Viscosity and Shear Strength of Natural-Rubber-Based Adhesives in the Presence of Gum Rosin and Petroresin

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ABSTRACT: The viscosity and shear strength of pressure-sensitive adhesives based on natural rubber (standard Malaysian rubber grade L) were studied with gum rosin and petroresin as the tackifying resins. Effects of the concentration of the tackifying resin and the molecular weight of rubber on the two properties were systematically investigated. Toluene was used as the solvent throughout the study to prepare the adhesives. The viscosity and shear strength of the adhesives were determined with a rotary viscometer and a texture analyzer, respectively. For the shear test, a hand coater was used to coat the adhesives on the release paper substrate to provide coating thicknesses of 60 and 120 μm. The results indicated that the viscosity increased with the resin loading and molecular weight of rubber increasing. The viscosity of the adhesive prepared from petroresin had a higher value than that of the gum-rosin-based adhesive. The shear strength of the adhesives decreased gradually with increasing resin content for both tackifying resins and coating thicknesses, and this observation was attributed to the decrease in the cohesive strength due to the dilution effect of the resins. However, the shear strength passed through a maximum at a molecular weight of rubber of 8.5×10^4 for both resins. The gum-rosin-based adhesive consistently showed higher shear strength than that of the petroresin/natural rubber adhesive because of the better cohesiveness and compatibility of the former system. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 4079–4083, 2008

Key words: adhesives; resins; rubber; shear; viscosity

INTRODUCTION

We have recently carried out several studies on the viscosity and adhesion properties of natural-rubber-based pressure-sensitive adhesives with coumarone–indene resin as the tackifying resin.[1–5] The results have shown that the viscosity and tack of the adhesives increase with the resin content because of the concentration effect of the tackifying resin. The peel strength increases with the resin content up to a maximum value of 40 phr resin, at which optimum wettability of the substrate is achieved. However, the shear strength decreases gradually with increasing resin content, and this observation has been attributed to the decreasing cohesive strength of the adhesives as the resin loading is increased.[3,4] We have also extended our study to rubber blend systems using coumarone–indene resin as the tackifier.[6,7] There have been very few studies on the adhesion properties of natural-rubber-based pressure-sensitive adhesives prepared from tackifiers other than coumarone–indene resin. To understand better the effects of other tackifiers, here we report our findings on the effects of the tackifier concentration and molecular weight of rubber on the viscosity and shear strength of natural-rubber-based adhesives using two other tackifier types, that is, gum rosin and petroresin.

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EXPERIMENTAL

Materials

Standard Malaysian rubber grade L (SMR L) was used as the natural rubber to prepare the pressure-sensitive adhesives in this study. The technical specifications of SMR L[8] are given in Table I. Gum rosin and petroresin were freshly supplied by Euro-Chemo-Pharma Co. (Prai, Penang, Malaysia). Toluene was used as the solvent to prepare the adhesives throughout the experiments.

Determination of the molecular weight of rubber

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 ([η]) was measured according to the method described by Billmeyer.[9] The viscosity-average molecular weight (M_v) of the rubber was computed with the Mark–Houwink equation:[10]

TABLE I
Technical Specifications of SMR L

Dirt content (maximum wt %)	0.03
Ash content (maximum wt %)	0.50
Nitrogen (maximum wt %)	0.60
Volatile matter (maximum wt %)	0.80
Plasticity retention index (minimum %)	60

$$[\eta] = kM_v^a$$

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

Adhesive preparation

The rubber with the highest molecular weight, that is, 1.32×10^5, was used to study the effect of the tackifier concentration on the viscosity and shear properties of the adhesives. Five grams of the milled rubber sheet was shredded and dissolved in 30 mL of toluene. The rubber solution was then kept in a conditioned room for 24 h. For each tackifying resin, five different weights of the pulverized resin, that is, 1, 2, 3, 4, and 5 g corresponding to 20, 40, 60, 80, and 100 phr resin, were then added slowly to the rubber solution with constant stirring to produce the pressure-sensitive adhesives. A control sample to which no resin was added was used for comparison. The effect of the molecular weight of the rubber on the viscosity and shear properties of the adhesives was determined with a 40 phr concentration of the tackifying resins.

