Effect of Molecular Weight of Epoxidized-Natural Rubber on Viscosity and Tack of Pressure-Sensitive Adhesives

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ABSTRACT: The effect of molecular weight of rubber on viscosity and loop tack of rubber-adhesives were studied using two grades of epoxidized-natural rubber, i.e., ENR 25 and ENR 50. Coumarone–indene resin, gum rosin, and petro resin were used as tackifiers. Toluene was used as the solvent throughout the experiment. The adhesive was coated on polyethylene terephthalate (PET) substrate using a SHEEN hand coater. Viscosity was determined by a HAAKE Rotary Viscometer, whereas loop tack was measured by a Llyod Adhesion Tester operating at 10 cm/min. Results show that viscosity increases gradually upto a critical molecular weight of 6.8×10^4 and 3.9×10^4 for ENR 25 and ENR 50, respectively, before a rapid increase in viscosity is observed. Loop tack indicates maximum value at the respective critical molecular weights for the three tackifiers investigated suggesting the culmination of wettability. For both rubbers, loop tack increases with coating thickness due to the concentration effect of adhesive. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1120–1124, 2010

Key words: viscosity; tack; rubber; molecular weight

INTRODUCTION

Recently, we have reported the effect of molecular weight of rubber on the viscosity and shear strength of SMR L-based adhesives in the presence of gum-rosin and petro-resin tackifiers.[1] For both tackifying resins, viscosity increases gradually with molecular weight upto 9.7×10^4 after which it increases rapidly with further increase in molecular weight of rubber due to the effect of entanglement of rubber chains. On the other hand, shear strength of the SMR L-based adhesive increases with molecular weight upto 8.5×10^4, after which it drops with further increase in molecular weight of rubber for the two coating thickness investigated.

The effect of molecular weight of rubber on tack and peel strength of SMR L-based pressure-sensitive adhesives using gum rosin and petro resin as tackifiers were also investigated.[2] Maximum loop tack and peel strength were observed at a molecular weight of 8.5×10^4 of SMR L. Several studies on the adhesion properties of epoxidized-natural rubber (ENR) were studied, including the effect of coumarone–indene resin, zinc oxide, and calcium carbonate on adhesion property of ENR-based pressure-sensitive adhesives.[3–5] However, the effect of molecular weight of ENR on the adhesion behavior of ENR-based adhesives is unknown. In view of the absence of research in this field of interest, we have carried out a systematic study on the dependence of viscosity and loop tack of adhesives on molecular weight of epoxidized-natural rubber using two grades of ENR, i.e., ENR 25 and ENR 50.

EXPERIMENTAL

Materials

Two grades of epoxidized-natural rubber, i.e., ENR 25 and ENR 50 having 25 mol % and 50 mol % of epoxidation, respectively, were used as the elastomers. The technical specifications of ENR[6] are shown in Table I. The rubbers were supplied by Rubber Research Institute of Malaysia (RRIM). Coumarone–indene resin, gum rosin, and petro resin were freshly supplied by EuroChemo-Pharma Company (Malaysia). Commercial grade toluene was used as the solvent throughout the experiment.

Molecular weight determination

ENR 25 and ENR 50 were masticated on a two-roll mill for 5, 10, 15, and 20 min to obtain different molecular weights of rubber. Viscometric method was adopted to determine the molecular weights of masticated- and unmasticated-rubber. For each rubber sample, five different concentrations (C) of dilute rubber solutions were prepared in toluene and the respective flow times (t) were determined using an

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TABLE I
Technical Specification of ENR

	ENR 25	ENR 50
Glass transition temperature (°C)	−45	−20
Specific gravity	0.97	1.03
Mooney viscosity, $M_{L,\ 1+4}$ (100°C)	110	140

Ubbelohde viscometer. The flow time of toluene (t_o) was also measured. Since the densities of solvent and dilute rubber solution are approximately the same, the specific viscosity of the rubber solution (η_{sp}) is given in eq. (1).

$$\eta_{sp} \simeq (t - t_o)/t_o \tag{1}$$

A plot of reduced-viscosity (η_{sp}/C) versus C was carried out. The intrinsic viscosity $[\eta]$ was determined from the intercept at $C = 0$ by extrapolation. The viscosity-average molecular weight (M_v) of the rubber sample was then calculated using the Mark-Houwink equation as shown by eq. (2) below.[7,8]

$$[\eta] = k\, M_v^a \tag{2}$$

where $k = 5.00 \times 10^{-4}$ dL/g and $a = 0.67$ in toluene.

