Effect of Molecular Weight of Epoxidized Natural Rubber on Shear Strength of Adhesives

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ABSTRACT: The dependence of shear strength of epoxidized natural rubber (ENR)-based adhesives on molecular weight of the rubber is studied using coumarone–indene resin, gum rosin, and petro resin as tackifiers. The adhesive was coated on polyethylene terephthalate (PET) film substrate using a SHEEN hand coater at various coating thickness. The shear strength of adhesives was determined by a Texture Analyzer. Results show a maximum at 6.63 $\times 10^4$ and 4.14 $\times 10^4$ for ENR 25 and ENR 50, respectively, after which the shear strength decreases with further increases in molecular weight for all the coating thickness. This observation is attributed to varying degree of cohesiveness which culminates at the respective optimum molecular weight of ENR. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3976–3979, 2009

Key words: shear strength; molecular weight; adhesive; ENR

INTRODUCTION

In formulating a rubber-based pressure-sensitive adhesive, an elastomer provides the elastic component, whereas a low-molecular-weight tackifying resin imparts the viscous component. Scientific research on rubber-based adhesives—particularly natural rubber—seems scarce. Kraus et al.[1,2] have studied the adhesive behavior of the styrene-diene-based pressure-sensitive adhesives. Leong et al.[3] have investigated the viscoelastic properties of natural rubber pressure-sensitive adhesive using acrylic resin as a tackifier. It was discovered that for a good pressure-sensitive adhesive, the ratio of storage modulus at high frequencies to low frequencies should be high. Fujita et al.,[4] on the other hand, reported the effects of miscibility and viscoelasticity on shear creep resistance of natural-rubber-based pressure-sensitive adhesives. They found that holding time of miscible pressure-sensitive adhesive systems tended to decrease as the tackifier content is increased, whereas the holding time of an immiscible adhesive system varies with the tackifier used. However, with respect to epoxidized natural rubber (ENR)-based pressure-sensitive adhesive, very few research works has been published. Thongnuanchan et al.[5] have carried out a study on epoxidized natural rubber-bonded para rubber wood particleboard. The adhesion of the epoxidized natural rubber adhesive with parawood sawdust was observed to improve by reducing the molecular weight of epoxidized natural rubber molecules. It was suggested that lower molecular weight exhibited greater ability to wet or cover the wood particle surfaces. Recently, we have carried out several studies on the adhesion behavior of ENR-based pressure-sensitive adhesives. These include the effect of zinc oxide, calcium carbonate, and rubber blends on the viscosity, tack, and peel strength of ENR-based pressure-sensitive adhesives.[6–8] We have also investigated the shear property of ENR-based adhesives.[9] It is found that shear strength decreases with increasing coumarone–indene resin for all the coating thickness studied. The rate of decrease is greatest for the thicker coating sample. ENR 25 shows higher shear strength than ENR 50 due to the greater flexibility and compatibility with resin in the former system. The previous study was carried out using unmasticated ENR. No investigation was reported so far on the dependence of shear strength on the molecular weight of ENR. In view of the lack of scientific research in this field of interest, we have carried out a systematic research on the effect of molecular weight of ENR on the shear strength of the adhesive in the presence of various tackifiying resins.

EXPERIMENT

Materials

ENR 25 and ENR 50 having 25 mol % and 50 mol % of epoxidation, respectively, were used as the elastomers, which were supplied by Rubber Research Institute of Malaysia (RRIM). The gel content of ENR is estimated to be less than 5%. Coumarone–indene

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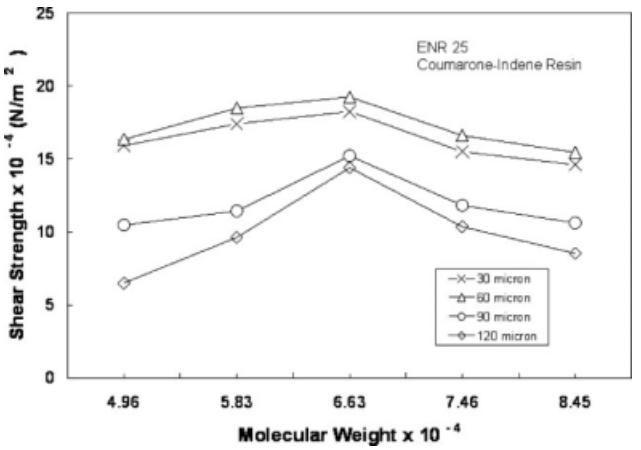

Figure 1 Variation of shear strength with molecular weight of ENR 25 containing coumarone–indene resin.

resin, gum rosin, and petro resin were obtained from EuroChemo-Pharma Company (Malaysia). Laboratory grade toluene was used as the solvent throughout the experiment.

