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ADHESION PROPERTIES OF STYRENE-BUTADIENE RUBBER-BASED ADHESIVE CROSSLINKED BY BENZOYL PEROXIDE

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ABSTRACT

Adhesion properties of benzoyl peroxide crosslinked styrene-butadiene rubber (SBR)-based pressure-sensitive adhesive were investigated using coumarone-indene, toluene and polyethylene terephthalate (PET) film as the tackifier, solvent and coating substrate respectively. The dosage of benzoyl peroxide ranged from 0 to 5 parts per hundred parts of rubber (phr). Four coating thicknesses, i.e. 30μm, 60μm, 90μm and 120 μm were used in this study. The modes of peel tests were 90°, 180° and T- peel tests. Loop tack, peel and shear strength were determined by a Lloyd Adhesion Tester operating at 10-60 cm min^{-1}. Results show that loop tack and peel strength increase with benzoyl peroxide dosage up to 2 phr before decreasing with further addition of benzoyl peroxide. This observation is attributed to the optimum crosslinking of SBR where optimum cohesive and adhesive strength occurs at 2 phr of benzoyl peroxide. Shear strength, however, increases steadily with increasing benzoyl peroxide dosage, an observation which is attributed to the steady increase in cohesive strength. In all cases, the adhesion properties of adhesives increase with testing rate and coating thickness.

Keywords: adhesive; rubber; benzoyl peroxide; adhesion; rate of testing.

1. INTRODUCTION

Many studies on the adhesion behaviour of pressure-sensitive adhesives have been carried out using linear, uncrosslinked polymers as the matrix. However, literature review reveals that very few adhesion studies involving crosslinked polymer were published. Verdier et al. (1998) studied the peel property of crosslinked and uncrosslinked acrylic pressure-sensitive adhesive. It was observed that cohesive failure cannot be obtained with slightly crosslinked adhesive. Hamed and Preechatiwong (2001) reported the effect of crosslinking on the rate and temperature response of peel adhesion of natural rubber bonded to polyethylene terephthalate. The study showed that for lightly crosslinked natural rubber, interfacial failure between rubber and PET film occurred. The highly crosslinked natural rubber has low peel strength due to reduction in normal viscoelastic energy dissipation as well as the loss of strain crystallization. Meanwhile, Wang et al. (2006) observed remarkable increase in cohesive strength, tensile and thermal properties with organic monmorillonite loading up to 10 phr in vulcanized silicone rubber adhesive system. The effect of UV crosslinkable microsphere

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pressure-sensitive adhesives on adhesive properties was also investigated by Kajtna and Krajnc (2011). They observed that the decrease in adhesion may be correlated with higher crosslinking density. On the other hand, Nakamura et al. (2013) reported that the interfacial adhesion increases while the cohesive strength decreases as crosslinking and probe rate decreases. The researchers have recently carried out a few studies on the adhesion properties of natural rubber and epoxidized natural rubber adhesives crosslinked by benzoyl peroxide (Poh & Cheong, 2012; Poh & Suid, 2014; Poh & Lim, 2014). Results revealed that the loop tack and peel strength of the adhesives show maximum values at an optimum dosage of benzoyl peroxide loading. However, the shear strength of the adhesives increases steadily with benzoyl peroxide dosage due to the increase in cohesive strength. Nevertheless, reports on the adhesion properties of crosslinked synthetic rubber adhesives are very limited. Owing to the scarcity of research on the adhesion behavior of crosslinked synthetic rubber adhesive, it is thus the objective of this article to discuss systematically on our research findings on the adhesion properties of styrene-butadiene rubber adhesive crosslinked by benzoyl peroxide.

2. METHODOLOGY

2.1 Materials

Styrene-butadiene rubber (SBR) was used as the synthetic elastomer for the preparation of the pressure sensitive adhesives. It was supplied by Bayer Company (Penang, Malaysia) and has a 33.5% by weight of target-bound styrene. Coumarone-indene resin, toluene, PET film and benzoyl peroxide were used as the tackifier, solvent, substrate and crosslinking agent respectively throughout the study. All the chemicals were used as received without further purification.

