

Adhesion Behavior of Natural Rubber-Based Adhesives Crosslinked by Benzoyl Peroxide

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ABSTRACT: The loop tack, peel, and shear strength of crosslinked natural rubber adhesive were studied using coumarone-indene and toluene as the tackifying resin and solvent, respectively. The concentration of benzoyl peroxide—the crosslinking agent—was varied from 1 to 4 parts per hundred parts of rubber (phr). A SHEEN hand coater was used to coat the adhesive on the polyethylene terephthalate substrate at various coating thickness. Loop tack, peel, and shear strength were measured by a Llyod adhesion tester operating at 30 cm min⁻¹. Result shows that loop tack and peel strength of the adhesive increases up to 2 phr of benzoyl peroxide concentration after which it decreases with further benzoyl peroxide content. This

observation is attributed to the optimum crosslinking of natural rubber where optimum cohesive and adhesive strength occurs at 2 phr peroxide loading. However, for the shear strength, it increases with increasing benzoyl peroxide concentration where higher rate of increase is observed after 2 phr of peroxide content, an observation which is associated to the steady increase in cohesive strength of crosslinked rubber. In all cases, the adhesion properties of adhesives increase with increase in coating thickness. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1031–1035, 2012

Key words: natural rubber; adhesive; tack; peel; shear

INTRODUCTION

The adhesion properties of rubber-based adhesives have been widely studied. These include the effects of miscibility and viscoelasticity on peel strength and shear creep resistance of natural-rubber-based pressure-sensitive adhesives,^{1,2} the relationship between peel and rheology of pressure-sensitive adhesive³ and modeling of the peel performance of adhesives.⁴ On the other hand, Phillips et al.^{5,6} have studied the singlet oxygen generation and adhesive properties in polymer blends adhesives. Mingaleeva et al.⁷ have reported the improvement of the adhesion strength of adhesive joints of fabric-backed vulcanized rubbers by the additional sand papering of a rubber surface. Recently, we have reported several studies on the adhesion properties of rubber-based pressure-sensitive adhesives. These include adhesion properties of pressure-sensitive adhesives prepared from rubber blends,⁸ viscosity and shear strength of natural-rubber-based adhesives in the presence of gum rosin and petro resin.⁹ Results show that viscosity of petro resin-based adhesive indicates higher value than that of gum rosin. Shear strength

of adhesive decreases gradually with increasing resin content and coating thickness, an observation which is associated to the decrease in cohesive strength. The effect of molecular weight of natural rubber and epoxidized natural rubber on the adhesion properties of the rubber-based adhesives was also systematically investigated.^{10–13} Maximum values of loop tack, peel strength, and shear strength were obtained at an optimum molecular weight of rubber, an observation which is attributed to maximum wettability of adhesive on the substrate. Studies on the effect of fillers on adhesion properties of rubbers^{14–17} reveal that there is an optimum loading of fillers where maximum adhesion property occurs. All these investigations involved linear, uncrosslinked rubber chain molecules as the elastomer. With regard to crosslinked-rubber-based adhesives, Verdier et al.¹⁸ studied the peeling property of crosslinked and uncrosslinked acrylic pressure-sensitive whereas Hamed and Preechatiwong¹⁹ investigated the effect of crosslinking on rate/temperature response on the peel adhesion of natural rubber bonded to polyethylene terephthalate. The linear rheology of crosslinked polypropylene oxide as a pressure-sensitive adhesive was reported by Jensen et al.²⁰ Besides, Wu et al.²¹ described the preparation, characterization, and properties of crosslinked hydroxylated poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer. However, the adhesion property of peroxide-crosslinked rubber-based adhesive is not

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reported so far. It is thus the aim of this article to discuss some of our findings on the adhesion behavior of adhesive in the presence of peroxide-crosslinked rubber.

EXPERIMENTAL

Materials

Standard Malaysian Rubber (SMR L grade) was chosen as the natural rubber in this study. Its technical specification was given in our previous paper.⁹ It was supplied by Rubber Research Institute of Malaysia. Coumarone-indene resin (CUMAR R12 grade) supplied by Mukmin Enviro Company, Penang (Malaysia), was used as the tackifying resin. Benzoyl peroxide and toluene were used as the crosslinking agent and solvent, respectively, throughout the experiment. Polyethylene terephthalate (PET) film was selected as the coating substrate. All the materials and chemicals used in this research were freshly supplied and no purification was carried out prior to use.