Adhesive preparation

Toluene (30 mL) was used to dissolve 5 g rubber sample and the rubber solution was tightly closed in a conditioned room for 24 h. Tackifier (2 g) corresponding to 40 parts per hundred parts of rubber (phr) was slowly added to the solution with constant stirring. It was then left for at least 2 h before testing.

Viscosity measurement

Viscosity of adhesive was determined using a HAAKE Rotary Viscometer (Model PK 100) operating at room temperature which was maintained at 30 ± 1°C. The spindle head (PK1;1°) and the platform were cleaned with acetone to prevent contamination of the adhesive. The gap between spindle head and platform was adjusted to zero. A few drops of adhesive were placed at the middle of platform which was then raised upto squeeze the adhesive. Any excess adhesive around the spindle head was wiped off with a clean tissue containing acetone. Testing was carried out for 1 min or 10 rounds of spinning. At least five readings were noted and the average viscosity was calculated. The error involved in the measurement of viscosity was estimated to be 5%.

Loop tack determination

Loop tack test is the peel test involving low-contact pressure and short application time.[9] A polyethylene terephthalate (PET) substrate with dimension of 25 cm × 4 cm was coated at the center (4 cm × 4 cm) with the adhesive using a stainless steel SHEEN Hand Coater (Model 1107 Four Sided Applicator). The coating thickness was monitored by a micrometer. Four coating thickness, i.e., 30, 60, 90, and 120 μm were used in this study. It was then conditioned at 30 ± 1°C for 24 h. A loop was formed and the coated-adhesive area was carefully brought into contact with a glass plate. The debonding force of adhesive from the glass plate was measured by a Lloyd Adhesion Tester (Model LRXPlus with NEXYGEN software) operating at 10 cm/min. The average debonding force was calculated from the three highest peaks recorded. Loop tack of the adhesive was expressed as the average debonding force per unit area of contact (N/m^2).

RESULTS AND DISCUSSION

The effect of molecular weight of ENR on viscosity and loop tack of the adhesive is discussed as below.

Viscosity

The dependence of viscosity of adhesive on molecular weight of ENR 25 is shown in Figure 1 for various types of tackifiers. The viscosity increases gradually with molecular weight upto 6.8×10^4 before a rapid increase in viscosity is observed. The molecular weight of 6.8×10^4 can be regarded as the critical molecular weight for the onset of polymer chain entanglement where its effect on viscosity becomes significant. At lower molecular weight, the rubber chains flow freely under shear stress, thus lower viscosity is observed. However, as the molecular chain reaches a certain chain length, i.e., the critical molecular weight, physical entanglement between rubber

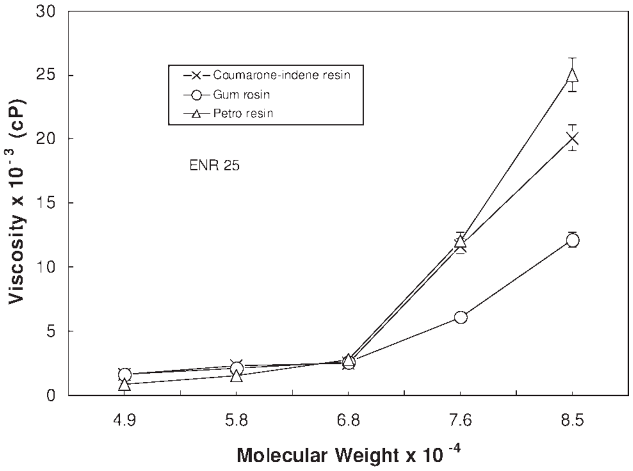

Figure 1 Variation of viscosity of adhesive with molecular weight of ENR 25 for various types of tackifiers.

