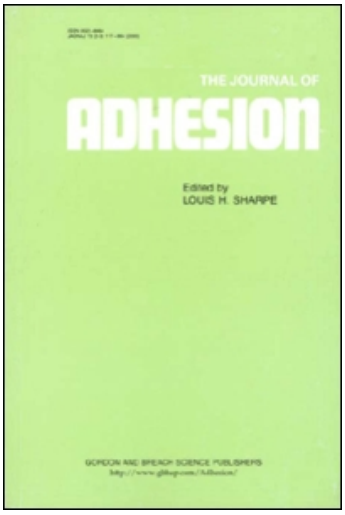

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Dependence of Peel Adhesion on Molecular Weight of Epoxidized Natural Rubber

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The effect of molecular weight of two grades of epoxidized natural rubber (ENR)—i.e., *ENR 25 and ENR 50—on the peel strength of an adhesive is studied using coumarone-indene resin, gum rosin, and petro resin as tackifiers. Toluene and polyethylene terephthalate (PET) film acted as the solvent and substrate, respectively. A SHEEN hand coater was used to coat the adhesive on the substrate to give coating thicknesses of 30, 60, 90, and 120 μm. The peel strength of adhesive was determined using a Lloyd Adhesion Tester operating at 30 cm/min. Results show that peel strength has a maximum value at a molecular weight of 6.8×10^4 and 3.9×10^4 for ENR 25 and ENR 50, respectively, an observation which is attributed to the combined effects of wettability and mechanical strength of the rubber at the respective optimum molecular weight of ENR. Peel strength increases with coating thickness for all the tackifiers investigated, with a gum rosin-based adhesive exhibiting the highest peel strength.*

Keywords: Adhesive; Molecular weight; Peel strength; Rubber

INTRODUCTION

Recently, we have carried out several studies on the adhesion behavior of epoxidized natural rubber (ENR)-based pressure-sensitive adhesives using unmasticated rubber. Results show that the maximum peel strength of ENR 25 and ENR 50-based adhesives occurs at 40 parts per hundred parts of rubber (phr) of coumarone-indene resin [1]. The shear strength shows a gradual decrease with increasing tackifier loading due to the decrease in cohesive strength of adhesive. On the other hand, viscosity and loop tack of ENR 25-based adhesive increases with

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increasing zinc oxide concentration [2]. Peel strength increases with zinc oxide up to 30–40 phr and drops after the maximum value. We have also reported the adhesion properties of pressure-sensitive adhesives prepared from ENR blends [3]. However, with respect to the effect of molecular weight of ENR on the adhesion behavior of adhesives, there is no investigation published so far, although we have studied the effect of molecular weight of SMR L—one grade of unmodified natural rubber—on the adhesion properties of the rubber adhesives [4,5]. In view of the absence of research in this field of interest, we have carried out a systematic study on the dependence of peel strength on the molecular weight of ENR using three types of tackifying resins. Results obtained are reported and discussed in this article.

EXPERIMENTAL

Materials

ENR 25 and ENR 50 having 25 mol % and 50 mol % of epoxidation, respectively, were used as the rubbers with technical specifications given in our previous paper [1]. Both rubbers were supplied by Rubber Research Institute of Malaysia (RRIM, Kuala Lumpur). Coumarone-indene resin (CUMAR RIZ), gum rosin (ww grade), and petro resin (Nisseki 120) were obtained from EuroChemo-Pharma Company (Prai, Penang, Malaysia). Toluene (lab grade) was used as the solvent throughout the experiment.

Molecular Weight Determination

Different molecular weights of ENR were prepared by masticating the rubbers on a two-roll mill for 5, 10, 15, and 20 minutes. The molecular weight of masticated and unmasticated rubber was determined by a viscometric method. The dilute rubber solution used for the molecular weight determination did not contain an insoluble fraction. The viscosity-average molecular weight (M_v) of the rubber was computed from the intrinsic viscosity [η] using the Mark-Houwink equation as shown below [6,7].

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

where $k = 5.00 \times 10^{-4}$ dl/g and $a = 0.67$ in toluene.

Adhesive Preparation

5 g rubber sample was dissolved in 30 ml of toluene. The rubber solution was tightly enclosed and kept in a conditioned room for 24 hours.