Molecular weight determination

Viscometric method was used to determine the molecular weights of ENR before and after masticating the rubbers on a two-roll mill for 5, 10, 15, and 20 min. The shearing action during mastication will break down the entangled rubber molecules, hence reduces the molecular weight of ENR. Molecular weight decreases with increase in mastication time. Five different concentrations (C) of dilute rubber solutions were prepared in toluene for each rubber sample. An Ubbelohde viscometer was used to determine the flow time of each rubber solution (t) and toluene (t_o). 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).

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

The reduced viscosity (η_{sp}/C) was plotted against C and the intrinsic viscosity [η] was determined from the intercept at $C = 0$ by extrapolation. The viscosity-average molecular weight (M_v) of the various rubber samples was obtained from the intrinsic viscosity [η] using the Mark-Houwink eq. (2) as shown below.[10,11]

$$[\eta] = kM_v^a \quad (2)$$

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

Adhesive preparation

The adhesive was prepared by dissolving 5 g of rubber sample in 30 mL of toluene. The rubber solution formed was kept in a conditioned room for 24 h. A 2 g of tackifier—corresponding to 40 parts per hundred parts of rubber (phr)—was then added slowly to the rubber solution with constant stirring to ensure complete dissolution. The adhesive obtained was subsequently left for at least 2 h before testing.

Shear test

Polyethylene terephthalate (PET) film was used as the substrate. The dimension of the test sample was 25 mm × 150 mm. Adhesive coating was carried at the center of the substrate with 25 mm × 50 mm dimension using a SHEEN Hand Coater to give coating thickness at 30, 60, 90, and 120 μm. The coated sample was then conditioned at room temperature at 30°C and relative humidity of 60% for 24 h before testing. A TA-HDi Texture Analyzer (Model-Stable Micro System) was used to determine the shear strength of the coated sample. The testing speed was set at 1 mm/s up to 50 s, and the testing distance was 50 mm corresponding to the length of coated area. Shear strength was expressed as the force per unit area of testing.

RESULTS AND DISCUSSION

The effect of molecular weight of rubber and coating thickness on shear strength of ENR 25 and ENR 50-based adhesive containing coumarone–indene resin, gum rosin, and petro resin is discussed below.

Effect of molecular weight of ENR

The dependence of shear strength of adhesive on molecular weight of ENR 25 containing coumarone–indene resin is shown in Figure 1 for various coating thickness. The increase in shear strength with molecular weight of ENR 25 is attributed to the increase in cohesive strength—a measure of holding power—until 6.63×10^4 which is the optimum rubber chain length that is needed to achieve the maximum cohesive and adhesive strength during shearing action.[12]

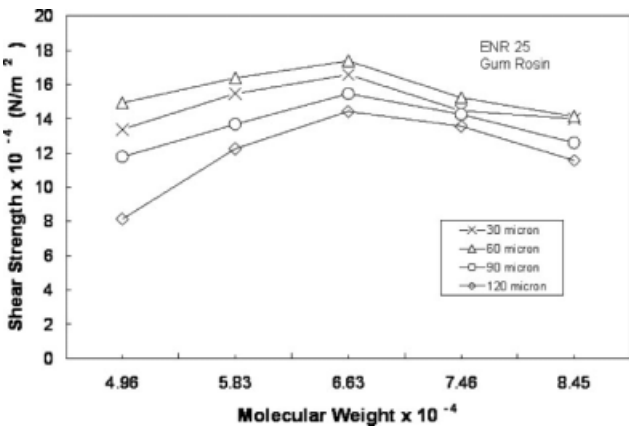

Figure 2 Variation of shear strength with molecular weight of ENR 25 containing gum rosin.

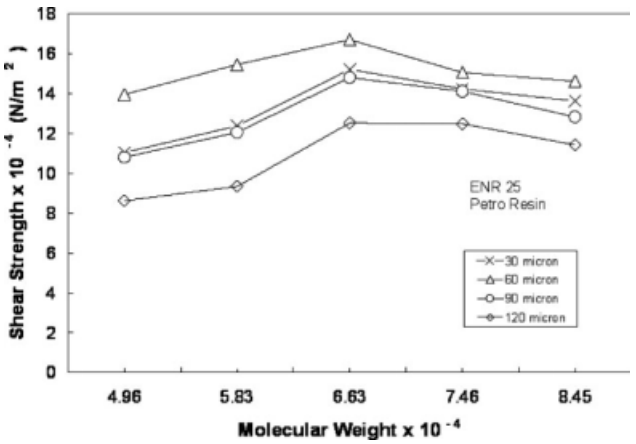

Figure 3 Variation of shear strength with molecular weight of ENR 25 containing petro resin.