2.2 Preparation of Adhesive

SBR was masticated on a two roll-mill for 10 minutes. 5 g of the masticated rubber was shredded into small pieces to facilitate easy dissolution in 30 mL of toluene. The rubber solution was then left overnight at 30°C. 2 g of pulverized coumarone-indene resin which corresponded to 40 phr of tackifying resin was gently added into the rubber solution and left for 2 hours. Five different loadings of benzoyl peroxide, i.e., 0.05, 0.10, 0.15, 0.20, and 0.25 g corresponding to 1, 2, 3, 4, and 5 phr of benzoyl peroxide were added to the adhesive solution. One control sample without benzoyl peroxide was also prepared for the purpose of comparison.

2.3 Measurements

2.3.1 Tack

A SHEEN hand coater (SHEEN Instruments Ltd., Teddington, Middlesex, UK) was used to coat a polyethylene terephthalate (PET) substrate of dimensions 4 cm x 25 cm at its centre (4 cm x 4 cm) at various adhesive coating thicknesses. The coated sample was left at room temperature for 24 hours before heating in oven at 80°C for 30 minutes to crosslink the rubber. The adhesive-coated area of the substrate was gently brought into contact with a glass plate. A Lloyd Adhesion Tester (Model LRX Plus with NEXYGEN software) operating at various testing rates ranging from 10-60 cm min^{-1} was used to determine the debonding force from the glass plate. The average debonding force was calculated from the three highest

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peaks from the load-propagation plot. Loop tack is expressed as the bonding force per area of contact with the glass plate (N m^{-2}).

2.3.2 Peel Strength

Table 1 shows the dimensions of PET substrates used for the T-, 90º and 180º peel tests. The adhesive was coated from the end of the substrate at a coating area of 10 cm x 4 cm to form the base stock at various coating thicknesses. The uncoated substrate (face stock) was carefully laid on the base stock. The test specimen was then left at room temperature for 24 hours before heated in an oven at 80°C for 30 minutes to crosslink the rubber. Peeling force for the three modes of peel test was measured by a Lloyd Adhesion Tester operating at 10-60 cm min^{-1}. The average peeling force was calculated from the three highest peaks from the load-propagation plot. Peel strength is expressed as the average load per width of the bond line required to separate progressively a flexible member (ASTM D 907).

Table 1. Dimensions of Peel Test Sample.

Mode of Peel Test	Base Stock	Face Stock
T- Peel	20 cm x 4 cm	20 cm x 4 cm
90° Peel	20 cm x 4 cm	15 cm x 7 cm
180° Peel	25 cm x 4 cm	10 cm x 10 cm

2.3.3 Shear Strength

A 20 cm x 4 cm PET film was used for the shear test. A SHEEN hand coater was used to coat the substrate from the end of the film at a coated area of 10 cm x 4 cm at various coating thicknesses. One end of the uncoated substrate was gently laid on the coated area of the base stock to form a shear test specimen. It was then conditioned at room temperature for 24 hours before heated in oven at 80°C for 30 minutes to crosslink the rubber. The shear force was determined using a Lloyd Adhesion Tester operating at 10-60 cm min^{-1}. The testing distance was set at 10 cm which corresponded to the length of the coated area. The peak force recorded from a plot of force against time was taken as the shear force. Shear strength was expressed as the shear force per unit area of testing (N m^{-2}).

3. RESULTS AND DISCUSSION

The effects of benzoyl peroxide loading and testing rate on the adhesion properties of SBR-based adhesive are discussed systematically below.

3.1 Tack

Figure 1 shows the dependence of loop tack on benzoyl peroxide loadings at 30 cm min^{-1} for various coating thicknesses. The graph clearly indicates that tack increases with benzoyl peroxide up to 2 phr dosage, after which it decreases with further increase in the benzoyl peroxide loading for all the coating thicknesses studied. The increase in tack up to an optimum value of benzoyl peroxide at 2 phr is attributed to the increase in the crosslinking of the rubber chains which enhances the cohesiveness of the adhesive. This enhancement culminates at 2 phr benzoyl peroxide as shown by the maximum tack value. However, after the optimum amount of the crosslinking agent, the rubber chains are over-crosslinked and this