2 g of tackifier corresponding to 40 parts per hundred parts of rubber (phr) was then added to the rubber solution with constant stirring. The ENR-based adhesive produced was then left for at least 2 hours before testing.

Peel Strength Determination

Three different modes of peel adhesion tests, *i.e.*, T-peel test, 90° peel test, and 180° peel test, were carried out using polyethylene terephthalate (PET) film of 0.07 mm thickness as the coating substrate. The dimensions of T- and 90° peel tests specimens were 20×4 cm. The dimensions of 180° peel test, however, were 25×4 cm for the base stock and 12×6 cm for the face stock. A SHEEN hand coater (Teddington, Middlesex, UK) was used to coat the ENR-based adhesive from the end of the PET substrate (base stock) over a coating area of 10×4 cm. Another PET film (face stock) was then laid on the base stock with no external pressure. Four different coating thicknesses, *i.e.*, 30, 60, 90, and 120 μm, were used in this study. The coated specimen was conditioned at room temperature (30°C) for 24 hours prior to testing on a Lloyd adhesion tester (Hampshire, UK) operating at 30 cm/min. The three highest peaks of the load-propagation graph were used to compute the average peeling force. Peel strength is defined as the average load per unit width of the bondline required to separate progressively a flexible member from a rigid member or another flexible member (ASTM D 907). The average reading of peel strength for each test was taken from three replicates.

RESULTS AND DISCUSSION

The dependence of peel strength of ENR 25 and ENR 50-based adhesive, on the molecular weight and coating thickness for the three tackifiers is discussed below.

Effect of Molecular Weight

Figure 1 shows the effect of molecular weight of ENR 25 on the peel strength of the adhesive using coumarone-indene resin as the tackifier at 120 μm coating thickness for the three modes of peel tests. The peel strength increases with molecular weight up to 6.8×10^4, after which it decreases with further increase in molecular weight of the rubber. This observation is attributed to the combined effects of wettability and mechanical strength of rubber. It is well known that the wetting effect decreases with increase in molecular

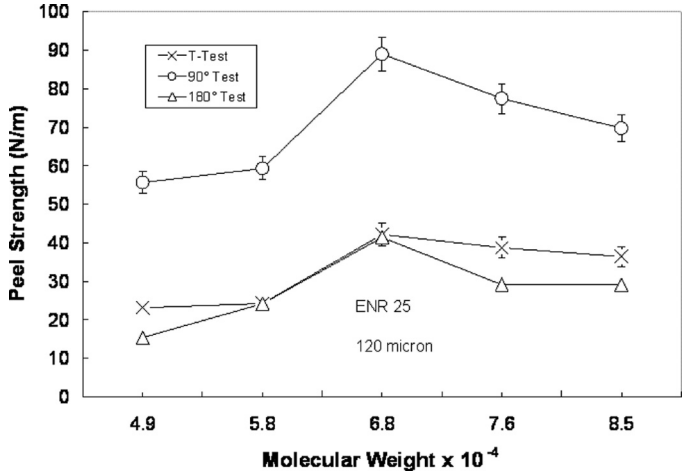

FIGURE 1 Variation of peel strength with molecular weight of ENR 25 in the presence of coumarone-indene resin.

weight of polymer. However, mechanical strength of bulk polymer increases with molecular weight and levels off at a certain molecular weight [8,9]. The increase in mechanical strength enhances the cohesive strength of the adhesive as the molecular weight of rubber is increased. This phenomenon would offset the decline in adhesive strength caused by the decrease in wettability due to the increase in molecular weight of rubber. Consequently, an optimum performance in peel strength is reached in the mid-range of molecular weight of ENR 25 as shown in Fig. 1. Similar behavior is observed for the dependence of shear strength on molecular weight of unmodified natural rubber (SMR L)[5] where optimum molecular weight is 8.5×10^4. Figure 2 shows the DSC scan of ENR 25-based adhesive at the optimum molecular weight. From the thermograph, one T_g is observed, indicating compatibility of the rubber/tackifier adhesive system.

