized Natural Rubber (ENR 50)-Based Adhesives

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ABSTRACT: The dependence of peel strength and shear strength of epoxidized natural rubber (ENR-50)-based pressure sensitive adhesive on molecular weight and rate of testing was investigated using coumarone-indene as the tackifying resin. Toluene and polyethylene terephthalate were used as the solvent and substrate respectively, throughout the study. A SHEEN hand coater was used to coat the adhesive on the substrate at a coating thickness of 120 μm . All the adhesion properties were determined by a Llyod Adhesion Tester operating at different rates of testing. Result shows that peel strength and shear strength increases up to an optimum molecular weight of 4.2×10^4 of ENR 50. For peel strength, the observation is attributed

to the combined effects of wettability and mechanical strength of rubber at the optimum molecular weight, whereas for the shear strength, it is ascribed to the optimum cohesive and adhesive strength which enhances the shear resistance of the adhesive. Peel strength and shear strength also increases with increase in rate of testing, an observation which is associated to the viscoelastic response of the adhesive. DSC and FTIR study confirms the miscibility of tackifier and the ENR 50. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2641–2647, 2011

Key words: molecular weight; rate of testing; adhesion; epoxidized natural rubber

INTRODUCTION

Epoxidized natural rubber (ENR) is a chemically modified form of the *cis*-1,4-polyisoprene rubber, whereby some of the unsaturation is converted into epoxides groups, which are randomly distributed along the polymer chain.¹ It is known as a compatibilizer for incompatible blends and a processing aid. The incorporation of ENR-50 into the rubber blends has improved process ability, stiffness, resilience and oil resistance, reduced air permeability, good damping, and wet grip performance.² The concept of physically blending two or more existing polymers to obtain a new product has not been developed as fully as the chemical approach to blending, but the physical approach is now attracting widespread interest and is being used commercially. The main aim of blending the rubber is to improve the physical and mechanical properties as well as modify processing characteristics and reduce the cost of the final product.

The adhesion properties are characterized via measurements of two basic applicative properties: peel strength (the ability to resist removal by peeling), and shear resistance (the ability to resist flow when shear forces are applied). The adhesion properties are primarily influenced by the inherent properties of the polymer such as molecular weight. They have an influence on the polymer properties directly and as well as indirectly through their influence on the physical properties (e.g., T_g).³ FTIR study has been used to see differences in peaks with changes in molecular weight of ENR 50 and variation of coumarone-indene resin content. Our previous study focuses on the dependence of adhesion property on molecular weight at different coating thickness.^{4–7} The aim of this study is to investigate the effect of molecular weight and testing rate on adhesion property of ENR. We have also studied effects of zinc oxide,⁸ calcium carbonate,⁹ silica,¹⁰ magnesium oxide,¹¹ kaolin,¹² and sodium sulfate¹³ on the adhesion properties of ENR-based pressure-sensitive adhesives. This work is novel as no author has studied adhesion property with molecular weight and testing rate.

The end-use properties of the PSAs will depend upon balance of peel strength and shear resistance and the balance between these properties must be changed according to the specific end use of the PSA.¹⁴ Commercial use of PSAs covers abroad range of label, medical, and cosmetic products.^{15,16} Fujita

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et al.¹⁷ have investigated the effects of miscibility and viscoelasticity on shear creep resistance of natural rubber-based pressure-sensitive adhesives. Hayaishi et al.¹⁸ have investigated the relationship between the miscibility of pressure-sensitive adhesives (PSAs) acrylic copolymer/hydrogenated rosin systems and their performance. Akiyama et al.¹⁹ studied the phase behavior and pressure-sensitive adhesive properties in blends of poly(styrene-*b*-isoprene-*b*-styrene) with tackifier resin. Kajtna et al.²⁰ investigated the effect of polymer molecular weight and crosslinking reactions on the adhesion properties of microsphere water-based acrylic pressure-sensitive adhesives. Taghizadeh et al.²¹ studied the miscibility and tack of blends of poly(vinylpyrrolidone) (PVP)/acrylic pressure-sensitive adhesive (PSA). Choi et al.²² have investigated the molecular weight effects in adhesion. Blending of polymers provides an efficient way of developing new materials with tailored properties and thus has received much attention from both academia and industry.^{23–25}