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would restrict the chain mobility and hence lower the wettability of adhesive as shown by the lower tack value with further addition of benzoyl peroxide. In other words, the viscous component of the adhesive is greatly reduced after the optimum benzoyl peroxide dosage of 2 phr. For a fixed benzoyl peroxide content, tack increases with coating thickness. This observation is attributed to the increase in adhesive amount as coating thickness is increased, whereby the viscoelastic property of the adhesive is greatly enhanced (Leong et al., 2003). The shift from cohesive to adhesive failure occurs when coating thickness is increased (Poh & Chee, 2007). The effect of testing rate on the tack behavior is shown in Figure 2 at 2 phr for 30 μm and 120 μm coating thicknesses. For both coating thicknesses, tack increases steadily with testing rate. This observation is explained by the difference in viscoelastic response when the testing rate is varied (Satas, 1982). At low testing rate, the viscoelastic response is predominantly viscous and cohesive failure occurs, whereas at high testing rate, the viscoelastic response is predominantly elastic whereby failure mode is essentially adhesive in nature.

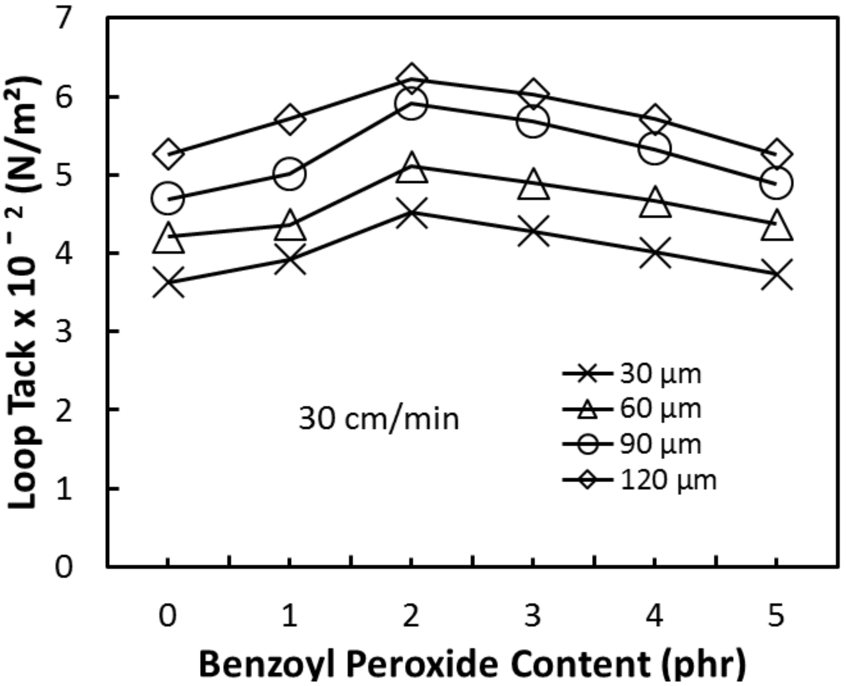

Figure 1: Variation of Loop Tack of SBR-Based Adhesive with Benzoyl Peroxide Content at Various Coating Thicknesses.