As the molecular weight of rubber is further increased, a drop in peel strength is observed. This finding can be explained by the decrease in wettability resulting from the increase in chain entanglement of rubber molecules as the molecular weight of rubber is increased. Entanglement molecular weight of ENR 25 and ENR 50 obtained from a previous viscosity study indicates values of 6.8×10^4 and 3.9×10^4, respectively. The response of the pressure-sensitive adhesive to the stress is of a viscoelastic nature [10]. For molecular weight lower than the optimum molecular weight, adhesion failure

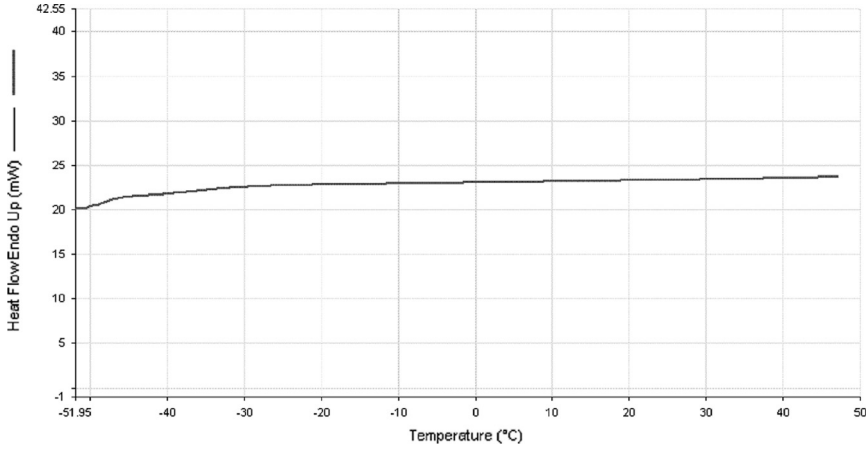

FIGURE 2 A DSC scan of ENR 25/coumarone-indene resin blend at the optimum molecular weight. Note that there is only one Tg, indicating compatibility.

is associated with both cohesive and adhesive failure. However, for higher molecular weight rubber, the failure mode is essentially adhesive in nature.

For a fixed molecular weight, 90° peel test exhibits the highest peel strength compared with T- and 180° peel tests. This observation is associated with the angle of testing where higher strain-induced crystallization [11,12] of ENR chains occurs in the 90° peel test and, consequently, the adhesive layer itself cannot easily be ruptured [13], thus, higher peel strength is observed. Figures 3 and 4 show the dependence of peel strength on the molecular weight of ENR 25 containing gum rosin and petro resin, respectively, at 120 μm coating thickness. The two graphs also indicate similar behavior as observed in the case of the coumarone-indene resin system. Peel strength exhibits a maximum value at 6.8×10^4 molecular weight of ENR 25, an observation which is attributed to maximum wettability by the adhesive on the substrate. Again, the 90° peel test shows the highest peel strength compared with the other two testing modes.

The effect of molecular weight of ENR 50 on the peel strength of adhesives is shown in Figs. 5–7 for coumarone-indene resin, gum rosin, and petro resin systems, respectively. In all cases, the peel strength shows a maximum value at 3.9×10^4 molecular weight of ENR 50, suggesting that optimum performance occurs at this optimum molecular weight results from the combined effects of wettability and mechanical strength of the rubber as discussed earlier for ENR 25.

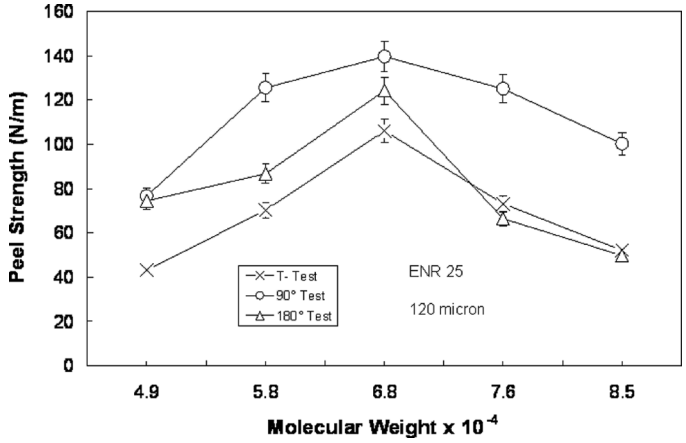

FIGURE 3 Variation of peel strength with molecular weight of ENR 25 in the presence of gum rosin.

