

EFFECT OF CROSS -LINKING ON ADHESION PROPERTY OF BENZOYL-PEROXIDE-CURED EPOXIDIZED NATURAL RUBBER (ENR 25)/ ACRYLONITRILE-BUTADIENE RUBBER (NBR) BLEND ADHESIVE

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Abstract – The effect of benzoyl peroxide loading on the adhesion properties of cross-linked epoxidized natural rubber (ENR 25) / acrylonitrile-butadiene rubber (NBR) blend adhesives were studied using coumarone indene resin resin and toluene as tackifier and solvent respectively. Throughout the study, benzoyl peroxide was used to crosslink the rubber blend adhesive with the loading from 1 to 5 parts per hundred part of rubber (phr) at 80°C for 30 min. The SHEEN hand coater was used to coat the adhesive on polyethylene terephthalate (PET) at 30 µm and 120 µm coating thickness. The adhesion properties were determined by a Lloyd adhesion tester operating at 30 cm min⁻¹. Results shows that the loop tack and peel strength of the ENR 25/NBR adhesive pass through a maximum value at 2 phr of benzoyl peroxide. This observation is attributed to the optimum crosslinking of rubber blend chains where optimum cohesive and adhesive strength is obtained. The shear strength, however, increases steadily with increasing benzoyl peroxide loading due to the steady increase in the cohesive strength of crosslinked rubber blend adhesive. In all cases, the adhesion properties of adhesives increase with increase in coating thickness.

Keywords: Adhesion, Adhesive, Rubber, Crosslinking, Tackifier.

I. INTRODUCTION

Rubber can be divided into two groups, natural rubber (NR) and synthetic rubber. Standard Malaysian Rubber (SMR) and epoxidized natural rubber (ENR) belong to NR whilst acrylonitrile-butadiene rubber (NBR) is one type of synthetic rubber used in this research. Natural rubber obtained from trees was the only source of rubber until the advent of the synthetic polymers in the early part of 20th century. The mechanical properties of NR are generally superior to those of synthetic rubber. However, NR cannot compete with the speciality synthetic elastomers with regard to such properties as gas permeability and oil resistance.

Therefore, NBR which have the superior properties to be used for its resistance to various organic oils, fuels and chemicals in seals, gaskets and hoses is used to blend with ENR 25 [1, 2]. Pressure sensitive adhesive (PSA) are viscoelastic materials that can adhere strongly to solid surfaces upon application under light pressure in very short time without heating or heavy pressure. They do not undergo any physical transformation or chemical reaction during the bonding process [3, 4]. Sulfur, peroxide and other crosslinking agent are applied to chemically react with rubber or plastic to form a three-dimensional network structure. The process increases strength and resiliency of polymers, endowing them with versatile applications. Crosslinking with peroxides has been known since 1915 when Ostromyslenski disclosed that natural rubber could be transformed into a

crosslinked state with dibenzoyl peroxide. However, there was little interest in peroxide crosslinking until the development of fully saturated ethylenepropylene copolymers in the early 1970s [1, 5]. It is desirable to have PSA that possess high cohesive strength in most applications. This desired property is generally incorporated through optimum crosslinking of the adhesive polymers. For solvent-based adhesives, crosslinking is introduced after the polymer synthesis to avoid making high viscosity solutions that are difficult to coat. Post-crosslinking is also commonly employed for water based PSA and thermally induced through formations of ionic or covalent links [6].

In this study, we report the study of applying benzoyl peroxide within pressure sensitive adhesives to achieve crosslinking to enhance PSA performance. With regard to crosslinked rubber based adhesive, we have carried out several studies on adhesion properties of the adhesive. Poh and Cheong [7] have studied the adhesion behaviour of natural rubber-based adhesives (SMR-L) crosslinked by benzoyl peroxide. On the other hand, Poh and Suid [8] observed the dependence of adhesion properties of cross-linked epoxidized natural rubber (ENR 25)-based pressure-sensitive adhesives on benzoyl peroxide loading in the presence of gum rosin and petroresin tackifiers. Meanwhile, Poh and Lim [9] also investigated effect of cross-linking on adhesion property of benzoyl-peroxide-cured epoxidized natural rubber (ENR 50) adhesives. Besides, Poh and Teh

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[10] have studied the dependence of adhesion property of epoxidized natural rubber (ENR 25)/ethylene-propylene-diene rubber blend adhesives crosslinked by benzoyl peroxide. In view of the scarcity of data reported on the adhesion properties of crosslinked rubber blend adhesives, it is thus the aim of this article to discuss some of our research results on adhesion property of of ENR 25/NBR based adhesives.