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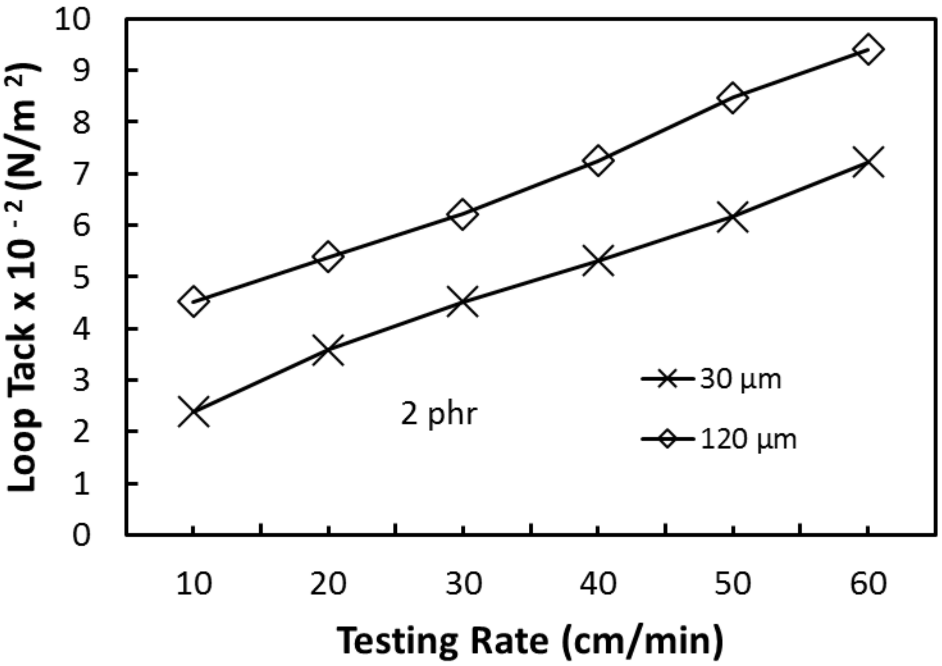

Figure 2: Dependence of loop tack on rate of testing at 2 phr Benzoyl Peroxide content for 30 µm and 120 µm coating thicknesses.

3.2 Peel Strength

Figures 3-5 show the variation of peel strength with benzoyl peroxide loading for the T-, 90º and 180º peel samples respectively at various coating thicknesses. In all cases, peel strength increases with benzoyl peroxide up to 2 phr dosage and thereafter, decreases with further addition of benzoyl peroxide. The initial increase in peel strength is again attributed to the increase in cohesive strength due to the increase in crosslinking of rubber chains. The decrease in peel strength after the optimum loading of benzoyl peroxide is associated to the over crosslinking of rubber chains which decreases the chain mobility and hence decreases the wettability of the adhesive. The elastic component of the viscoelastic response increases with crosslinking of rubber chains. This means that higher interfacial debonding, i.e. adhesive failure occurs as benzoyl peroxide loading is increased. Figure 6 shows the dependence of peel strength on coating thickness for the three modes of peel tests. It is obvious that peel strength increases with coating thickness, an observation which is consistent with the general belief that peel force increases with increasing adhesive thickness up to a certain limit (Satas, 1982). This observation is attributed to the increase in the amount of adhesive which enhances the viscoelastic response as discussed earlier in the case of tack behaviour. Figure 6 also shows that the 90º peel test consistently exhibits the highest peel value for all coating thicknesses, an observation which is associated to the angle of testing. Higher peel force is needed in the 90º peel test where the rubber chains undergo more strain-induced crystallization (Davies et al., 1983) which enhances the resistance to rupture under an applied load, so that the adhesive layer itself cannot easily be ruptured (Skeist, 1990). The dependence of peel strength (90° peel test) on the testing rate at 2 phr benzoyl peroxide loading is shown in Figure 7 for 30 µm and 120 µm coating thicknesses. For both coating thicknesses, peel strength increases with testing rate. This observation can be similarly

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explained by the changes in viscoelastic responses when testing rate is increased. At lower rate of testing, the viscoelastic response is primarily viscous and cohesive failure occurs whereas at higher rate of testing, the viscoelastic response is predominantly elastic resulting in adhesive failure mode.