EXPERIMENTAL

Materials

The rubbers were supplied by Rubber Research Institute of Malaysia. ENR-50 having 50 mol % of epoxidation was used as the elastomer for the preparation of the pressure sensitive adhesive. Coumarone-indene resin, which is freshly supplied by Mukmin Enviro Company (Malaysia), was used as the tackifier in this study. Toluene and polyethylene terephthalate (PET) film were chosen as the solvent and substrate, respectively. All the materials used in this experiment were freshly supplied commercial grades. No purification was carried out prior to use.

Preparation of adhesive

Two gram of unmasticated and masticated rubber was shredded into small pieces and dissolved in 15 mL of toluene. The rubber solution was then left overnight to ensure complete dissolution. With constant stirring, 0.2, 0.6, and 1.0 g of pulverized coumarone-indene resin that corresponded to 10, 30, and 50 parts per hundred parts (phr) respectively, of tackifying resin was slowly put into the rubber solution. The coumarone-indene resin was pounded into a fine powder to facilitate easy dissolution in the rubber solution.

Determination of molecular weight

Five rubber samples were obtained by mastication with a two-roll mill. A viscometric method was used to determine the molecular weight of each masticated sample. The intrinsic viscosity ($[\eta]$) was measured

according to the method described by Billmeyer.²⁶ The viscosity-average molecular weight (M_v) of the rubber was computed with the Mark-Houwink equation²⁷

$$[\eta] = kM_v^a \quad (1)$$

where k is 5.00×10^{-4} dL/g and a is 0.67 in toluene.

MEASUREMENT

Peel strength

For the T- and 90° peel tests, the dimensions of PET substrates (base stock and face stock) were 20 cm × 4 cm. The adhesive was coated from the end of the PET film at a coating area of 10 cm × 4 cm for various coating thickness using a SHEEN Hand Coater. The face stock was then placed on the coated PET film (base stock). The sample was then conditioned at room temperature for 24 h before testing on a Lloyd Adhesion Tester operating at different rates (cm/min). The average peeling force was determined from the three highest peaks recorded from the load-propagation graph. Peel strength is defined as the average load per width of the bond line required to separate progressively a flexible member from a rigid member or another flexible member (ASTM D 907).

Shear strength

The dimension of the PET film was 15 cm × 2.5 cm. A SHEEN Hand Coater was used to coat the adhesive from the end of the substrate with 5 cm × 2.5 cm dimension. It was then conditioned at room temperature for 24 h before testing on a Lloyd Adhesion Tester operating at different rates (cm/min). The testing distance was 5 cm which corresponded to the length of the coated area. Shear strength was expressed as the shear force per unit area of testing (N/m²).

Infrared spectroscopy (FTIR)

FTIR spectra were measured by direct transmittance by means of the KBr pellet technique using a Nicolet Impact 400 FTIR spectrometer equipped with a DTGS detector. The respective adhesive was coated on the KBr pellet, and then a spectrum was recorded. Spectra were measured at a spectral resolution of 4 cm⁻¹. Good quality FTIR spectra were obtained based on the smoothness of the baseline and resolution. Peak heights of spectra were measured using OMNIC software.

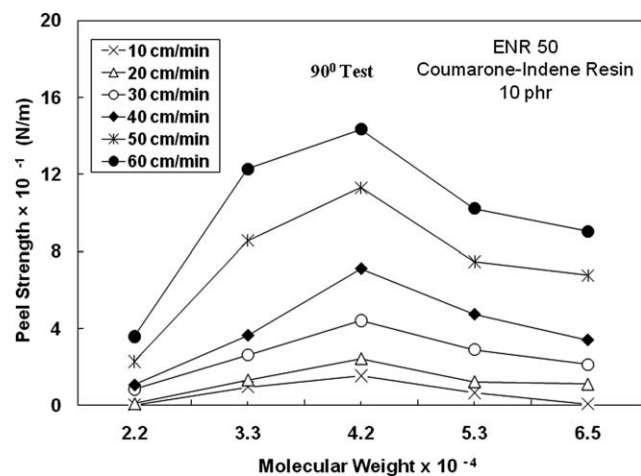


Figure 1 Variation of peel strength (90° test) with molecular weight for various testing rate for 10 phr of coumarone-indene resin at the coating thickness of 120 μm .