2. Experiment

2.1. Materials. ENR 25 having 25 mol % of epoxidation was used as the elastomer for the preparation of PSA. The rubbers were supplied by Rubber Research Institute of Malaysia (Kuala Lumpur, Malaysia). Acrylonitrile-butadiene rubber (NBR) which has a bound acrylonitrile content of 33% was supplied by Bayer Company (Penang, Malaysia). Coumarone indene resin was used as the tackifier. It was freshly supplied by Mukmin Enviro Company, Penang (Malaysia). Toluene and benzoyl peroxide were used as the solvent and crosslinking agent, respectively throughout the experiment. Polyethylene terephthalate (PET) film was chosen as the coating substrate throughout the experiment. All the materials and chemicals used were freshly supplied and no purification was carried out prior to use.

2.2 Preparation of adhesive. After mastication of rubber on a two-roll mill for 10 min, 5 g of masticated rubber were shredded into small pieces. Blends ratios in grams of ENR 25/NBR rubber blend is fix at 1/4, corresponding to 20% ENR 25 was prepared. The rubber blend was dissolved in 30 ml of toluene. The rubber solution was then left overnight (24 hours) to ensure complete dissolution. With constant stirring, 2 g of pulverized coumarone indene resin which corresponded to 40 phr of resin was added slowly to the rubber solution. The resulting adhesives were left for 2 hours at room temperature before the addition of benzoyl peroxide. Five different dosages of benzoyl peroxide, that is, 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. Besides, one control sample without benzoyl peroxide was also prepared for comparison purposes.

3. Measurement

3.1. Loop tack. Loop tack test, which is the peel test involving low contact pressure and short application time [11]. The adhesive was coated on a PET film with dimension of 4 cm × 25 cm using a SHEEN Hand Coater. The coated area was 4 cm × 4 cm at the center of the PET film at a coating thickness of 30 μm and 120 μm respectively. The sample was conditioned at room temperature (30°C) for 24 h before heating in an oven at 80°C for 30 minutes to crosslink the rubber blend. The PET film was then formed into a loop and brought into contact with a glass plate until the coated area was in full contact with the glass plate. A Lloyd Adhesion Tester operating at a testing rate of 30 cm/min was used to determine the pulling force to detach the loop from the glass plate. The loop tack value is expressed as the average debonding force per area of contact [N/m²].

3.2. Peel strength. Three modes of peeling tests were carried out, i.e. T-peel test, 90°-peel and 180°-peel tests. PET film was used for the base stock and face stock in the peel tests. The dimensions of PET film for the T- peel test were 20

cm x 4 cm. For the 90° peel test, the dimensions were 20 cm x 4 cm and 15 cm x 7 cm for the base stock and face stock respectively. The respective dimensions of the substrate were 25 cm x 4 cm and 10 cm x 10 cm for the 180° peel test. The adhesive was coated from the end of the PET film at a coating area of 10 cm × 4 cm film at a coating thickness of 30 μm and 120 μm respectively by using a SHEEN Hand Coater. The face stock was then placed on the coated PET film (base stock). The sample was then conditioned at room temperature (30°C) for 24 h before heating in an oven at 80°C for 30 minutes to crosslink the rubber blend. A Lloyd Adhesion Tester operating at a testing rate of 30 cm/min was used to determine the peeling force of the adhesive. The average peeling force was determined from the three highest peaks recorded from the load-propagation graph. Peel strength is defined 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).

3.3. 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 a coating thickness of 30 μm, and 120 μm respectively by using a SHEEN Hand Coater. One end of the face stock (10 cm × 4 cm) was gently placed on the coated area of the base stock. The sample was conditioned at room temperature (30°C) for 24 h before heating in an oven at 80°C for 30 minutes to crosslink the rubber blend. A Lloyd Adhesion Tester operating at a testing rate of 30 cm/min 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).