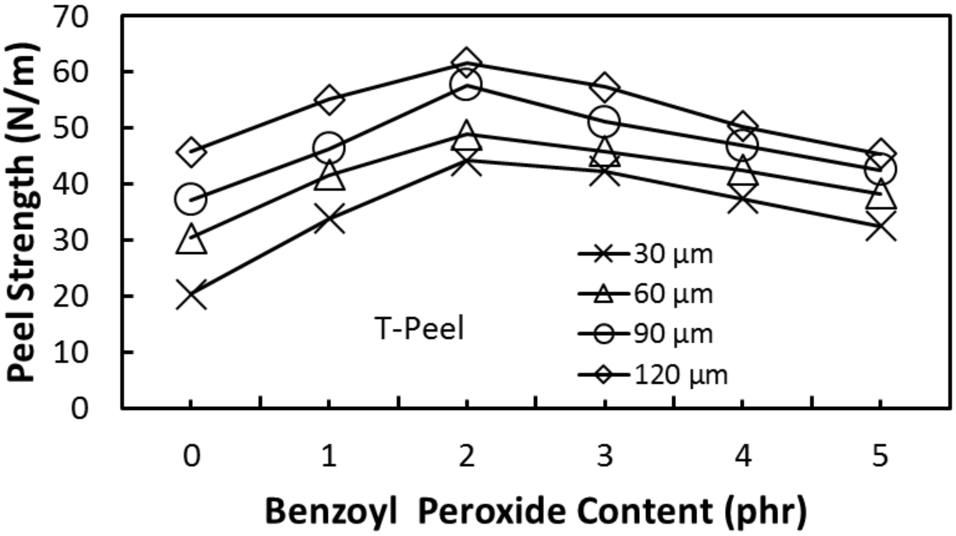

Figure 3: Variation of peel strength (T peel test) of SBR-based adhesive with benzoyl peroxide content at various coating thicknesses.

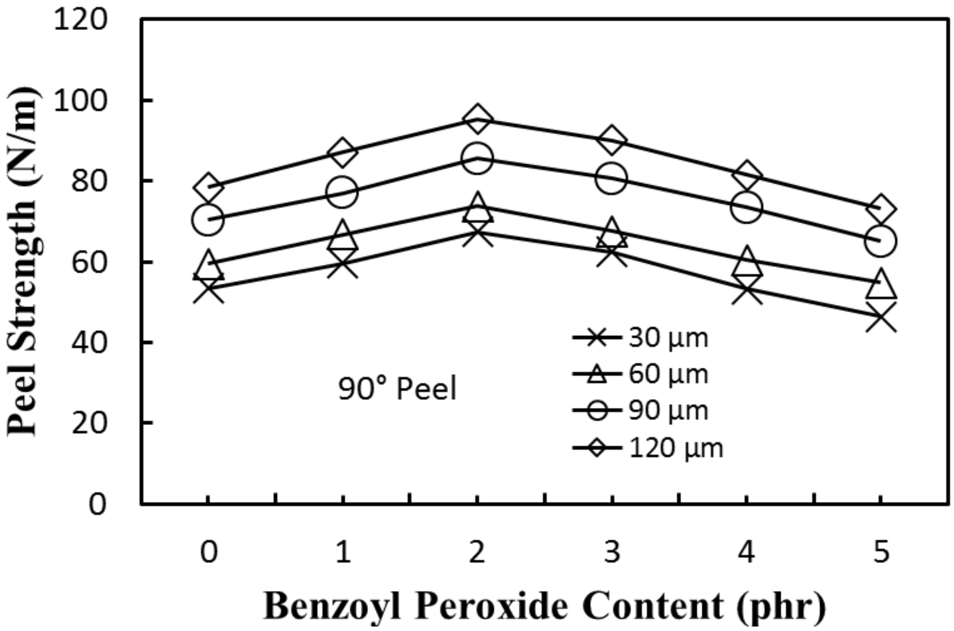

Figure 4: Variation of peel strength (90º peel test) of SBR-based adhesive with benzoyl peroxide content at various coating thicknesses.