Differential scanning calorimetry

The differential scanning calorimetric measurements were performed with a Perkin-Elmer-Pyris DSC-6 differential scanning calorimeter supported by a Perkin-Elmer computer for data acquisition. The samples (≤ 5 mg), sealed under aluminum pans were scanned in the temperature range of -60 to 100°C . The heating rate was $10^\circ\text{C min}^{-1}$ under the nitrogen atmosphere with a flow rate of 20 mL min^{-1} .

RESULTS AND DISCUSSION

The dependence of peel and shear strength of adhesive on the molecular weight of rubber and testing rate for various coumarone-indene resin content is discussed below.

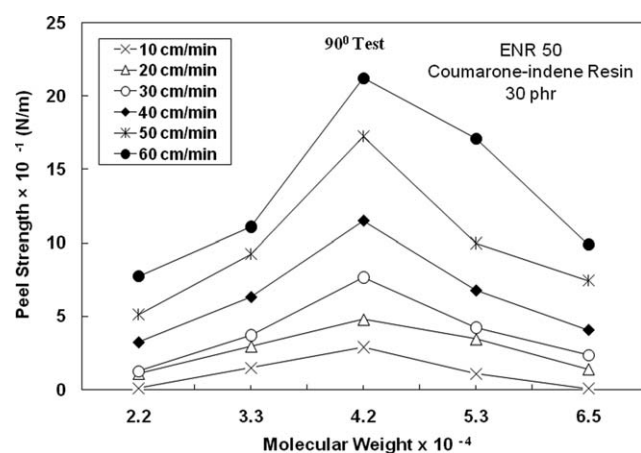


Figure 2 Variation of peel strength (90° test) with molecular weight for various testing rate for 30 phr of coumarone-indene resin at the coating thickness of 120 μm .

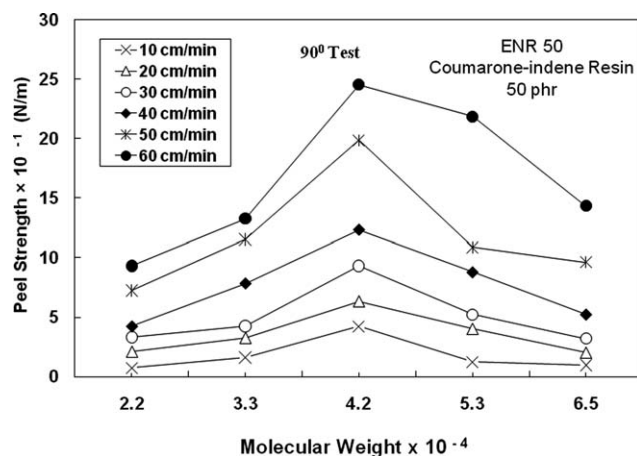


Figure 3 Variation of peel strength (90° Test) with molecular weight for various testing rate for 50 phr of coumarone-indene resin at the coating thickness of 120 μm .

Peel strength

Figures 1–6 shows the dependence of peel strength (T-test and 90°) of ENR 50 based adhesives on the molecular weight with different testing rates of 10, 20, 30, 40, 50, and 60 cm/min for various loadings of coumarone-indene resin at the coating thickness of 120 μm . From the graph, it indicates that the peel strength (T-test and 90°) increases with molecular weight of rubber up to 4.2×10^4 for ENR 50, and drops with further increase in molecular weight of rubber for all testing rate. This observation is attributed to the increasing wettability of adhesive up to a maximum value 4.2×10^4 for ENR 50, where maximum wettability is observed. At this adhesive formulation, mechanical interlocking and anchorage of the adhesive in pores and irregularities in the adherent are formed.^{15,28} The separation front is blunted, the stresses are minimized and separation is

