Effect of Zinc Oxide on the Viscosity, Tack, and Peel Strength of ENR 25-Based Pressure-Sensitive Adhesives

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ABSTRACT: Viscosity, loop tack, and peel strength of epoxidized natural rubber (ENR 25 grade)-based pressure-sensitive adhesive was studied in the presence of zinc oxide. The zinc oxide concentration was varied from 10–50 parts per hundred parts of rubber (phr). Coumarone–indene resin with loading from 20 to 100 phr was chosen as the tackifier resin. Toluene was used as the solvent throughout the experiment. The adhesive was coated on the substrate using a SHEEN hand coater to give a coating thickness of 60 μm. Viscosity of the adhesive was determined by a HAAKE Rotary Viscometer whereas the loop tack and peel strength were measured by a Llyod Adhesion Tester operating at 30 cm/min. Results show that viscosity and loop tack of adhesive increases with increasing zinc oxide concentration. For the peel strength, it increases with zinc oxide concentration up to 30–40 phr and drops after the maximum value. This observation is associated with the effect of varying degree of wettability of the adhesive on the substrate. However, for a fixed zinc oxide concentration, loop tack and peel strength exhibit maximum value at 80 phr resin loading after which both properties decrease with further addition of resin, an observation which is attributed to phase inversion. From this study, the optimum adhesion property is achieved by using 40 phr zinc oxide and 80 phr coumarone–indene resin. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 333–337, 2007

Key words: viscosity; tack; peel strength; zinc oxide; epoxidized natural rubber

INTRODUCTION

Recently, we have reported the viscosity, tack, peel, and shear strength of Standard Malaysian Rubbers (SMR L, SMR 10, and SMR 20 grades)-based pressure-sensitive adhesives.[1–3] Results have shown that viscosity of the adhesive decreases with mastication time because of the shortening of rubber chains. The study also shows that shear strength decreases gradually with increasing resin content. On the contrary, viscosity, tack, and peel strength of the adhesive generally increases with an increase in coumarone–indene resin which acts as a tackifying resin. This observation is essentially attributed to the better wettability of adhesive on the substrate as tackifying resin is increased. However, with respect to epoxidized natural rubber (ENR), the study on its adhesion properties seems scarce. Most of the study focused on the curing characteristics and mechanical properties of ENR in the bulk state.[4–6] Our recent study indicates that peel strength of ENR-based adhesive (without filler) passes through a maximum value at 40 phr coumarone–indene resin, but a gradual drop of shear strength with increasing tackifier loading is observed.[7] In view of the scarcity of data on the adhesion properties of ENR, we have carried out a systematic investigation on the viscosity, tack, and peel strength of ENR 25-based pressure-sensitive adhesives with and without zinc oxide which acts as a filler in the adhesive system. Zinc oxide was chosen as the filler because of its outstanding property in tack retention during shelf aging.

EXPERIMENTAL

Materials

One grade of epoxidized natural rubber, ENR 25, having 25 mol % of epoxidation was used as the elastomer for the preparation of the pressure-sensitive adhesive. Technical specification of the ENR 25 was given in our previous report.[8] Zinc oxide, coumarone–indene resin, and toluene were used as the filler, tackifier, and solvent, respectively, in this research. All the materials used in this experiment were freshly supplied commercial grades. No purification was carried out prior to use.

Preparation of adhesive

ENR 25 was masticated on a two-roll mill for 10 min to facilitate dissolution in the solvent. Then, 5 g of masticated rubber was dissolved in 20 mL of toluene and the rubber solution was tightly closed and kept

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for 24 h before the addition of coumarone–indene resin and zinc oxide. Five different weights, i.e., 1, 2, 3, 4, and 5 g of pulverized coumarone–indene resin corresponding to 20, 40, 60, 80, and 100 phr of resin were used. There was one control sample where no coumarone–indene resin was added. For the zinc oxide, the weights used were 0.5, 1, 1.5, 2, and 2.5 g corresponding to 10, 20, 30, 40, and 50 phr of filler were added into the adhesive once the coumarone–indene resin had completely dissolved in the adhesive. The adhesive was left for 24 h at room temperature (30°C) before testing.

Measurement

Viscosity

The viscosity of the adhesives was measured by a HAAKE Rotary Viscometer (Model PK 100) at room temperature (30°C). Spindle head (PK1; 1°) was wiped with acetone and fixed to the viscometer. The platform was also wiped with acetone and then raised up to touch the spindle head. 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 up to squeeze the adhesive. Excessive adhesive around the spindle head was wiped off with acetone. Testing was ended after 1 min or 10 rounds of spinning. At least five readings were taken and the average viscosity was calculated.