4. Results and Discussion

4.1. Tack. Tack is defined as an adhesion property, which indicates how quickly an adhesive can wet out and make intimate contact with a surface of substrate [12]. The dependence of loop tack on benzoyl peroxide content at 30 μm and 120 μm coating thickness is shown in Figure 1.

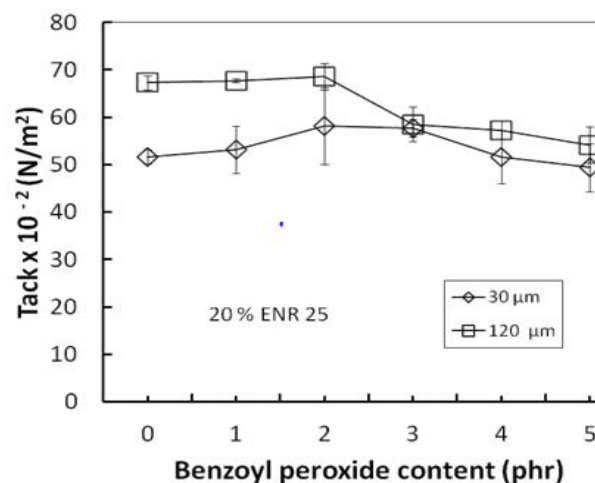


FIGURE 1: Variation of loop tack of ENR 25/NBR blend adhesive with benzoyl peroxide content at 30μm and 120 μm coating thickness.

The plot shows 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 ascribed to the increase in the cross-linking of ENR 25/NBR rubber blend chain - which enhances the cohesive strength of the adhesives - culminates at 2 phr of benzoyl peroxide loading. The initial increase in tack with benzoyl peroxide before 2 phr suggests that adhesive strength still dominates the failure mode. However, after the optimum amount of benzoyl peroxide of 2 phr, tack decreases rapidly with further loading of benzoyl peroxide.

This phenomenon is primarily attributed to the decrease in wettability of the adhesives due to the over crosslinking of the rubber blend adhesive. When the crosslinking of the rubber blend adhesive is increased, the viscous component of the adhesive is greatly reduced; hence wettability of the adhesive is decreases. In other word, the failure mode is predominantly adhesive in nature which occurs at interface between adhesive and adherend. Figure 1 also shows that for a fixed benzoyl peroxide loading, loop tack increases when thecoating thickness is increased where 120 μm coated sample indicates higher tack value than the 30 μm coated sample.

This observation is attributed to the increase of adhesive volume which enhances the viscoelastic property of the adhesive [13]. The failure mode shifts from cohesive to adhesive failure when coating thickness is increased [14].

4.2. *Peel strength.* The peel strength using a T-peel test experiment is shown in Figure 2. The plot shows that a T-peel test at 30 μm and 120 μm coating thickness, the peel strength increases

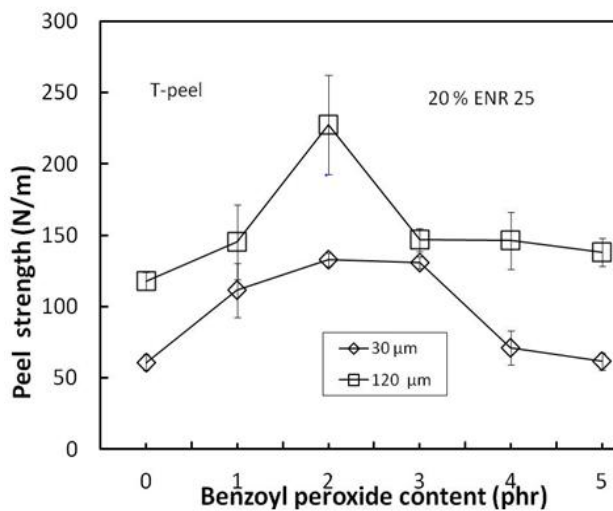


FIGURE 2: Variation of peel strength (T-test) of ENR 25/NBR blend adhesive with benzoyl peroxide content at 30 μm and 120 μm coating thickness.

with benzoyl peroxide loading up to 2 phr of benzoyl peroxide, after which the peel strength decreases with further addition of crosslinking agent. Again the initial increase in peel strength can be explained by the increase in cohesive strength of the adhesive as in the case of tack. After the

optimum loading of benzoyl peroxide, over crosslinking of rubber blend chain decreases the wettability of the adhesives as discussed earlier for the tack test. On the other hand, the highly crosslinked network make the rubber blend chain mobility decreases where wettability of adhesive is drops. At this stage, the elastic component of the rubber blend is also increased, which play the important role in the debonding process [15, 16]. A similar observation is also obtained for the 90° and 180° peel test as shown in Figure 3 and Figure 4, respectively.