Figure 8 shows a DSC scan for the ENR 50-based adhesive at the optimum molecular weight. One T_g is observed, indicating compatibility in the ENR 50/tackifier adhesive system. Further increase in molecular weight would result in a drop of peel strength due to the effect of chain entanglement as discussed earlier. For the three tackifier systems studied, the 90° peel test consistently indicates the highest peel strength, confirming our previous observation on the peel strength

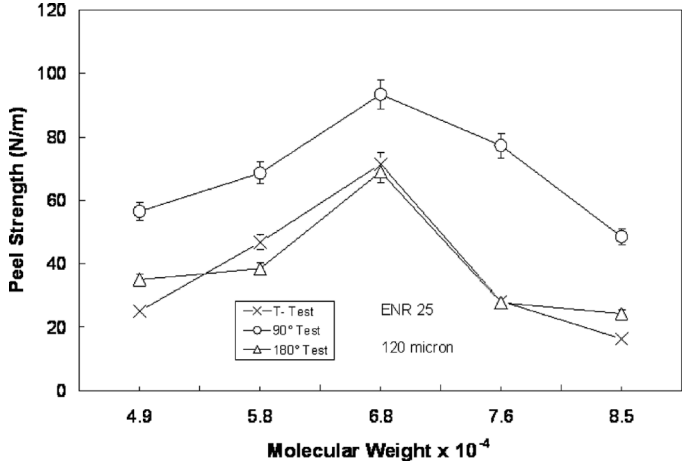

FIGURE 4 Variation of peel strength with molecular weight of ENR 25 in the presence of petro resin.

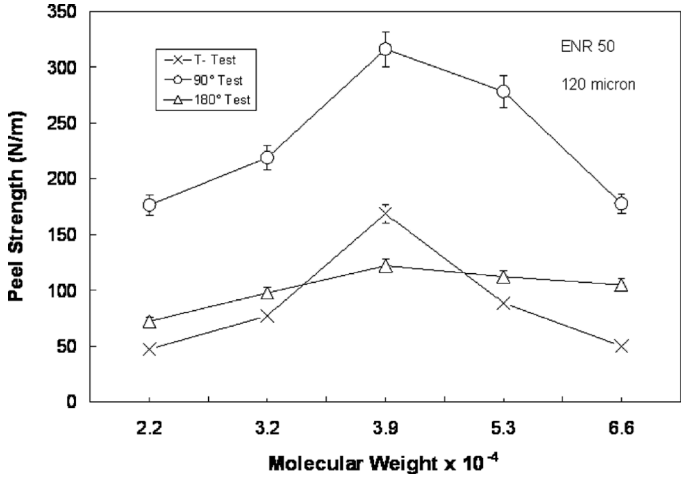

FIGURE 5 Variation of peel strength with molecular weight of ENR 50 in the presence of coumarone-indene resin.

study on the ENR 25-based adhesive [1]. One interesting observation is that the peel strength is maximum at a lower molecular weight of ENR 50 than ENR 25. This observation is ascribed to the higher degree of epoxidation in ENR 50 which enhances the compatibility and wettability of the adhesive. This means that more intermolecular

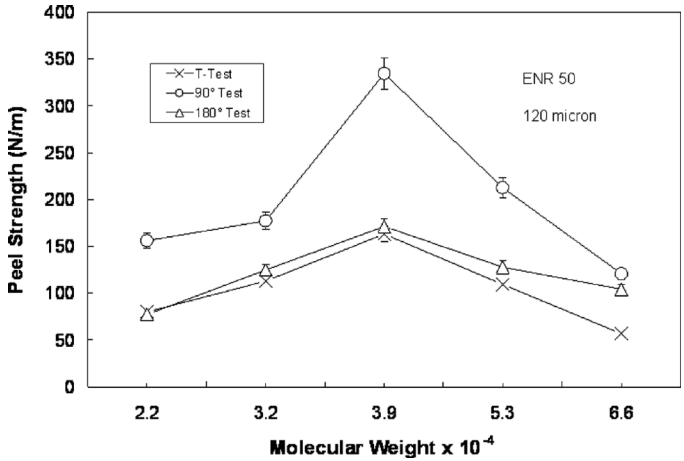

FIGURE 6 Variation of peel strength with molecular weight of ENR 50 in the presence of gum rosin.