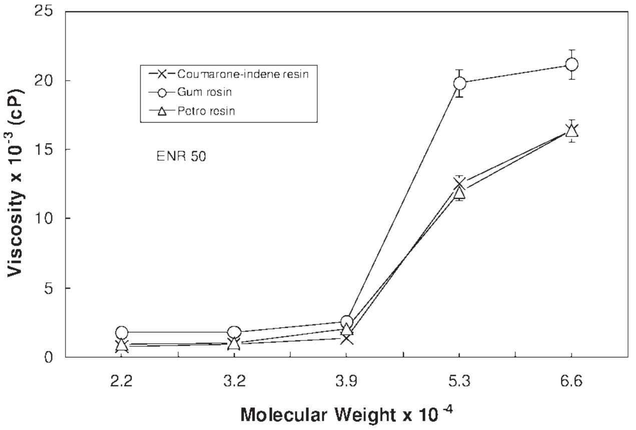

Figure 2 Variation of viscosity of adhesive with molecular weight of ENR 50 for various types of tackifiers.

chains occurs as indicated by the rapid increase in the viscosity. Petro resin comprises of polymerized C5 or C9 or polycyclic streams derived from the naphtha-cracking process.[10] The polymeric petro resin entangles with ENR 25 matrix to increase the viscosity of the adhesive. Gum rosin is obtained as oleoresin from the living trees. The gum rosin mildly entangles with ENR 25 matrix as indicated by the lowest viscosity as shown in Figure 1. Coumarone–indene resin, on the other hand, shows intermediate degree of entanglement with ENR 25 where the viscosity is between petro-resin and gum-rosin adhesive system.

Figure 2 shows the effect of molecular weight of ENR 50 on the viscosity of adhesive for various tackifier systems. The viscosity also increases gradually with molecular weight of rubber upto 3.9 × 10^4 after which a rapid increase in viscosity with molecular weight of rubber is observed. The rapid increase in viscosity in ENR 50 after the critical molecular weight of 3.9 × 10^4 is attributed to both chain entanglement and hydrogen bonding between ENR 50 and tackifiers. Since gum rosin is a natural occurring tackifying resin and more polar in nature than the other two synthetic tackifiers, stronger interaction between ENR 50 and gum rosin accounts for the highest viscosity. The critical molecular weight for the onset of entanglement is lower in the case of ENR 50, i.e., 3.9 × 10^4 compared with 6.8 × 10^4 of ENR 25, an observation which is ascribed to the chemical structure of ENR 50.

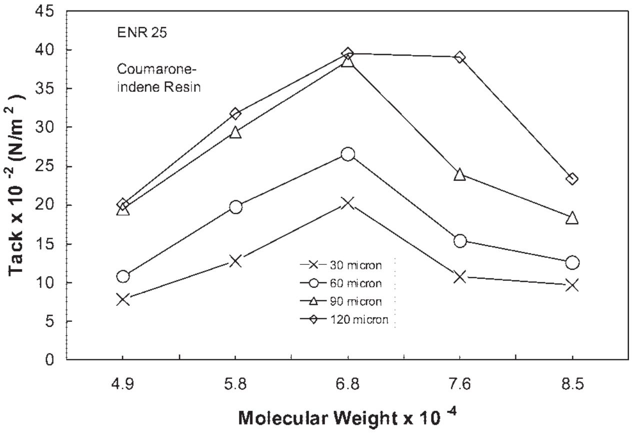

Figure 3 Variation of loop tack of adhesive with molecular weight of ENR 25 using coumarone-indene resin as tackifier for various coating thickness.