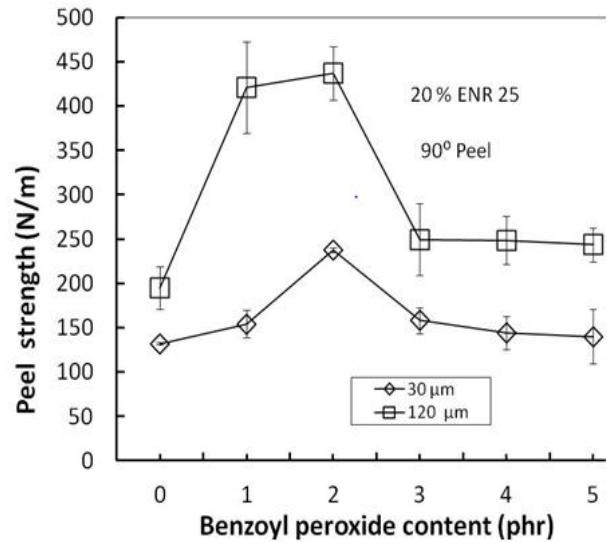


FIGURE 3: Variation of peel strength (90° -test) of ENR 25/NBR blend adhesive with benzoyl peroxide content at 30 μm and 120 μm coating thickness.

From both plots, an optimum loading of 2 phr benzoyl peroxide is also observed. At this optimum loading, maximum wettability and cohesive strength also occur as we discussed earlier in T-peel test. The drop in peel strength after 2 phr benzoyl peroxide is again attributed to the

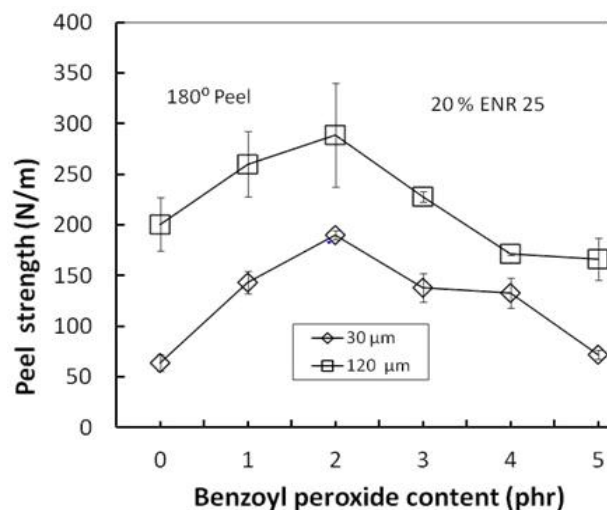


FIGURE 4: Variation of peel strength (180° - test) of ENR 25/NBR blend adhesive with benzoyl peroxide content at 30 μm and 120 μm coating thickness.

decrease in wettability when crosslinking of rubber blend adhesive increase. Figure 2-4 also shows that for the three modes of peel test at fixed benzoyl peroxide loading, the peel strength increases when coating thickness increases where 120 μm coated sample indicates higher peel strength value than the 30 μm coated sample. This observation is attributed to the increase in rubber blend content which enhances the viscoelastic behavior of the adhesive. Figure 5 shows the comparison of peel strength for the various modes of testing at the optimum loading of benzoyl peroxide, i.e., 2 phr. It is obvious that 90° peel test gives the highest peel strength, followed by the 180° peel test and T-peel test for both coating thickness. This phenomenon is attributed to the difference in the angle of testing where a higher force is needed in the case of 90° peel test to separate the mechanical interlocking and anchorage of the adhesive in pores and irregularities in the substrate [12, 14, 17]. Subsequently, the adhesive layer itself cannot easily be ruptured [18].