Tack

For the loop tack test which is the peel test involving low contact pressure and short application time,[9] a polyethylene terephthalate (PET) substrate with dimension of 4 cm × 25 cm was used. The adhesive was coated at the centre (4 cm × 4 cm) of the substrate using a SHEEN Hand Coater at a coating thickness of 60 μm. The coated sample was conditioned at room temperature for 24 h prior to testing. The PET strip was then formed into a loop and the adhesive area was brought into contact with a glass plate. A Lloyd Adhesion Tester (Model LRXPlus with NEXYGEN software) with a testing rate of 30 cm/min was used to measure the debonding force from the glass plate at room temperature (30°C). The average debonding force was calculated from the three highest peaks detected from the test. The loop tack value was expressed as the debonding force per area of contact (N/m^2). The testing was carried out in triplicate for each formulation and the median value was reported in this study.

Peel strength

The peel adhesion test was carried out at room temperature (30°C) by using polyethylene terephthalate (PET) film (base stock) and a A4 paper (face stock) as substrates. Three modes of peeling tests were carried out, i.e. T-Peel Test, 90° Peel Test, and 180° Peel Test.

T-peel, 90°, and 180° peel tests

The dimensions for the T- and 90° Peel Tests substrates were 20 cm × 4 cm. For the 180° Peel Test, the dimensions of PET film and paper substrates were 25 cm × 4 cm and 12 cm × 6 cm, respectively. The adhesive was coated from the end of the PET film at a coating area of 10 cm × 4 cm with a coating thickness of 60 μm. Then, the paper substrate was stuck on the coated PET film. The testing sample was conditioned for 24 h prior to testing on a Lloyd Adhesion Tester operating at 30 cm/min. Five specimens were used for each adhesive formulation in this test. The three highest peaks from the load-propagation graph were used to calculate the average peeling force. Peel strength is defined as the average load per width of the bondline required to separate progressively a flexible member from a rigid member or another flexible member (ASTM D 907).

RESULTS AND DISCUSSION

The results of this study are discussed with respect to the effect of zinc oxide on the viscosity, tack, and peel strength of ENR 25-based pressure-sensitive adhesives.

Viscosity

The dependence of viscosity of ENR 25-based adhesive on zinc oxide concentration is shown in Figure 1 for various coumarone–indene resin contents. It is obvious from the graph that viscosity of adhesive increases with increase in zinc oxide concentration, the rate of increase is faster as the resin content is increased. This observation is attributed to the thickening effect of the zinc oxide which acts as a filler in the adhesive formulation.[10] Even for the control sam-

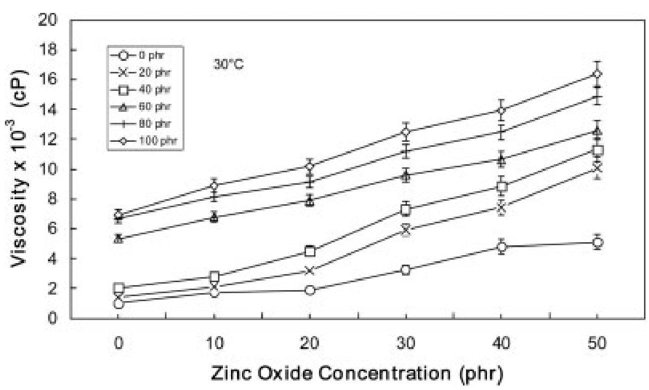

Figure 1 Variation of viscosity with zinc oxide concentration for various resin contents.

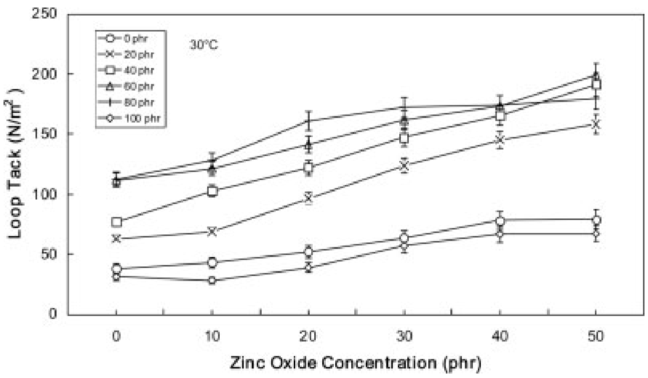

Figure 2 Variation of loop tack with zinc oxide concentration for various resin contents.