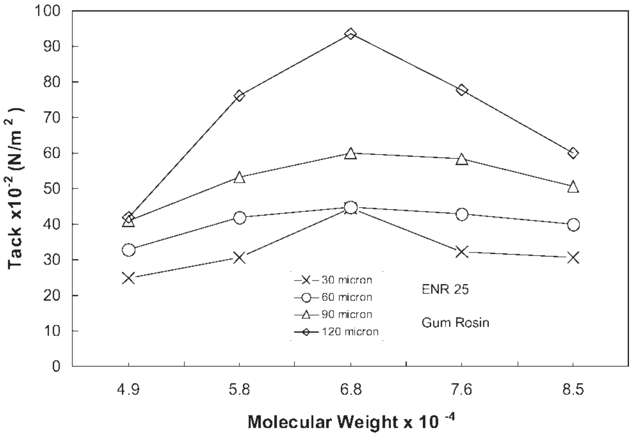

Figure 4 Variation of loop tack of adhesive with molecular weight of ENR 25 using gum rosin as tackifier for various coating thickness.

Loop tack

Figures 3, 4, and 5 show the effect of molecular weight of ENR 25 on the loop tack of adhesives containing coumarone–indene resin, gum rosin and petro resin, respectively, for various coating thickness. The graphs indicate that loop tack increases with increasing molecular weight of ENR 25 upto 6.8 × 10^4 and drops with further increase in molecular weight of rubber for all coating thickness. This observation is attributed to the increasing wettability

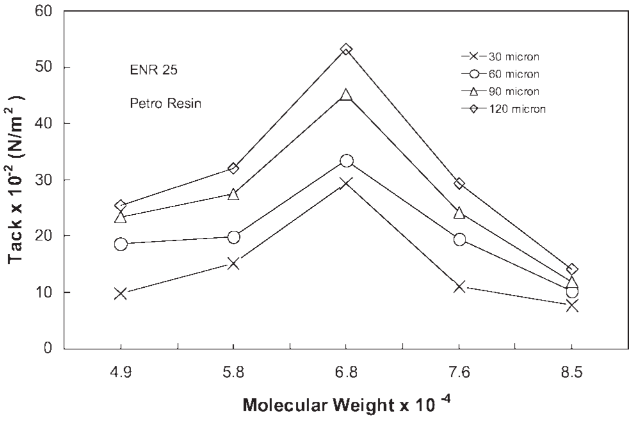

Figure 5 Variation of loop tack of adhesive with molecular weight of ENR 25 using petro resin as tackifier for various coating thickness.

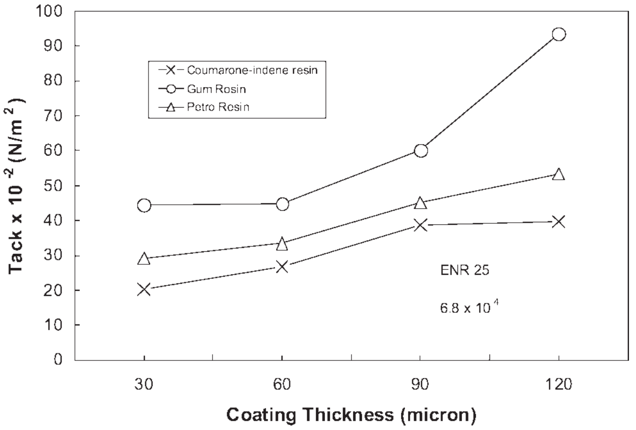

Figure 6 Variation of loop tack of ENR 25-based adhesive with coating thickness for various tackifiers.

of adhesive upto a maximum value at 6.8 × 10^4 where maximum wettability is observed. The response of the pressure-sensitive adhesive to the stress is of a viscoelastic nature.[10,11] The viscous component enhances wettability, i.e., the adhesive is able to conform to the irregularities of the adherend to give higher tack value. However, wettability decreases after the optimum molecular weight of 6.8 × 10^4 as reflected by the decline in tack values for all the coatings studied.