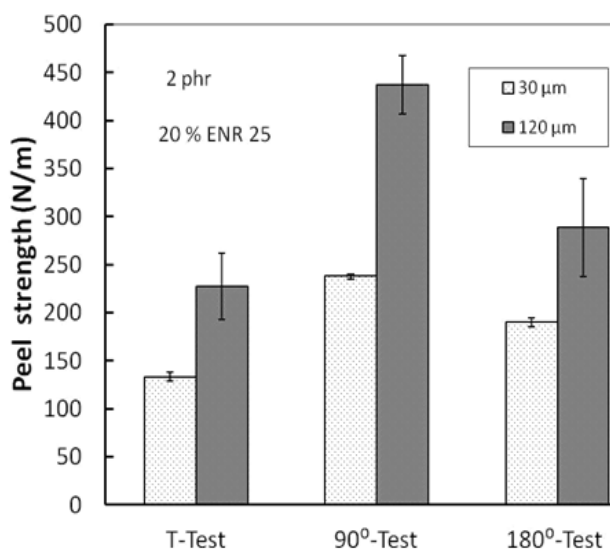


FIGURE 5: Comparison of peel strength between three modes of peel tests at 30 μm and 120 μm coating thicknesses.

4.3. Shear strength. Figure 6 shows the variation of shear strength of ENR 25/NBR blend adhesive with benzoyl peroxide content at 30 μm and 120 μm coating thickness. Shear strength of the adhesive increases continually with increasing benzoyl peroxide loading for both coating thickness. This observation can be explained by the increases cohesive strength of adhesive due to the increase in crosslinking of rubber blend as a benzoyl peroxide is increased.

As the crosslinking of rubber blend chain is increased, the holding power between the adhesive and adherent also increases correspondingly. This means that the higher the holding power, the higher the resistance towards shear action of adhesive. For a fixed benzoyl peroxide loading, shear strength increases when coating thickness increases where 120 μm coated sample indicates higher shear strength value than the 30 μm coated sample. This observation is attributed to the higher volume of adhesive in 120 μm coated sample which enhances the resistance to shearing action as coating thickness is increased, hence higher shear strength is observed.

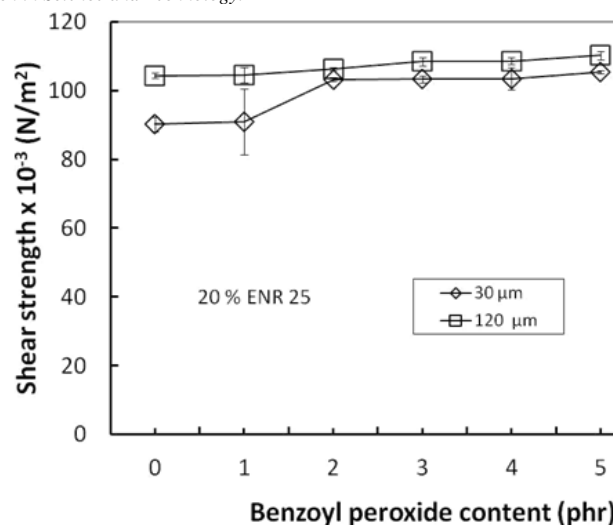


FIGURE 6: Variation of shear strength of ENR 25/NBR blend adhesive with benzoyl peroxide content at 30 μm and 120 μm coating thickness.

5. Conclusion

Loop tack and peel strength of ENR 25/NBR blend adhesive increase with benzoyl peroxide loading up to 2 phr for both coating thickness, after which it decreases with further addition of crosslinking agent. This observation is attributed to the crosslinking of rubber blend chains which enhances the cohesive strength of the adhesives. However, after 2 phr benzoyl peroxide loading, the wettability of the adhesives drops due to the over crosslinked rubber blend chains as shown by the lower loop tack and peel strength value. The 90° peel test exhibits higher peel strength followed by the 180° peel test and T-peel test for both coating thickness.

This phenomenon is ascribed to the angle of testing where greater strain-induced crystallization of rubber blend is experienced in 90° peel test. For the shear strength, it increases steadily with benzoyl peroxide loading for both coating thicknesses. This observation is attributed to the increase in cohesive strength resulting from the crosslinking of rubber blend chains. In all cases, the adhesion property increases with coating thickness, an observation that is attributed to the increase of adhesive amount as coating thickness is increased where the viscoelastic response of the adhesive is enhanced.

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