Measurement

Viscosity

A Haake (Karlsruhe, Germany) model PK 100 rotary viscometer was used to determine the viscosity of the adhesives at room temperature (30°C). The spindle head (PK1; 1°) was cleaned with acetone and fixed to the viscometer. The wiped platform was then raised up to touch the spindle head. The gap between the spindle head and platform was adjusted to zero. A few drops of the adhesive were put in the middle of the platform. It was then raised up to squeeze the adhesive. Acetone was also used to wipe off excessive adhesive around the spindle head. Testing was carried out for 1 min or 10 rounds of spinning. The average viscosity was computed from at least five readings.

Shear testing

The dimensions of the release paper substrate for shear testing were 2.5 cm × 15 cm. A Sheen hand coater (Teddington, Middx, England) was used to coat the center of the substrate with a coating area of 2.5 cm × 5 cm and with two different coating thicknesses, that is, 60 and 120 μm. Another piece of release paper was immediately placed on top of the coated substrate. The single lap shear specimen was then conditioned at room temperature for 24 h before testing. A TA-HDi Stable MicroSystem texture analyzer operating at a testing speed of 1 mm/s up to 50 s was used to measure the shear force as indicated by the peak force. The testing distance was 5 cm, which corresponded to the length of the coated area. The shear strength was expressed as the shear force per unit of area of testing.

RESULTS AND DISCUSSION

The dependence of the viscosity and shear strength of the adhesives on the tackifying resin content and molecular weight of rubber is discussed next.

Viscosity of the adhesives

Figure 1 shows the dependence of the viscosity of the adhesives on the gum rosin and petroresin content. For both tackifying resins, the viscosity increases with increasing resin loading, and this observation is attributable to the concentration effect of the resins. However, the viscosity of the adhesive prepared from petroresin is consistently higher than that of the gum-rosin-based adhesive. This is due to the nature of petroresin, which comprises polymerized C5 or C9 or polycyclic streams[11] derived from the naphtha cracking process. Because petroresin is a polymeric material, it can entangle with the rubber matrix to increase the viscosity of the adhesive. On the other hand, gum rosin is obtained as oleoresin from living trees. Gum rosin does not entangle with the rubber matrix, and hence a lower viscosity is obtained, as indicated in Figure 1. However, as the resin concentration is increased beyond 80 phr, the difference in the viscosity of the adhesives from

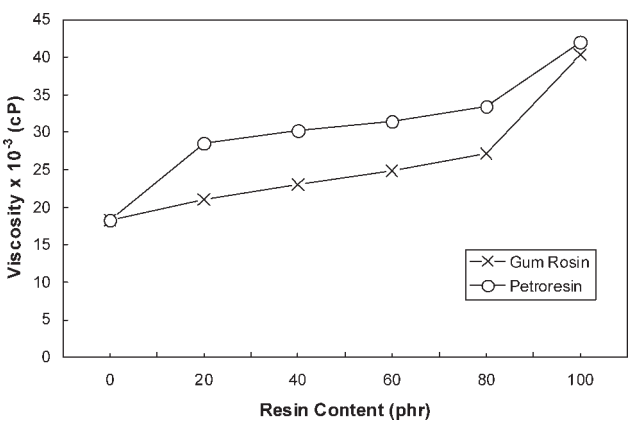

Figure 1 Variation of the viscosity of the adhesives with the gum rosin and petroresin content.

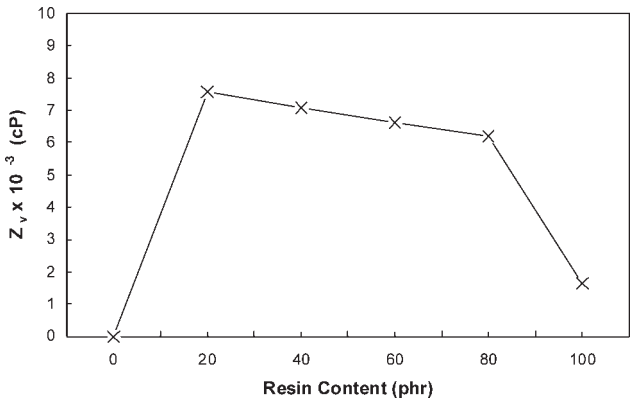

Figure 2 Variation of the difference in the viscosity of the petroresin-based and gum-rosin-based adhesives (Z_v) with the resin content.