One interesting observation is that for the three types of tackifiers investigated, the optimum molecular weight to achieve maximum tack occurs at the same molecular weight, i.e., 6.8 × 10^4. This suggests that molecular weight of ENR 25 exhibits the same effect on the tack property of the adhesive irrespective of the type of tackifier used though the absolute tack value varies with the tackifier system. Figure 6 shows the dependence of tack on the coating thickness at the optimum molecular weight of ENR 25.

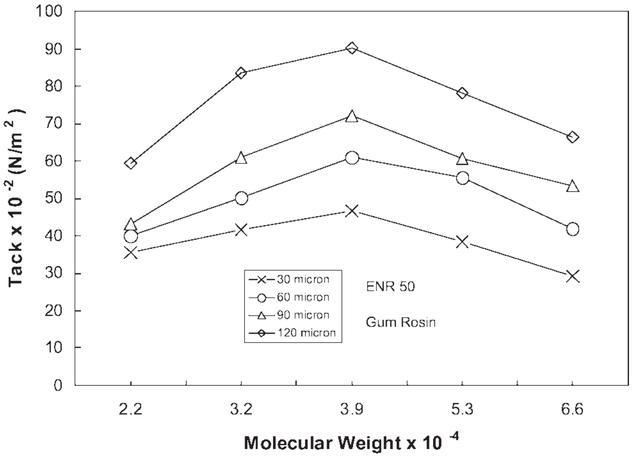

Figure 8 Variation of loop tack of adhesive with molecular weight of ENR 50 using gum rosin as tackifier for various coating thickness.

Results indicate that tack increases with coating thickness for all the three tackifiers studied, an observation which is associated with the increasing amount of rubber component present in the coating layer.

The effect of molecular weight of ENR 50 on the tack property of adhesive is shown in Figures 7, 8, and 9 for coumarone–indene resin, gum rosin, and petro resin, respectively. The peak tack value occurs at a lower molecular weight in ENR 50, i.e., 3.9 × 10^4 compared with 6.8 × 10^4 of ENR 25. The lower optimum molecular weight of ENR 50 is attributed to the higher degree of epoxidation in ENR 50 which means that the more polar ENR 50 achieves maximum wettability at shorter molecular chain length than the less polar ENR 25. Figure 10 shows the effect of coating thickness on the tack behavior for the three tackifiers at the optimum molecular weight of ENR 50, i.e., 3.9 × 10^4. Tack value increases

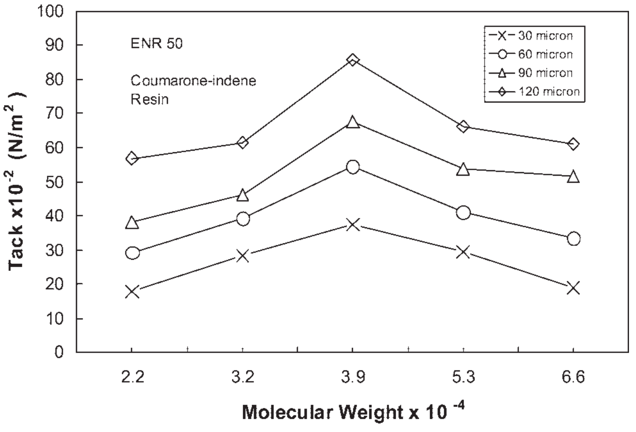

Figure 7 Variation of loop tack of adhesive with molecular weight of ENR 50 using coumarone-indene resin as tackifier for various coating thickness.

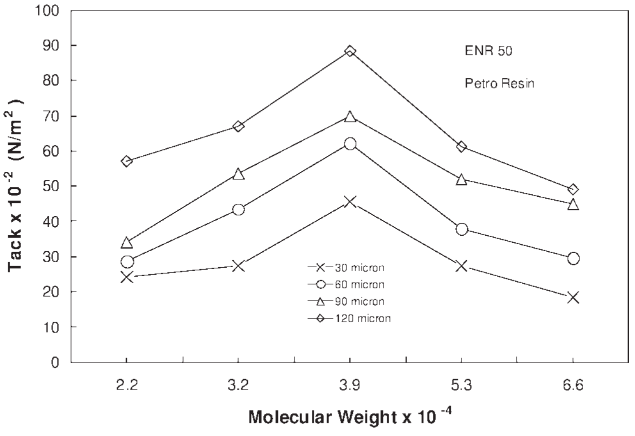

Figure 9 Variation of loop tack of adhesive with molecular weight of ENR 50 using petro resin as tackifier for various coating thickness.