ple, i.e. in the absence of resin loading, there is a gradual increase in viscosity as the zinc oxide concentration is increased. However, with the addition of resin up to 40 phr, marked increase in viscosity is observed, especially for zinc oxide loading higher than 20 phr. This finding suggests that greater interaction between the filler and adhesive system occurs. However, for resin concentration greater than 60 phr, viscosity increases steadily with zinc oxide concentration. This observation is attributed to the higher resin content which overshadows the effect of zinc oxide as the filler. For a fixed zinc oxide concentration, viscosity increases with increase in resin content. This observation is consistent with our previous results reported for SMR 10 and SMR 20-based pressure-sensitive adhesives.[1,2] The increase in viscosity is associated to the concentration effect of the resin. Higher resin loading will result in stronger rubber-resin interaction and chain entanglement between rubber chains and resin molecules may occur.[11]

Tack

Tack may be defined as the property of a material which enables it to form a bond of measurable strength immediately upon contact with another surface, usually with low applied pressure.[10] Tack gives an indication of how quickly an adhesive can wet and make intimate contact with a surface. Figure 2 shows the effect of zinc oxide concentration on loop tack of ENR 25-based adhesive for various resin contents. It can be seen from the figure that loop tack increases with increase in zinc oxide loading for all resin contents. This observation may be attributed to the lowering of surface tension to give the proper flow and wetting characteristics.[10] Tack is a function of the rheological properties of the adhesive as well as the surface energy characteristics of the adhesive and the bonded surface. The degree of wettability increases with increase in zinc oxide loading as shown by the higher tack value. For a fixed loading of zinc oxide, loop tack increases with tackifying resin up to a maximum value at 60–80 phr resin. The tack value decreases with further resin loading. At 60–80 phr resin, the adhesive attains maximum wettability and conform to the irregularities of the substrate, i.e. low surface energy condition is observed. The adhesive deformation in the bonding stage is mainly viscous and high ratio of viscous to elastic properties is achieved.[12] More of the adhesive is actively resisting bond rupture at any instant. The rubber and resin components indicate the optimum elastic and viscous property that is necessary for the maximum tack in a pressure-sensitive adhesive.[13] However, as the resin loading is increased beyond the optimum loading, phase inversion phenomenon occurs as exhibited by the 100 phr resin which gives the lowest tack value.

Peel strength

The effect of zinc oxide on peel strength of ENR 25-based adhesive is shown in Figure 3 using a T-Test mode. Except for the control sample and 100 phr resin content, the rest of the samples shows marked increase in peel strength with increasing zinc oxide concentration. For the 20 phr resin, maximum peel strength is observed at 30 phr zinc oxide which indicated maximum wettability at this particular composition. For the 40–80 phr resin loading, peel strength increases significantly after 20 phr of zinc oxide. This observation is attributed to the continuous lowering of surface tension by zinc oxide, and hence better wettability of adhesive on the substrate is obtained as shown by the increase in the peel strength. The increase in wettability enhances mechanical interlocking and anchorage of the adhesive in pores and irregularities in the adherent.[9,14] The response of the pressure-sensitive adhesive to the stress is of a viscoelastic nature.[12] At low rate of force application, the response is essentially viscous and the result is a

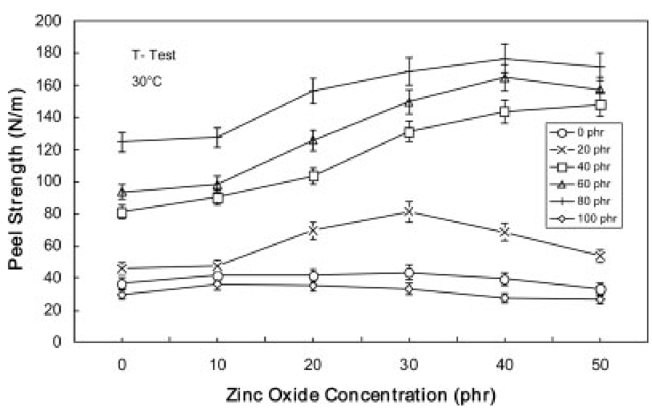

Figure 3 Variation of peel strength with zinc oxide concentration for various resin contents using T-peel test.