Preparation of adhesive

The rubber was masticated on a two-roll mill for 10 min. About 5 g of the masticated rubber were shredded into small pieces and dissolved in 30 mL of toluene. The rubber solution was tightly closed and kept overnight to ensure complete dissolution. Nearly 2 g of pulverized coumarone-indene resin which corresponded to 40 phr of tackifying resin was then slowly added into the rubber solution. The mixture was left for 2 h before the addition of benzoyl peroxide into the adhesive solution. Four different loadings of benzoyl peroxide, i.e., 0.05, 0.10, 0.15, and 0.20 corresponding to 1, 2, 3, and 4 phr of benzoyl peroxide were chosen. For comparison purposes, one control sample without benzoyl peroxide was also prepared.

Measurement

Tack

Loop tack is essentially a peel test involving low contact pressure and short application time.²² A SHEEN Hand Coater was used to coat a polyethylene terephthalate (PET) film (4 cm × 25 cm) at the center of coating area of 4 cm × 4 cm at various coating thickness i.e., 30, 60, 90, and 120 μm. The sample was then conditioned at 30°C for 24 h. It was then heated in oven at 80°C for 30 min to cure the rubber. The density of the rubber was 0.92 g cm⁻³. The adhesive-coated area of the PET film was slowly brought into contact with a glass plate. The debonding force from the glass plate was

TABLE I
Dimensions of PET Substrate for the Various Modes of Peel Tests

Mode of testing	Base stock	Face stock
T-	4 cm × 20 cm	4 cm × 10 cm
90°	4 cm × 20 cm	7 cm × 15 cm
180°	4 cm × 25 cm	10 cm × 10 cm

measured by a Lloyd Adhesion Tester (Model LRXPlus with NEXYGEN software) operating at a testing rate of 30 cm min⁻¹. The three highest peaks from the load-propagation graph were used to compute the average debonding force. The loop tack was defined as the debonding force per area of contact with the glass plate (N m⁻²).

Peel strength

The dimensions of PET substrates for the T-, 90° and 180° peel tests are shown in Table I. A SHEEN Hand Coater was used to coat the adhesive from the end of the PET film (base stock) at a coating area of 10 cm × 4 cm at 30, 60, 90, and 120 μm coating thicknesses. The face stock was then carefully laid on the coated PET film. As in the case of tack experiment, the test specimen was conditioned at 30°C for 24 h. It was then heated in oven at 80°C for 30 min to cure the rubber. The density of the rubber was 0.92 g cm⁻³. Peel property for the three modes of peel tests were determined by a Lloyd Adhesion Tester operating at 30 cm min⁻¹. The three highest peaks from the load-propagation graph were used to determine the average peeling force of the sample. Peel strength is expressed 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 20 cm × 4 cm for the shear test. The substrate was coated from the end of the film at a coated area of 10 cm × 4 cm using a SHEEN hand coater for various coating thickness. One end of the face stock with dimension 10 cm × 4 cm was gently placed on the coated area of the base stock. The sample was conditioned at 30°C for 24 h before heated in oven at 80°C for 30 min to cure the rubber. The density of the rubber was 0.92 g cm⁻³. A Lloyd Adhesion Tester operating at 30 cm min⁻¹ was used to determine the shear force of the adhesive. The testing distance was 10 cm which corresponded to the length of the coated area. Shear strength was defined as the shear force per unit area of testing (N m⁻²).

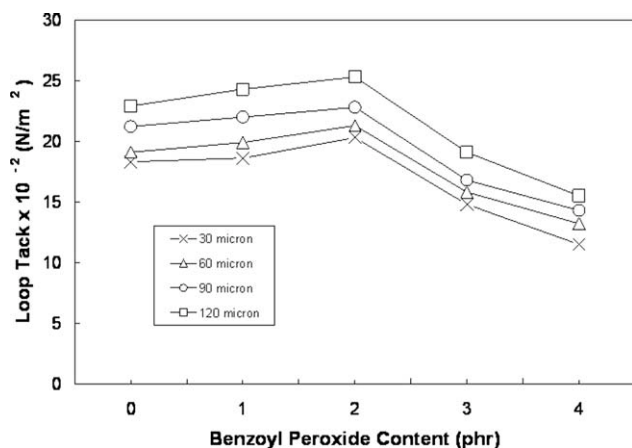


Figure 1 Variation of loop tack of adhesive with concentration of benzoyl peroxide at various coating thickness.