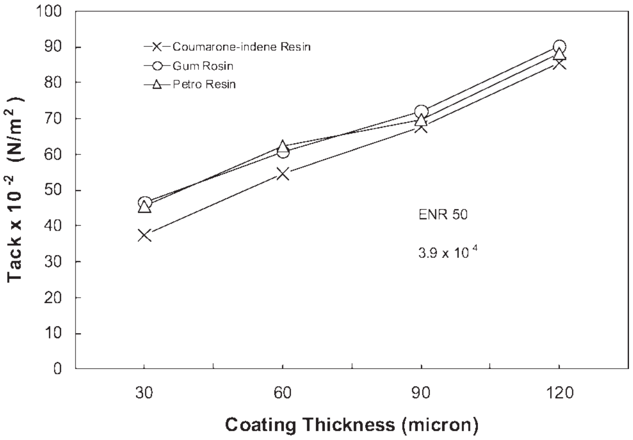

Figure 10 Variation of loop tack of ENR 50-based adhesive with coating thickness for various tackifiers.

gradually with increasing coating thickness due to the larger amount of rubber present which provides the viscoelastic behavior that is necessary for good tack. As in the case of ENR 25, gum rosin-based adhesive still indicates the highest tack value followed by petro resin and coumarone–indene resin system for all the coating thickness. The natural occurring gum rosin is more compatible with ENR 50 than the other two synthetic resins.

Table II summarized the viscosity and tack between ENR 25 and ENR 50 at the critical molecular weight of rubber.

TABLE II
Comparison of Viscosity and Tack Between ENR 25 and ENR 50 at the Critical Molecular Weight of Rubber

Tackifier	ENR 25	ENR 50
Viscosity × 10^{-3} (cP)		
Coumarone–indene resin	2.51	1.36
Gum rosin	2.61	2.61
Petro resin	2.77	2.04

Tackifier	Coating Thickness (μm)	ENR 25	ENR 50
Tack × 10^{-2} (N/m^2)			
Coumarone–indene resin	30	20.25	37.30
	60	26.63	54.53
	90	38.69	67.61
	120	39.62	85.67
Gum rosin	30	44.43	46.61
	60	44.86	60.82
	90	59.98	72.12
	120	93.54	90.24
Petro resin	30	29.25	45.64
	60	33.39	62.25
	90	45.28	69.72
	120	53.18	88.28

CONCLUSIONS

From this study, the following conclusions can be drawn.

1. Viscosity of ENR-based adhesive increases gradually upto a critical molecular weight of 6.8×10^4 and 3.9×10^4 for ENR 25 and ENR 50, respectively, after which it increases rapidly due to entanglement effect of rubber chain molecules. Differences in viscosity between the three tackifier systems investigated are associated to the varying degree of molecular interaction between the ENR and the tackifiers. ENR 50 which has a higher degree of epoxidation than ENR 25 exhibits a stronger interaction with tackifiers. Consequently, a lower critical molecular weight for the onset of entanglement is observed in ENR 50-based adhesive.
2. Loop tack increases with increasing molecular weight of ENR upto an optimum molecular weight of 6.8×10^4 and 3.9×10^4 for ENR 25 and ENR 50, respectively, after which it drops with further increase in molecular weight of ENR. This observation is attributed to the varying degree of wettability which culminates at the optimum molecular weights. For a fixed molecular weight of ENR, loop tack increases with coating thickness for all the three tackifiers studied, an observation which is ascribed by the increasing amount of rubber component which provides the viscoelastic response that is necessary for good tack. For both ENR 25 and ENR 50, gum rosin-based adhesive consistently shows the highest tack followed by petro resin and coumarone–indene resin systems.

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