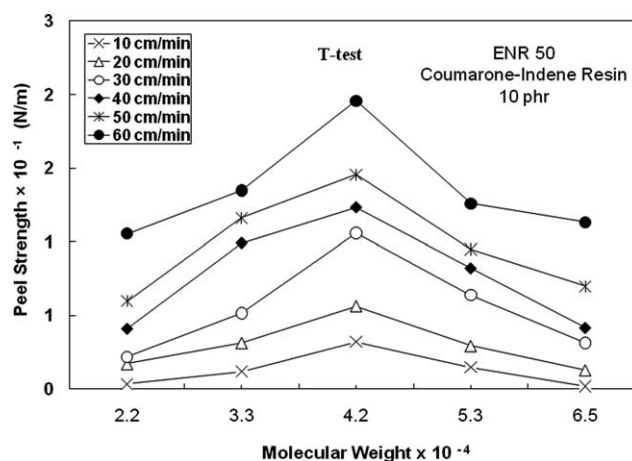


Figure 4 Variation of peel strength (T-test) with molecular weight for various testing rate for 10 phr of coumarone-indene resin at the coating thickness of 120 μm .

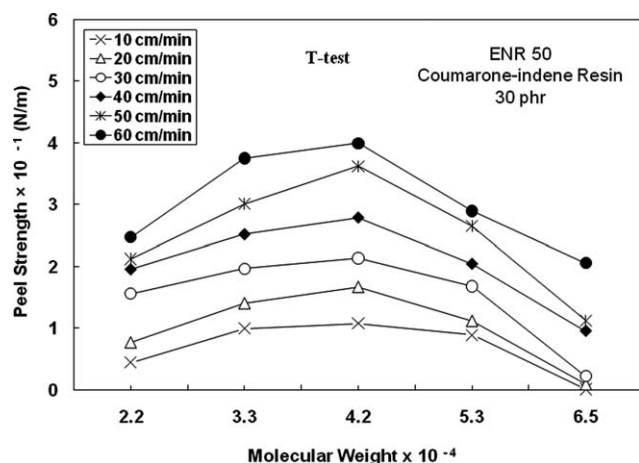


Figure 5 Variation of peel strength (T-test) with molecular weight for various testing rate for 30 phr of coumarone-indene resin at the coating thickness of 120 μm .

prevented,¹⁶ when the adhesive is able to flow like a yielding solid. At the optimum molecular weight the adhesive most probably hardens at high strain levels to become a tough solid; the adhesive layer itself cannot easily be ruptured and hence showing maximum peel strength. Higher molecular weight sample lowers the wettability of adhesive, probably due to the effect of entanglement as the entangled rubber chain does not flow effectively to produce good wettability on the substrate.

Figures 1–6 also show the effect of testing rate on the peel strength (T-test and 90°) of adhesives at 120 μm coating thickness. The plot indicates that peel strength increases with increase in the peeling rate. This observation is attributed to cohesive failure at the low peeling due to the predominantly viscous response. Cohesive failure is defined as the inability of an adhesive to resist internal separation. During

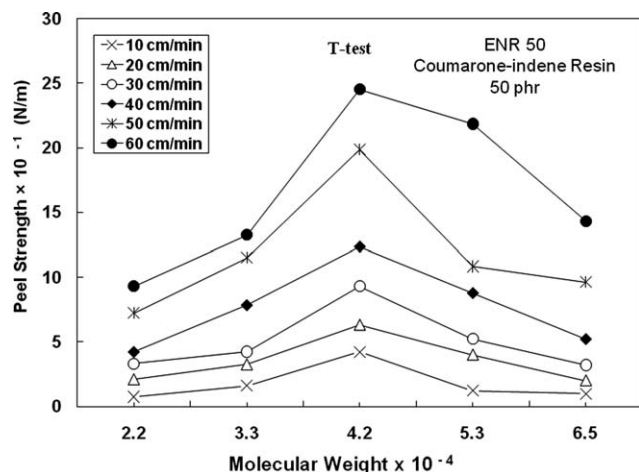


Figure 6 Variation of peel strength (T-test) with molecular weight for various testing rate for 50 phr of coumarone-indene resin at the coating thickness of 120 μm .