RESULTS AND DISCUSSION

Tack

The dependence of loop tack on benzoyl peroxide concentration is shown in Figure 1 for various coating thickness. The plot indicates that tack increases with benzoyl peroxide loading up to 2 phr, after which it decreases with further increase in the curing agent. This observation is attributed to the increase in the crosslinking of rubber chains which enhances the cohesiveness of the adhesive. However, after the optimum amount of benzoyl peroxide of 2 phr, increasing crosslinking of rubber chains would restrict the chain mobility, thus reduces the wettability of adhesive on the substrate as reflected by the lower tack value as benzoyl peroxide is further increased. The viscous component of the adhesive is greatly reduced as crosslinking increases, hence decreases the wettability of the adhesive. Figure 1 also shows that for a fixed benzoyl

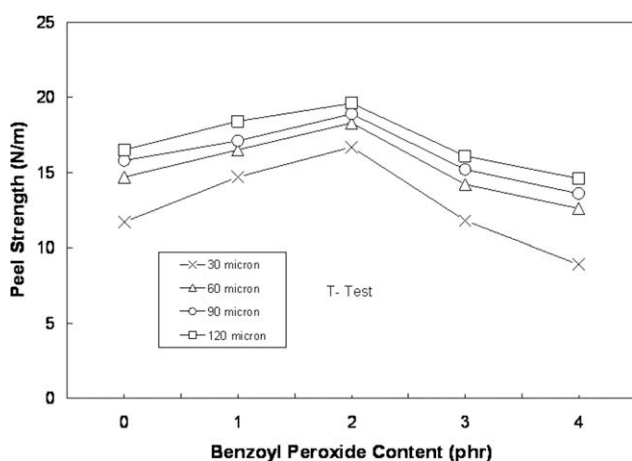


Figure 2 Variation of peel strength (*T*-test) of adhesive with concentration of benzoyl peroxide at various coating thickness.

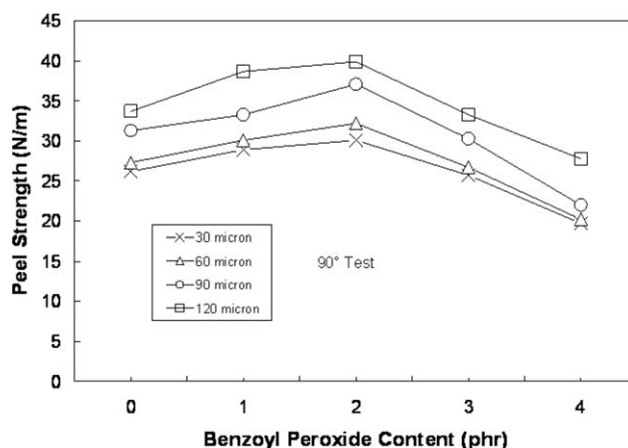


Figure 3 Variation of peel strength (90° test) of adhesive with concentration of benzoyl peroxide at various coating thickness.

peroxide loading, loop tack increases with increase in coating thickness where 120- μ m coated sample consistently indicates highest tack value than the other lower coating thickness. This observation is attributed to the increase in adhesive volume which enhances the viscoelastic property of the adhesive.²³ This observation is consistent to the general belief that peel force increases with increasing adhesive thickness up to a certain limit.²⁴ Increasing coating thickness causes the shift from cohesive to adhesive failure.^{25,26}

Peel strength

Figures 2–4 show the effect of benzoyl peroxide loading on the peel strength of natural rubber-based adhesives using *T*-, 90° and 180° peel tests, respectively. For the three modes of testing, peel strength increases gradually up to 2 phr benzoyl peroxide and drops after the optimum level of benzoyl