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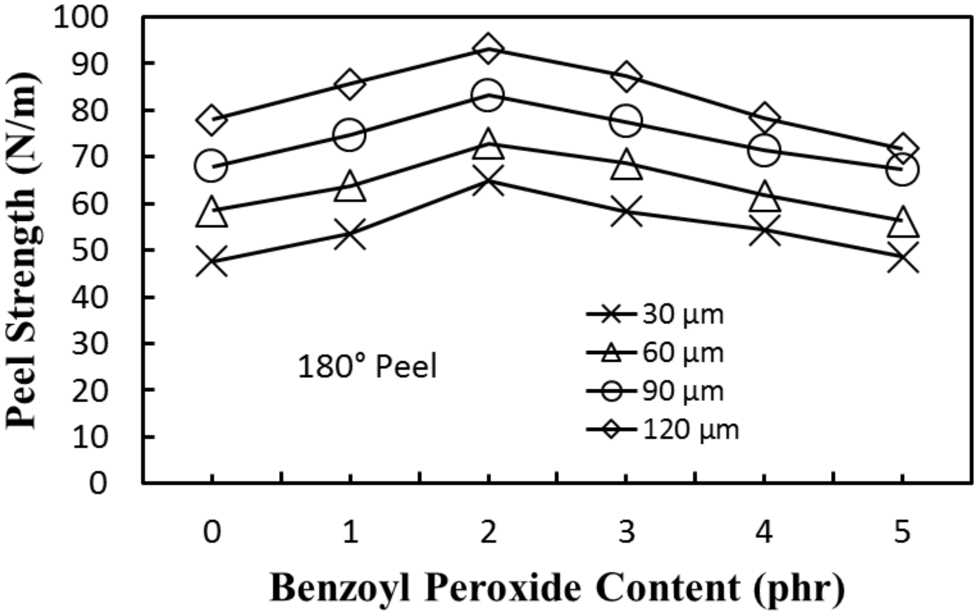

Figure 5: Variation of peel strength (180° peel test) of SBR-based adhesive with benzoyl peroxide content at various coating thicknesses.

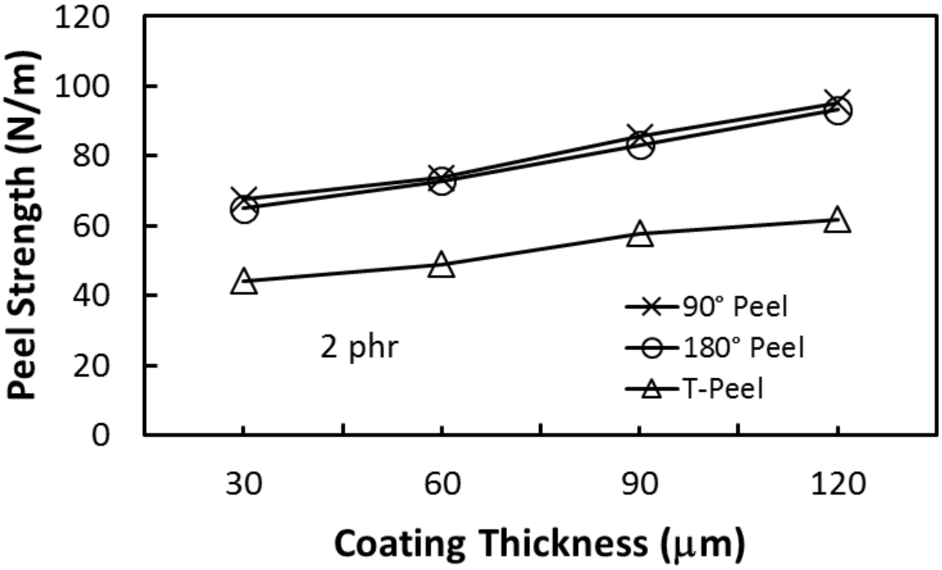

Figure 6: Variation of peel strength coating thickness for the three modes of peel tests at 2 phr of benzoyl peroxide loading.