cohesive failure, the adhesive sticks to both surfaces, but cannot hold them together. However, as the peeling rate is increased, the predominantly elastic response results in adhesive failure which is reflected by the higher peel strength. Adhesive failure occurs at the interface between the adhesive and the substrate. The transition from cohesive to adhesive failure in a peel test is observed in the region of maximum peel force versus molecular weight.³

Shear strength

The dependence of shear strength of ENR 50-based adhesives on molecular weight at 120 μm coating thickness is shown in Figure 7–9. From the figure, it is seen that shear strength increases with molecular weight up to 4.2×10^4 and drops with higher molecular weight of rubber for coating thicknesses of 120 μm . This observation is attributed to the optimum molecular weight that is necessary to provide for the maximum cohesive and adhesive strength during the shearing action. For lower molecular weight, cohesive failure is observed²⁸ due to shorter chain length of the rubber molecules. On the contrary, for high molecular weight, poor adhesive strength is observed as a result of poor wettability. Thus, at the optimum molecular weight of 4.2×10^4 , the optimum combination of cohesive and adhesive strength is achieved which contributes to the highest shear strength in the study. From the results, it is obvious that shear strength of adhesive increases with coating thickness. This observation is attributed to increasing amount of rubber component present in the coating layer which enhances the shear resistance of the adhesive.

As in the case of peel strength, shear strength also increases with increase in the rate of testing. This observation is attributed to the increasing effect of elastic component of the adhesive as the rate of testing

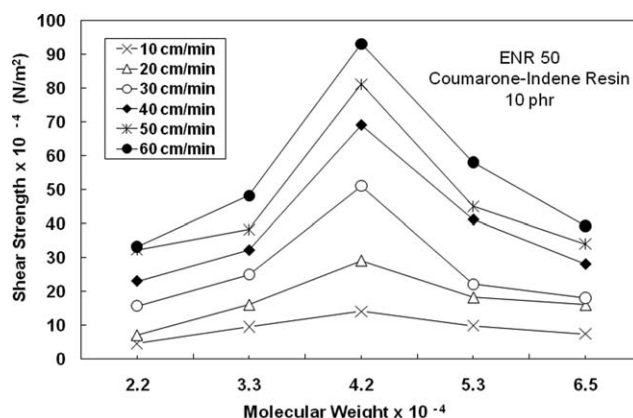


Figure 7 Variation of shear strength with molecular weight for various testing rate for 10 phr of coumarone-indene resin at the coating thickness of 120 μm .

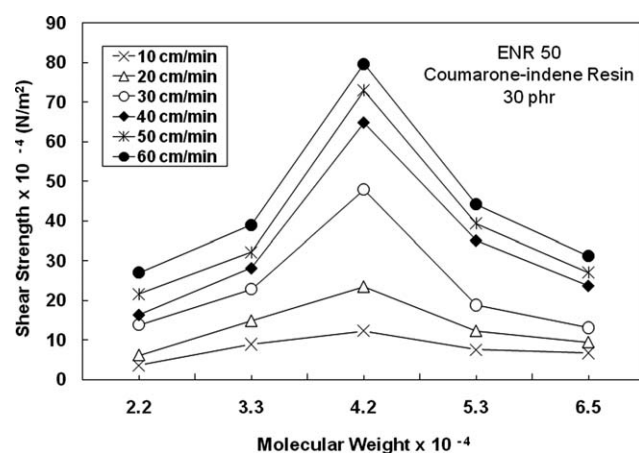


Figure 8 Variation of shear strength with molecular weight for various testing rate for 30 phr of coumarone-indene resin at the coating thickness of 120 μm .