the petroresin and gum rosin systems narrows. In fact, for a 100 phr resin content, the two tackifying resins exhibit similar viscosities. This observation is attributable to the dominance of the resin; that is, phase inversion occurs. The effect of entanglement in the petroresin/rubber system is significantly reduced as the effect of phase inversion becomes more dominant. The difference in the viscosity for the petroresin-based and gum-rosin-based adhesives (Z_v) is shown in Figure 2. The plot indicates the highest value with 20 phr resin, and this suggests that the entanglement in the petroresin/rubber system is greatest at this resin concentration. As the amount of petroresin is further increased, Z_v decreases gradually up to an 80 phr resin content, after which a sudden drop in Z_v is obtained. This decrease in Z_v after an 80 phr resin content is associated with the phase inversion, which diminishes the effect of entanglement of petroresin in the rubber matrix. Figure 3 shows the effect of the molecular weight of rubber on the viscosity of the adhesives containing gum rosin and petroresin. It is obvious

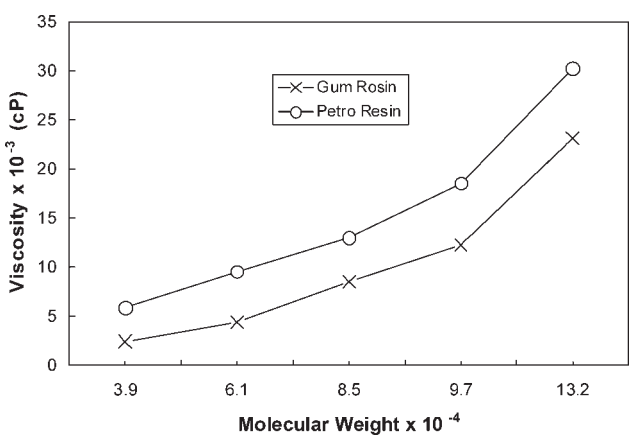

Figure 3 Variation of the viscosity of the adhesives with the molecular weight of rubber with 40 phr gum rosin and petroresin.

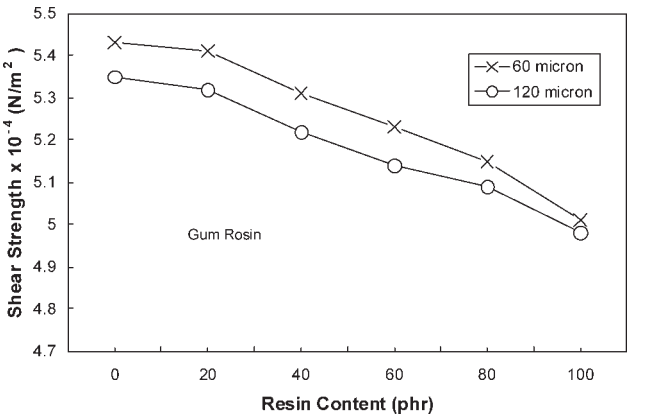

Figure 4 Dependence of the shear strength on the gum rosin content for 60- and 120-μm coating thicknesses.

that for both tackifying resins, the viscosity increases gradually with the molecular weight up to 9.7×10^4, after which it increases rapidly with a further increase in the molecular weight of rubber. The initial gradual increase in the viscosity is attributable to the increase in the rubber chain length. However, after the molecular weight of 9.7×10^4, the sudden increase in the viscosity is associated with the effect of entanglement of rubber chains.[12] Figure 3 also shows that the petroresin-based adhesive has a higher viscosity than that of the adhesive prepared from gum rosin. This observation is consistent with that made concerning the concentration effect of the tackifying resins, as discussed earlier.

Shear strength

The effect of the gum rosin loading on the shear strength of SMR L based pressure-sensitive adhesives is shown in Figure 4 for 60- and 120-μm coating thicknesses. For both coating thicknesses, the graph shows that the highest shear strength is exhibited by the control sample, that is, a zero concentration of the resin, after which the shear strength decreases gradually with increasing resin content. This observation is attributable to the decrease in the cohesive strength due to the dilution effect of the resin.[3] The rubber, which acts as the binder in the adhesive system, will lose its holding power as the resin content is increased because the shearing resistance of the resin is much weaker than that of the rubber component. Also, increasing the resin loading will increase its dilution effect, and this in turn will weaken the adhesive's ability to resist flow during shearing action. The addition of a low-molecular-weight diluent (resin) reduces the number of entanglements per unit of volume and increases long-term compliance and flow.[11] Figure 4 also indicates that the shear strength for the 60-μm-coating sample is consistently higher than that of the