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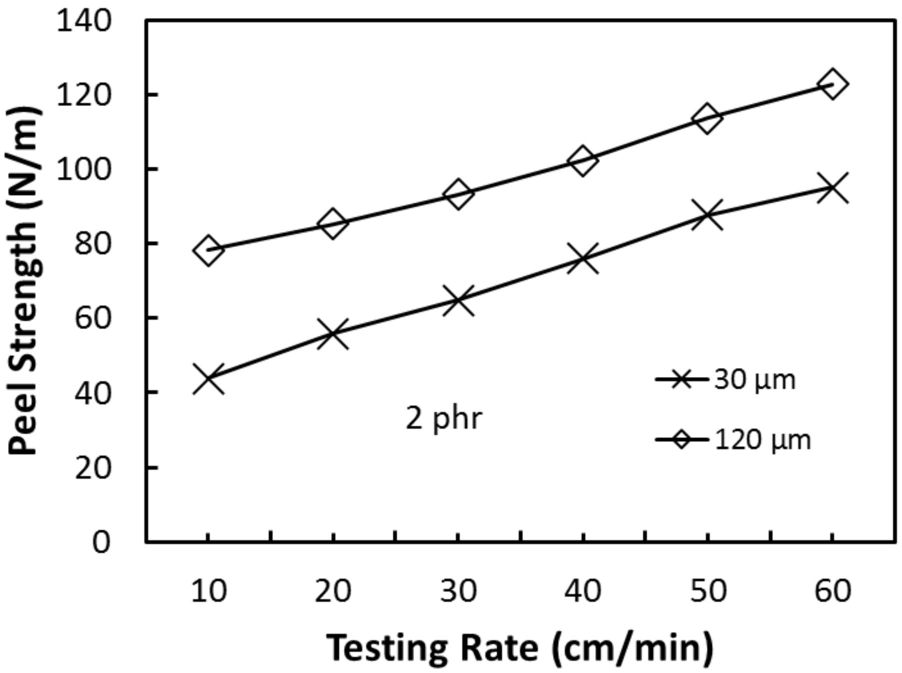

Figure 7: Dependence of peel strength (90° peel test) on rate of testing at 2 phr benzoyl peroxide content for 30 µm and 120 µm coating thicknesses.

3.3 Shear Strength

The variation of shear strength with benzoyl peroxide dosage for various coating thicknesses is illustrated in Figure 8. The plot indicates clearly that shear strength increases steadily with benzoyl peroxide dosage for all coating thicknesses investigated. This observation is attributed to the steady increase in the cohesive strength of the adhesive with increase in crosslinking of rubber chains due to further addition of benzoyl peroxide. The increase of cohesive strength of adhesive enhances the holding power of adhesive as shown by the higher shear strength as crosslinking is increased. For a fixed benzoyl peroxide loading, shear strength increases with coating thickness, similar to the results observed for tack and peel strength. This phenomenon is again ascribed to the increase in the amount of adhesive which increases the shearing resistance as coating thickness is increased. Figure 9 indicates the effect of testing rate on the shear strength of the adhesive at 2 phr benzoyl peroxide loading for 30 µm and 120 µm coating thicknesses. Shear strength also increases steadily with testing rate for both coating thicknesses. This observation is attributed to the different viscoelastic responses at low and higher testing rates, i.e. viscous and elastic responses resulting in the cohesive and adhesive failure modes respectively. From Figure 9, it is observed that the rate of increase in shear strength is slower after 30 cm min $^{-1}$ testing rate. This finding suggests that the effect of elastic response at a higher testing rate is less significant compared to viscous response at a lower testing rate, i.e. below 30 cm min^{-1}.

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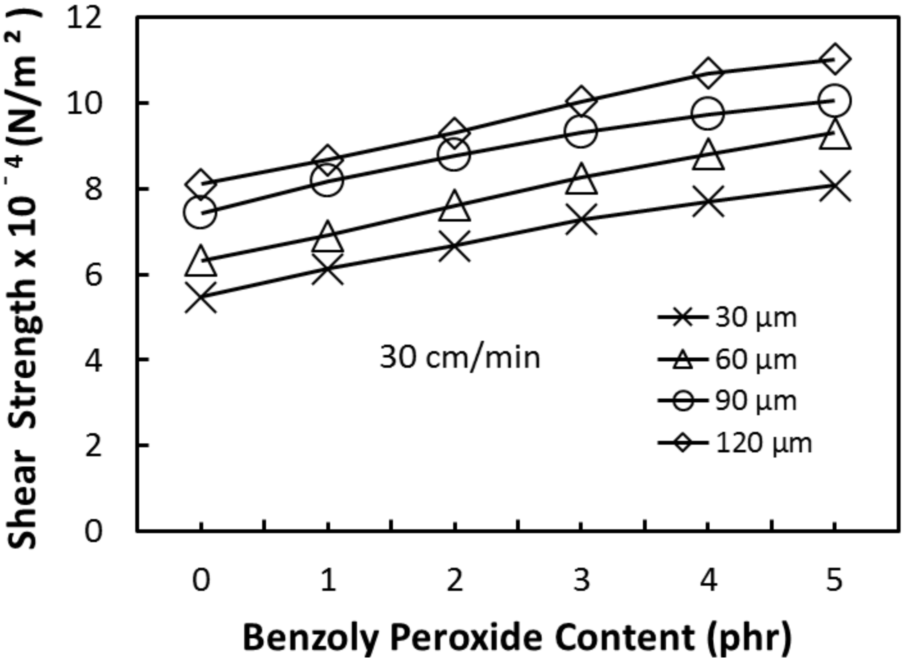