is increased. The response of pressure-sensitive adhesive to the shear stress is of a viscoelastic nature. Adhesive hardens at high strain levels to become a tough solid; the adhesive layer itself cannot easily be ruptured.¹⁶

Thermal analysis

The properties of the PSAs are known to be strongly dependent on the glass transition temperature of the adhesive. Figure 10 represent the DSC thermograms at the optimum molecular weight of the ENR 50. The peak around -40°C corresponds to desorption of any moisture present within the sample as shown in Figure 10. It was reported earlier²⁹ that the glass transition temperature T_g , which marks the characteristic transition of the amorphous region of the blend from glassy state to a rubbery state, is the most convenient and popular way of investigating

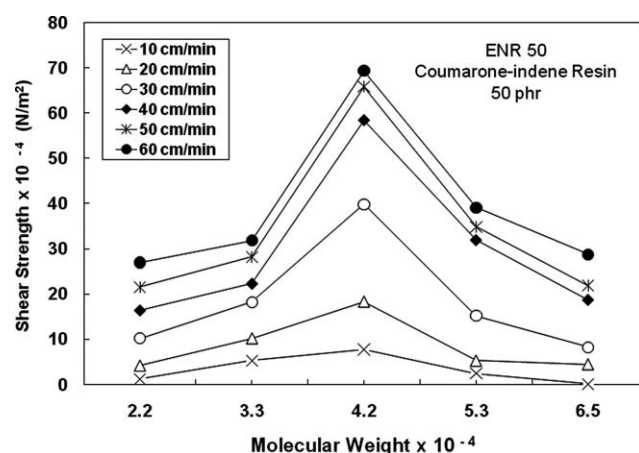


Figure 9 Variation of shear strength with molecular weight for various testing rate for 50 phr of coumarone-indene resin at the coating thickness of 120 μm .

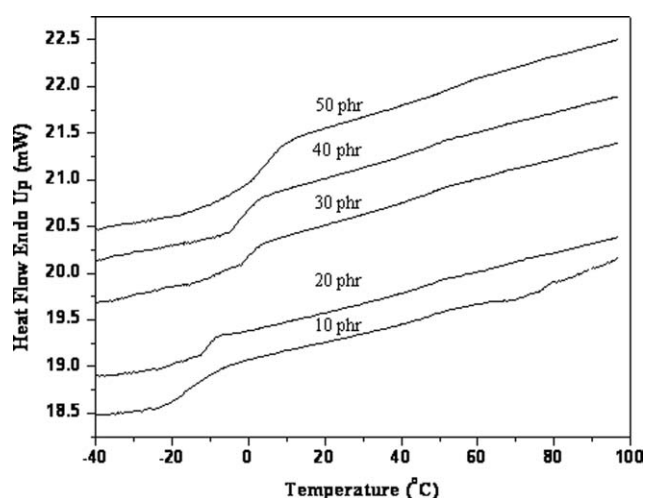


Figure 10 DSC scan of ENR 50/coumarone-indene resin blends at the optimum molecular weight for various resin concentration (phr).

the miscibility or immiscibility of the of polymers and tackifier. The presence of one single glass transition temperature in Figure 10 indicates the miscibility of polymer and tackifier hence the good compatibility of the blend.^{30,31} The presence of only one single peak indicates very clearly that this blend system is a compatible blend. For binary miscible systems, the dependence of T_g on composition can be presented by well known Fox equation.³² The thermal study of pure ENR-50 has been previously reported³³ and is in close agreement with our results. The T_g of ENR 50 is found to be -20°C and taking softening point of coumarone-indene (100°C) as glass transition temperature we have calculated the T_g values from Fox equation. The T_g has been reported in our previous study¹⁰ also. The softening point of coumarone-indene resin has been previously reported³⁴ as 100°C which is agreement with our result. The Fox equation is quite applicable for predicting the T_g of a miscible blend with certain T_g and weight fractions of component polymers.