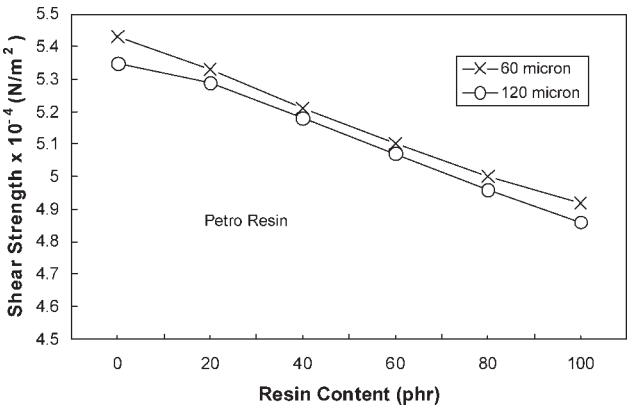

Figure 5 Dependence of the shear strength on the petroresin content for 60- and 120-μm coating thicknesses.

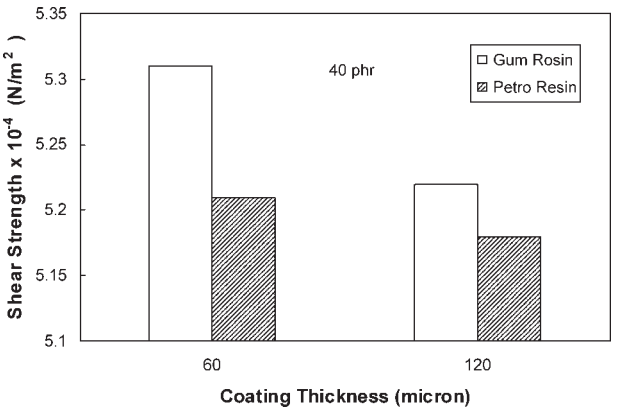

Figure 7 Comparison of the shear strength for gum rosin and petroresin with 60- and 120-μm coating thicknesses.

120-μm-coating sample. This may be associated with the lower coating thickness, which results in better adhesion and hence increases its resistance to shearing action. A similar observation is reported for the pressure-sensitive adhesive prepared from petroresin, as shown in Figure 5. The shear strength again decreases steadily with increasing petroresin as a result of decreasing cohesive strength, as discussed earlier. The shear strength for the 60-μm coating thickness also indicates higher shear strength compared to the corresponding value for the 120-μm coating thickness. However, in this case, the difference in the shear strength for the 60- and 120-μm coating thicknesses is not as great as in the gum rosin system. For comparison, the difference in the shear strength for the two coating thicknesses (Z_s) is plotted against the resin content, as shown in Figure 6. One interesting feature is that for the gum rosin, Z_s drops after a 60 phr resin loading, and this suggests that the shear strength becomes less dependent on the coating thickness for a higher gum rosin loading. On the other hand, for the petroresin, Z_s reaches a minimum value between resin concentrations of 40 and 60 phr and then increases with the further addition of petroresin; this observation is contrary to that reported for the gum rosin system. This discrepancy is attributable to the greater effect of phase inversion in the case of petroresin. Figure 7 compares the shear strengths of the adhesives prepared from gum rosin and petroresin at a 40 phr resin loading. It is obvious that for the two thicknesses investigated, the gum rosin system consistently exhibits higher shear strength than the petroresin system. Gum rosin, as stated earlier, consists of oleoresin, a natural product from living trees, whereas petroresin is a synthetic resin derived from the polymerization of petroleum cracked products. The result shows that the naturally occurring tackifying resin, that is, gum resin, gives higher shear strength as a result of better cohesiveness and compatibility between the gum rosin and natural rubber, both of which are naturally occurring materials. Figures 8 and 9 show the dependence of the shear strength on the molecular weight of rubber for adhesives prepared from gum rosin and petroresin, respectively. The results indicate that the shear strength increases with the

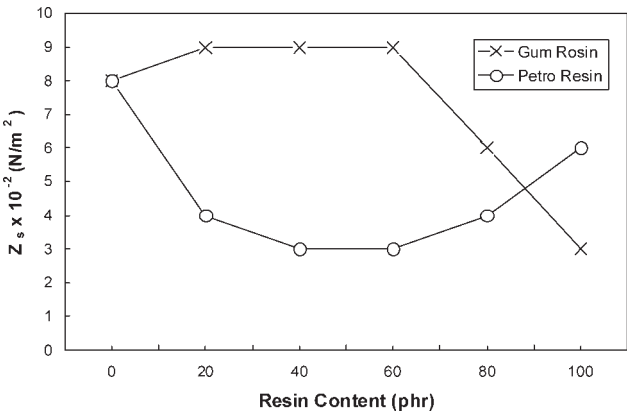

Figure 6 Variation of the difference in the shear strength for coating thicknesses of 60 and 120 μm (Z_s) with the gum rosin and petroresin content.