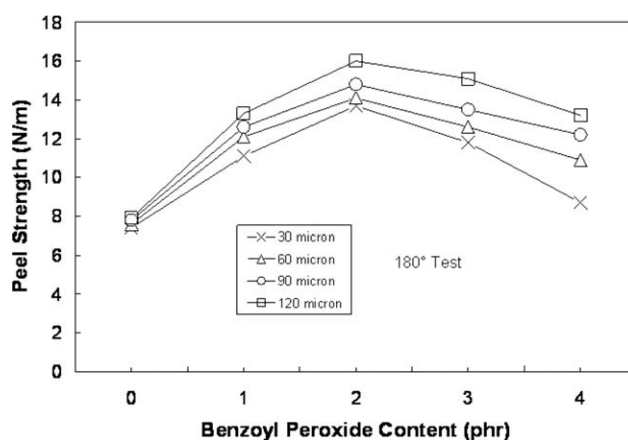


Figure 4 Variation of peel strength (180° test) of adhesive with concentration of benzoyl peroxide at various coating thickness.

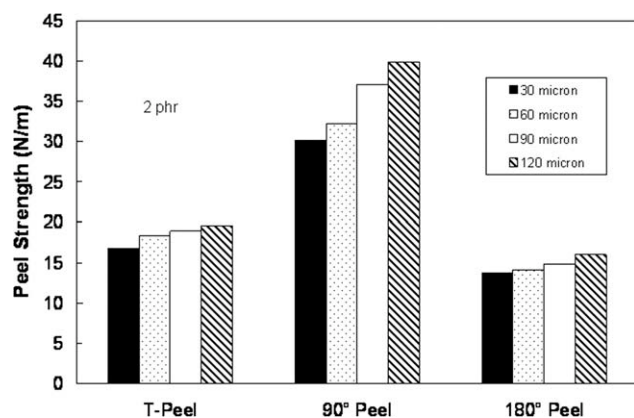


Figure 5 Comparison of peel strength between various coating thickness for three modes of peel tests at 2 phr of benzoyl peroxide.

peroxide. Again, the initial increase in peel strength is associated with the increase in crosslinking of rubber chains which enhances the cohesive strength of the adhesive. However, after the optimum loading of benzoyl peroxide, peel strength decreases due to the over crosslinking of rubber chains. The highly crosslinked network decreases the chain mobility and hence wettability drops. The crosslinked network increases the elastic component of the rubber and adhesive failure occurs.²⁴ The gradual drop in peel strength after 2 phr of benzoyl peroxide loading is due to the decrease in wettability resulting from the increase in crosslinking which increases the elastic component of the adhesive. All the three modes of peel tests consistent show the same behavior as illustrated in Figures 2–4. Comparison of peel strength for the various modes of testing is indicated in Figure 5 at the optimum loading of benzoyl peroxide, i.e., 2 phr. For all coating thickness, the 90° peel test consistently shows the highest peel value followed by T- and 180° peel tests. This observation

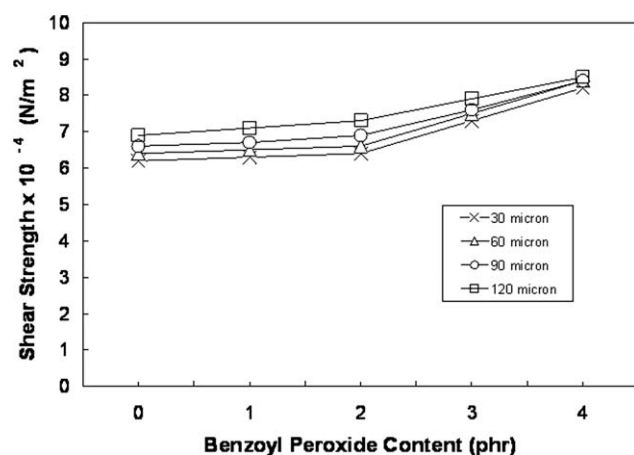


Figure 6 Variation of shear strength of adhesive with concentration of benzoyl peroxide at various coating thickness.

is attributed to the angle of testing where greater strain-induced crystallization of natural rubber^{27,28} occurs in the 90° peel test, thus the adhesive layer itself cannot easily be ruptured.²⁹ As in the case of loop tack, peel strength increases with coating thickness for all the modes of peel tests as shown in Figure 5. This increase is again associated to the increase in adhesive volume which in turn enhances the viscoelastic property of the adhesive. In addition, the cohesive strength of the adhesive is increased following the increase in adhesive volume for thicker coating thickness.