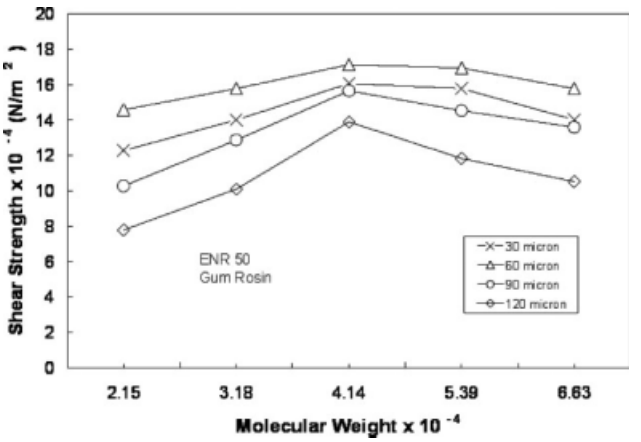

Figure 5 Variation of shear strength with molecular weight of ENR 50 containing gum rosin.

Below the optimum molecular weight of rubber (M_{op}), lower shear strength is attributed to the cohesive failure[13] due to shorter chain length of the rubber molecules. The higher the molecular weight of rubber, the higher is the extent of entanglement as reflected by the drop of shear strength as shown in Figure 1. Similar observation is obtained when gum rosin and petro resin were used as tackifiers as illustrated in Figures 2 and 3, respectively. In all cases, maximum shear strength is obtained at M_{op} of 6.63 $\times 10^4$ where maximum cohesive and adhesive strength occurs. The effect of molecular weight of ENR 50 on shear strength of adhesive is shown in Figures 4–6 containing coumarone–indene resin, gum rosin, and petro resin, respectively. As in the case of ENR 25, shear strength increases with molecular weight of ENR 50 and decreases after reaching M_{op} of 4.14 $\times 10^4$ for all coating thickness investigated in this study. At the M_{op} of ENR 50, maximum cohesive and adhesive strength occurs which is indicated by the maximum shear strength for all tackifying resin systems. Comparison between ENR 25 and ENR 50 reveals that M_{op} to attain maximum shear strength occurs earlier in ENR 50-based adhesive system than ENR 25, i.e., 4.14 $\times 10^4$ and 6.63 $\times 10^4$, respectively. In fact, our previous study[12] on the shear strength of adhesives prepared from natural rubber (i.e., zero epoxidation) shows that M_{op} of natural rubber occurs at much higher M_{op}, i.e., 8.5 $\times 10^4$. The optimum rubber chain length at M_{op} provides the maximum cohesive and adhesive strength during shear test. Below M_{op}, cohesive failure occurs due to shorter chain length of the rubber molecules. On the other hand, higher molecular weight of rubber exhibits weak adhesive strength which contributes to the lower shear strength. As epoxidation is increased, the modified natural rubber becomes more polar and hence increases intermolecular interaction between ENR and the tackifiers. This phenomenon enhances better compatibility as reflected by the lower M_{op} observed for ENR 50.

Effect of coating thickness

Figure 7 shows the effect of coating thickness on the shear strength of ENR 25 and ENR 50-based

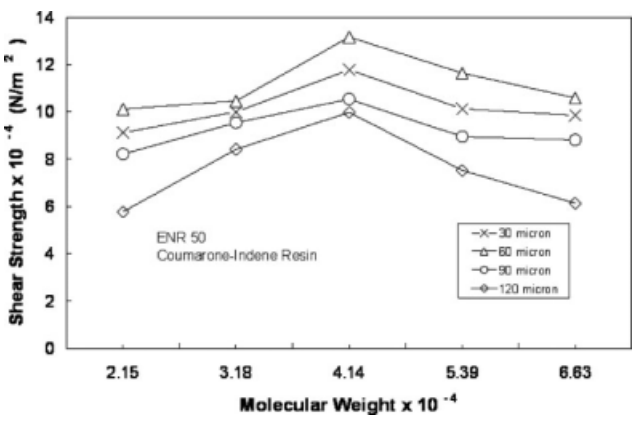

Figure 4 Variation of shear strength with molecular weight of ENR 50 containing coumarone–indene resin.