cohesive failure. On the other hand, at higher rate of force application, the response is mainly elastic in nature and the failure becomes adhesive. The adhesive hardens at high strain levels to become a tough solid, it cannot easily be ruptured. However, for the control sample (i.e. without the addition of tackifying resin), the peel strength is essentially independent on the zinc oxide concentration although a slight decrease in peel strength is observed after 30 phr zinc oxide. Addition of zinc oxide in the absence of tackifying resin does not enhance the peel strength of ENR 25- based adhesives. Zinc oxide only acts as the filler for the adhesive and no molecular interaction between filler and rubber chain molecules is observed. Further addition of zinc oxide in fact dilute the adhesion property and cause the slight decrease in peel strength. On the other hand, for the 100 phr resin, phase inversion occurs as discussed earlier. The elastic component from ENR 25 has diminished significantly as reflected by the sharp drop in peel strength. Increase in zinc oxide concentration for the 100 phr resin adhesive also does not indicate much effect on the peel strength suggesting dilution phenomenon also occurs in this adhesive system. Figure 3 also shows that peel strength increases with resin content up to 80 phr resin for all zinc oxide concentration studied, an observation which is attributed to the maximum wettability of adhesive on the substrate at this resin content. Similar observations of the effect of zinc oxide on peel strength obtained from the 90° and 180° Peel Tests are shown in Figures 4 and 5, respectively. Again, peel strength increases up to 30–40 phr zinc oxide concentration after which it drops with further addition of the filler. The 80 phr resin system exhibits the highest peel strength for all the zinc oxide concentration investigated. On the other hand, adhesive containing 100 phr resin consistently indicates the lowest peel strength for the 90° and 180° Peel Tests because of phase inversion as discussed earlier.

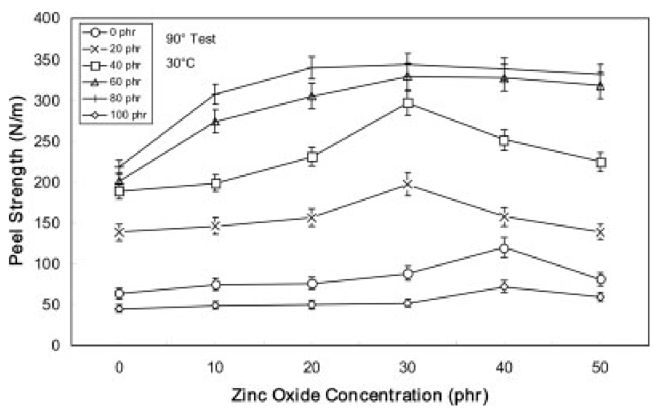

Figure 4 Variation of peel strength with zinc oxide concentration for various resin contents using 90° peel test.

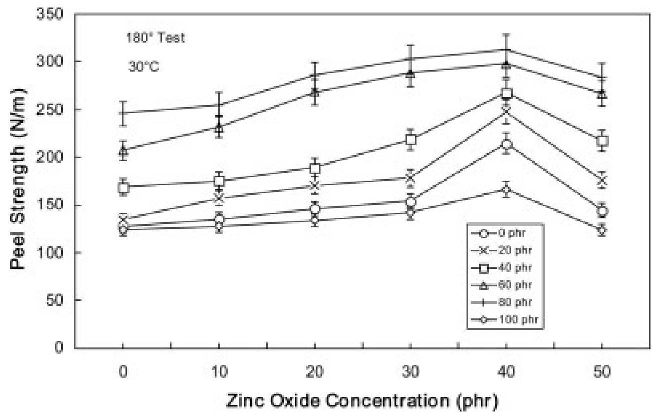

Figure 5 Variation of peel strength with zinc oxide concentration for various resin contents using 180° peel test.

CONCLUSIONS

From this study, the following conclusions can be drawn.

1. The viscosity of ENR 25-based adhesive increases with increase in zinc oxide concentration for all resin loadings. However, the rate of viscosity increase with zinc oxide is greater for higher resin content. This observation is attributed to the thickening effect of zinc oxide in the adhesive system. For a fixed zinc oxide concentration, viscosity of the adhesive increases with an increase in resin loading because of the concentration effect of the latter.
2. Loop tack increases with increase in zinc oxide loading for all resin concentration studied, an observation which is associated with the lowering of surface tension and enhancement of wettability of adhesive on the substrate. For a fixed loading of zinc oxide, maximum loop tack is obtained at 60–80 phr resin where maximum wettability is achieved. However, for the adhesive containing 100 phr resin, the lowest tack value obtained is attributed to the phenomenon of phase inversion in the adhesive system.
3. Peel strength increases significantly with increasing zinc oxide concentration for resin loading between 20 and 80 phr. This observation is associated to the continuous lowering of surface energy by zinc oxide which enhances better wettability of adhesive on the substrate. However, zinc oxide does not exhibit marked effect on the peel property of adhesive without tackifying resin. Similar to that of tack, adhesive containing 100 phr resin consistently shows the lowest peel strength. For

all zinc oxide loadings, adhesive containing 80 phr resin indicates the highest peel strength for the three modes of peel tests.

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