Fox equation

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (2)$$

where T_{g1} , T_{g2} , and T_g is the glass transition of the rubber, tackifier, and mixture, and w_1 and w_2 is the weight fraction of rubber and tackifier, respectively. The transition temperatures determined by DSC measurements and theoretical calculated values according to Fox equation is shown in Table I. The experimental values and theoretical values by Fox equation are in close agreement for 10, 20, 30, 40, and 50 phr tackifier. This agreement, in turn, proves the validity of the Fox equation for these blends and

TABLE I
Composition of Rubber-Resin, Values of Glass Transition Temperatures of Blend, Measured Experimentally, and Calculated Theoretically

Rubber-resin ratio (phr)	Glass transition temperature ($^{\circ}\text{C}$)	
	Experimental	Calculated according to Fox equation
90 : 10	-15.06	-12.38
80 : 20	-8.60	-5.67
70 : 30	-0.55	0.29
60 : 40	2.48	5.61
50 : 50	7.50	10.39

the fact of complete miscibility in the ENR 50 and coumarone-indene systems.

FTIR analysis

Infrared spectroscopy has been proven to be a powerful tool for investigating specific interactions between polymers. There are two types of hydrogen

bonding that exist in this polymeric system, intermolecular and intramolecular hydrogen bonding among polymers and the tackifier. The FTIR study of pure ENR 50 has previously reported by one of the authors³⁵ where the peaks are in quite agreement with our results. Figure 11 shows the FTIR spectra of ENR 50/coumarone-indene resin blend at optimum molecular weight. Broad peak in the region $3400\text{--}3200\text{ cm}^{-1}$ is associated with the presence of hydroxyl groups. The incorporation of coumarone-indene resin in ENR 50 gradually decrease intermolecular hydrogen bonding as indicated by increase in the hydroxyl stretching frequency from 3444.63 to 3474.38 cm^{-1} . Peak around $3018.18\text{--}3026.69\text{ cm}^{-1}$ clearly indicates the presence of aromatic ring in the polymer blend. Peak at $2912.40\text{--}2902.48\text{ cm}^{-1}$ and $2895.87\text{--}2857.93\text{ cm}^{-1}$ are due to asymmetric and symmetric stretching vibration of methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2$) group, respectively. Aromatic combination band appeared between 1660 and 2200 cm^{-1} . Absorption bands at $1450.58\text{--}1455.98\text{ cm}^{-1}$ and around 1370.21 cm^{-1} are characteristic peaks of $-\text{C}-\text{H}$ bending vibrations of methylene ($-\text{CH}_2$) group. The $\text{C}-\text{O}-\text{C}$ asymmetric stretching