Shear strength

The effect of the benzoyl peroxide loading on the shear strength of SMR L-based pressure-sensitive adhesives is shown in Figure 6. For all the coating thickness investigated, shear strength increases gradually with increasing benzoyl peroxide content up to 2 phr benzoyl peroxide, after which a greater rate of increase in shear strength is observed. This observation is attributed to the increase in the cohesive strength due to the increase in crosslinking of rubber chains. After 2 phr of benzoyl peroxide loading, the failure mode is essentially adhesive in nature as crosslinking increases further. In other words, the holding power of adhesive is significantly enhanced at higher benzoyl peroxide loading due to the increase of cohesive strength of adhesive. Figure 7 shows the effect of coating thickness on the shear strength of adhesives for various loadings of benzoyl peroxide. For benzoyl peroxide loading below 2 phr, shear strength increases gradually with increasing coating thickness, an observation which is attributed to the increase in volume of adhesive which enhances the resistance to shearing action as coating thickness is increased. However, as benzoyl peroxide

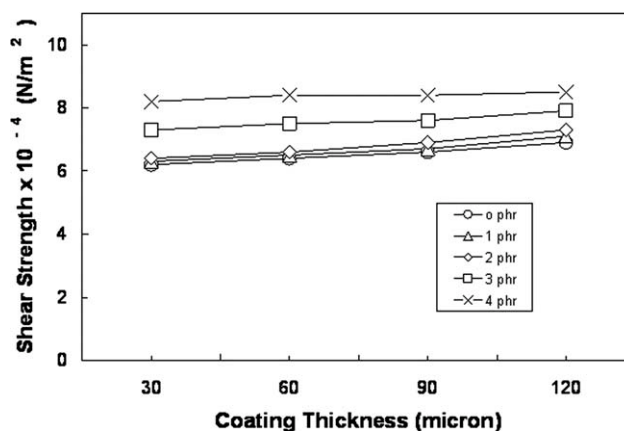


Figure 7 Variation of shear strength of adhesive with coating thickness for various concentration of benzoyl peroxide.

loading is further increased, shear strength shows less dependence on coating thickness especially for 4 phr benzoyl peroxide content. The shear strength at 4 phr benzoyl peroxide is in fact virtually independent on coating thickness. This observation suggests that shear strength is not sensitive to coating thickness when a critical crosslinking of rubber chains is achieved. At this critical crosslinking state, the effect of crosslinking of rubber chains, i.e., network constraint, eclipses the effect of adhesive volume on the shear behavior of natural rubber-based pressure-sensitive adhesives.

CONCLUSIONS

From this study, the following conclusions can be drawn:

1. Loop tack of crosslinked natural rubber-based adhesive passes through a maximum value at 2 phr of benzoyl peroxide loading. This observation is attributed to the effect of crosslinking of rubber chains which enhances the cohesive strength of the adhesive. Further addition of benzoyl peroxide beyond 2 phr reduces the wettability of adhesive due to the reduction of chain mobility of over crosslinked rubber chains. Loop tack increases with increase in coating thickness, an observation which is attributed to the increase in adhesive volume which enhances the viscoelastic property of the adhesive.
2. For the three modes of peel testing, peel strength increases up to 2 phr benzoyl peroxide loading, an observation which is attributed to the increase in cohesive strength resulting from the crosslinking of adhesive. However, for higher benzoyl peroxide loading, over crosslinked rubber network decreases the rubber chain mobility and hence reduces the wettability of adhesive on substrate as shown by the lower peel strength. The 90° peel test exhibits the highest peel strength due to the greater strain-induced crystallization of natural rubber. Peel strength also increases with coating thickness for the three modes of peel tests.
3. Shear strength increases gradually with increasing benzoyl peroxide loading up to 2 phr, after which shear strength indicates a greater rate of

increase with further loading of benzoyl peroxide. This observation is attributed to the steady increase in the cohesive strength resulting from increasing crosslinking of rubber chains. Shear strength is virtually independent on coating thickness at high loading of benzoyl peroxide. This finding suggests that the effect of adhesive volume on shear strength becomes insignificant for highly crosslinked adhesive.

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