Figure 8: Variation of shear strength of SBR-based adhesive with benzoyl peroxide content at various coating thicknesses.

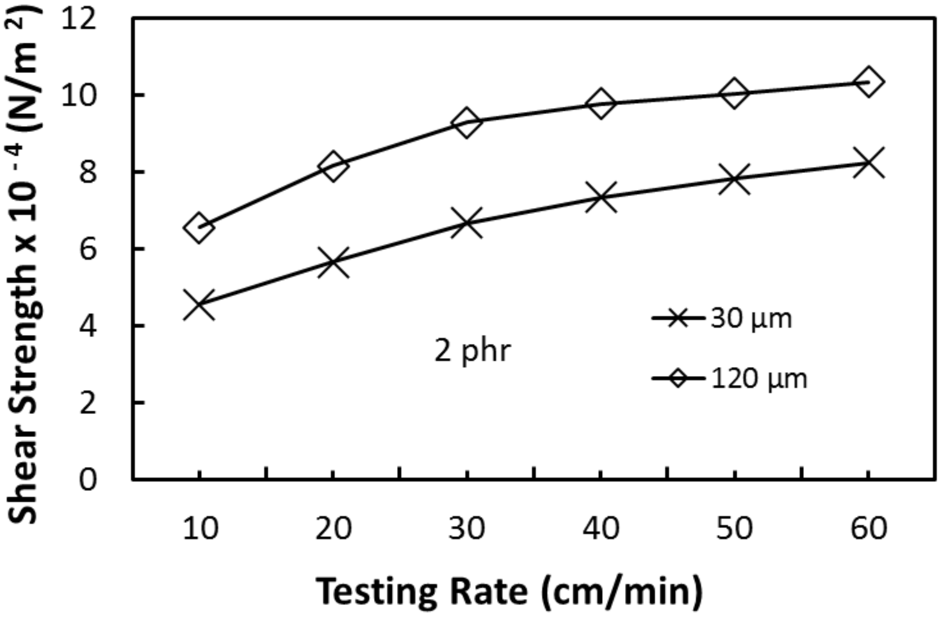

Figure 9: Dependence of shear strength on rate of testing at 2 phr benzoyl peroxide content for 30 µm and 120 µm coating thicknesses.

4. CONCLUSIONS

Loop tack and peel strength of SBR-based adhesive increases with benzoyl peroxide loading up to 2 phr before it decreases with further addition of benzoyl peroxide. This observation is attributed to the increase in crosslinking of the rubber chains which enhances the cohesive

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strength culminating at 2 phr benzoyl peroxide. Over crosslinking decreases the tack and peel strength of the adhesive due to the decrease in wettability of adhesive. However, for the shear strength, it increases steadily with benzoyl peroxide as a result of steady increase in cohesive strength. The 90º peel test consistently shows the highest peel strength compared to the T-peel and 180° peel tests, an observation which is associated to the angle of testing where higher peel force is needed in the former. The adhesion property increases with coating thicknesses, an observation which is attributed to the higher amount of adhesive in thicker coated sample which enhances the viscoelastic responses of the adhesive. In all cases, the adhesion properties increase with the rate of testing. This phenomenon is ascribed to the changes in viscoelastic responses. At a low rate of testing, the viscoelastic response is predominantly viscous whereby cohesive failure occurs. However, as the rate of testing is increased, the viscoelastic response changes to elastic response and failure mode is essentially adhesive in nature. The dependence of shear strength on testing rate is less significant above the testing rate of 30 cm min^{-1}.

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