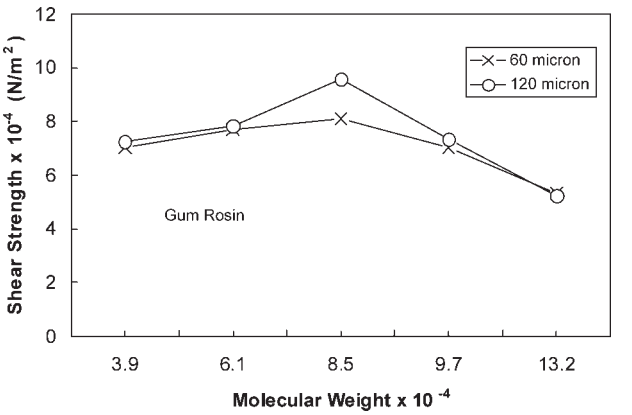

Figure 8 Variation of the shear strength with the molecular weight of rubber with 60- and 120-μm coating thicknesses for 40 phr gum rosin.

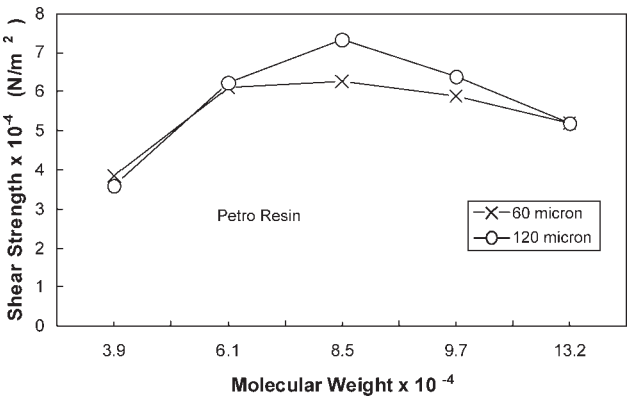

Figure 9 Variation of the shear strength with the molecular weight of rubber with 60- and 120-μm coating thicknesses for 40 phr petroresin.

molecular weight up to 8.5×10^4, after which it decreases with an increase in the molecular weight of rubber for the two coating thicknesses investigated. The maximum shear strength observed at the optimum molecular weight of 8.5×10^4 is ascribed to the optimum rubber chain length needed to achieve the maximum cohesive and adhesive strength during shearing action. The lower shear strength observed below the optimum molecular weight of rubber is attributable to the cohesive failure[11] due to the shorter chain length of the rubber molecules. Conversely, for a higher molecular weight of rubber, the weak adhesive strength contributes to the lower shear strength because of poor wettability of the adhesive on the substrate.

CONCLUSIONS

The following conclusions can be drawn from this study.

First, the viscosity of adhesives prepared from gum rosin and petroresin increases with increasing resin loading, and this observation is attributable to the concentration effect of the resin. However, the viscosity of the petroresin-based adhesive is consistently higher than that of the gum-rosin-based adhesive. This observation is associated with the varying degree of entanglement between the rubber matrix and petroresin. Beyond a resin concentration of 80 phr, the difference in the viscosity for the petroresin-based and gum-rosin-based adhesives narrows, and this indicates that the effect of phase inversion has overshadowed the entanglement effect in the petroresin/rubber system. The viscosity of the adhesive increases with the molecular weight of rubber. The initial gradual increase in the viscosity is attributable to the increase in the rubber chain length. However, the sudden increase in the viscosity after a molecular weight of 9.7×10^4 is attributable to the effect of entanglement of rubber chains.

Second, for both tackifying resins, the shear strength of the adhesive decreases gradually with increasing resin content. This observation is attributable to the decrease in the cohesive strength due to the dilution effect of the resin. The shear strength for the 60-μm-coating sample is consistently higher than that of the 120-μm-coating sample because of better adhesion in the former sample. For both thicknesses investigated, the gum rosin system consistently exhibits higher shear strength than the petroresin system. This phenomenon is ascribable to better cohesiveness and compatibility between the gum rosin and natural rubber than between the petroresin and natural rubber. The shear strength passes through a maximum value at a molecular weight up to 8.5×10^4, and this observation is attributable to the optimum rubber chain length necessary to achieve the maximum cohesive and adhesive strength during shearing action.

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