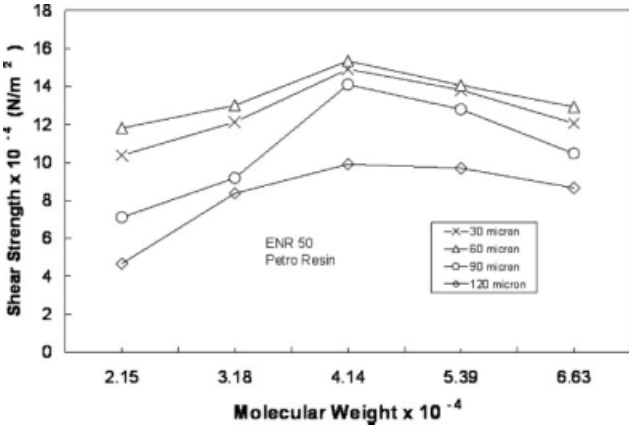

Figure 6 Variation of shear strength with molecular weight of ENR 50 containing petro resin.

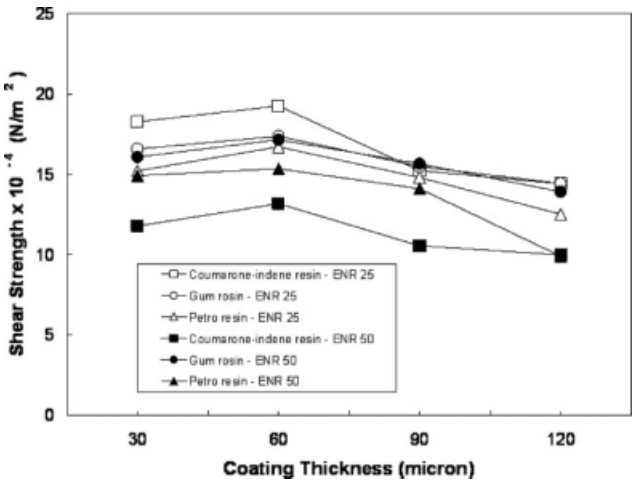

Figure 7 Dependence of shear strength on coating thickness for ENR 25 and ENR 50-based adhesives at the optimum molecular weight.

adhesives at 6.63×10^4 and 4.14×10^4 molecular weight, respectively. From the plot, shear strength indicates maximum value at 60 μm coating thickness for all the systems investigated in this study. This observation suggests that at 60 μm coating thickness, the adhesive exhibits optimum cohesive, and adhesive strength that enhances its resistance to shearing action. This finding is consistent with our previous study[12] on shear strength of natural-rubber-based adhesive where the 60-μm-coating sample is consistently higher than that of 120-μm-coating sample because of better adhesion in the former sample. For ENR 25-based adhesive, Figure 7 also shows that for a fixed coating thickness, coumarone–indene resin system shows the highest shear strength, followed by gum rosin and petro resin systems. This behavior is attributed to varying degree of molecular interaction between ENR 25 and the respective resin, i.e., compatibility is resin dependent. However, for ENR 50-based adhesive at a fixed coating thickness, gum rosin system exhibits the highest shear strength followed by petro resin and coumarone–indene resin. Greater cohesiveness and compatibility between ENR 50 and gum rosin prevails because both are natural occurring materials. Gum rosin is a mixture of rosin acids which consists of abietic acid and pimaric acid. Petro resin is the product of polymerization of C-5 petroleum fraction, mainly *cis*- and *trans*-piperylene and some amount of isoprene. Coumarone–indene resin consists of aromatic petroleum resins produced from cationic solution polymerization of indene (principal monomer) and coumarone. Generally, for a fixed tackifier system, ENR 25-based adhesive shows higher shear strength compared with that of ENR 50 adhesive system. This observation is attributed to the flexibility and better crystallizability of ENR 25 when subjected to shearing action. The greater flexibility of ENR 25 is due to its lower T_g (−45°C) compared with ENR 50 (−20°C) as a result of higher epoxidation in the latter.[9]

CONCLUSIONS

From this study, the following conclusions can be drawn.

1. Shear strength increases with increasing molecular weight of ENR until an optimum molecular weight of 6.63×10^4 and 4.14×10^4 for ENR 25 and ENR 50, respectively, is reached. This observation is attributed to the maximum cohesive and adhesive strength obtained at the optimum molecular weight of ENR. Further increase in molecular weight of ENR results in the decrease of shear strength due to the effect of chain entanglement which decreases the wettability of adhesive. As epoxidation of natural rubber is increased, intermolecular interaction between ENR and resin is enhanced resulting in better compatibility as reflected by the lower optimum molecular weight observed for ENR 50.
2. Shear strength shows maximum value at 60 μm coating thickness for all the adhesive systems studied, an observation which is attributed to the optimum cohesive and adhesive strength occurring at this coating thickness. For a fixed coating thickness, coumarone–indene resin exhibits the highest shear strength in ENR 25 adhesive. However, the highest shear value in ENR 50 system is shown by gum rosin tackifier. This discrepancy is ascribed to the difference in polarity between ENR 25 and ENR 50 due to the varying degree of epoxidation.

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