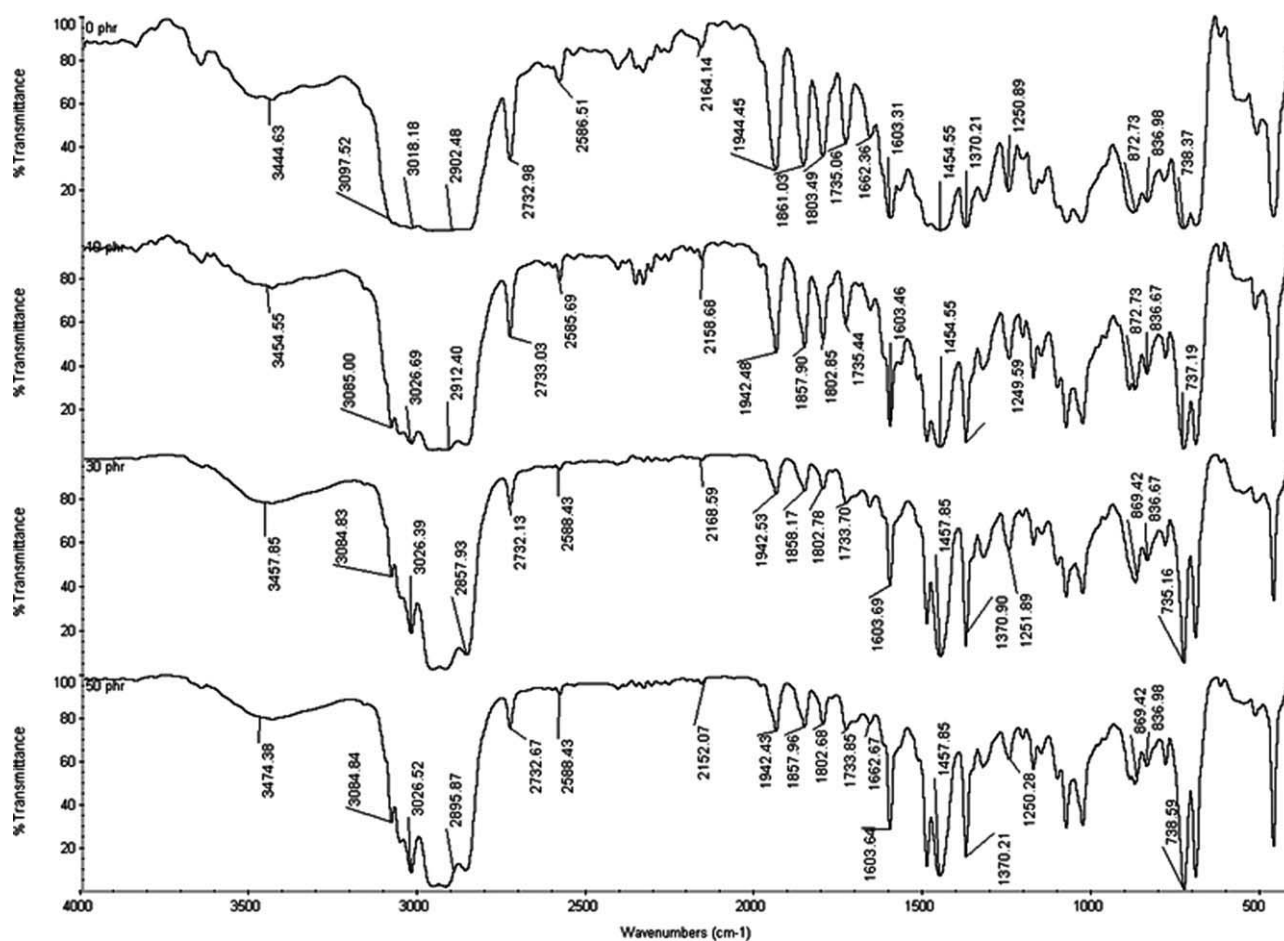


Figure 11 FTIR spectra of ENR 50/coumarone-indene resin blend at optimum molecular weight.

of epoxides showed strong absorption cross section in the region of 836.98 cm^{-1} . Peaks at $1600\text{--}1615\text{ cm}^{-1}$ clearly indicates aromatic ring pattern which gradually get intensify on increasing concentration of tackifier. Absorption peak at $869.42\text{--}870.73\text{ cm}^{-1}$ and at $737.19\text{--}738.59\text{ cm}^{-1}$ clearly showed meta-substituted benzene and ortho-substituted benzene, respectively. Peaks at $\sim 1250\text{ cm}^{-1}$ again confirm the presence of epoxy moiety.

CONCLUSIONS

From this study, the following conclusions can be drawn.

1. Peel strength and shear strength increases with molecular weight of rubber up to an optimum molecular weight of 4.2×10^4 of ENR 50. For peel strength, this observation is attributed to the combined effects of wettability and mechanical strength of rubber at the optimum molecular weight. However, in the case of shear strength, it is ascribed to the optimum cohesive and adhesive strength during the shearing action.
2. Peel strength of ENR 50-based adhesives increases with increasing rate of testing, an observation which is attributed to the viscoelastic response of the adhesive. At low rates of testing, the response is predominantly viscous and cohesive failure occurs whereas at higher rates of testing, the response becomes predominantly elastic which results in adhesive failure. Shear strength of the rubber-based adhesive also increases with increasing rate of testing which is attributed to the increasing effect of elastic component of the adhesive as the rate of testing is increased.
3. The DSC and FTIR study confirms the miscibility of tackifier and ENR 50 in the adhesive system.

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