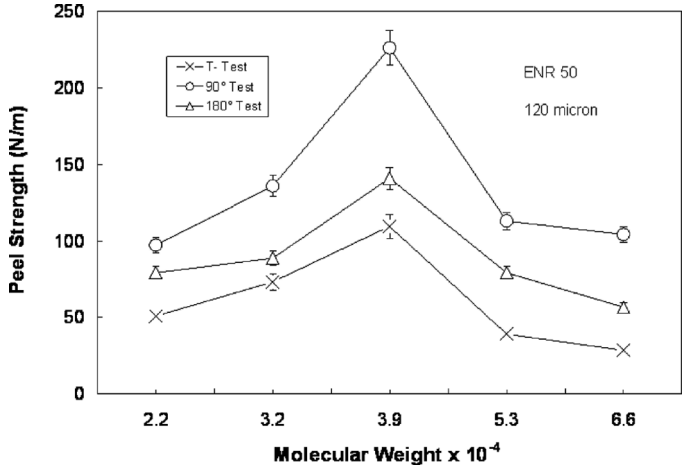

FIGURE 7 Variation of peel strength with molecular weight of ENR 50 in the presence of petro resin.

interaction (*e.g.*, H-bonding) between ENR 50 and tackifier occurs compared with that in ENR 25. Hence, a shorter molecular chain length is needed to attain the maximum peel strength compared to the ENR 25-based adhesive system. From this study, it is noted that the optimum molecular weight to achieve maximum wettability does not depend on the tackifier system used for a particular ENR.

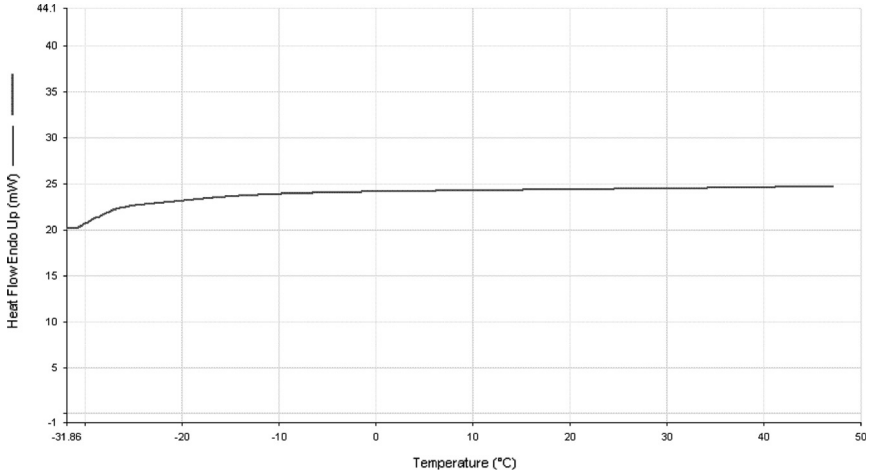

FIGURE 8 A DSC scan of ENR 50/coumarone-indene resin blend at the optimum molecular weight.

Effect of Coating Thickness

Figure 9 shows the variation of maximum peel strength of ENR 25-based adhesive with coating thickness for the three tackifiers studied using the 90° peel test. From the plot, it can be seen that peel strength increases with coating thickness for the three tackifiers studied, similar to that obtained by Gardon [14,15]. We believe that this is due to increasing amount of rubber component present in the coating layer. The viscoelastic behavior of the rubber component [16] enhances the wettability of the adhesive—as reflected by the increase in peel strength—as coating thickness is increased. The result obtained in this study is consistent with the general belief that peel force increases with increasing adhesive thickness up to a certain limit [10]. Since there is no maximum observed in Fig. 9, it can be inferred that the critical coating thickness to achieve maximum peel strength has not been reached. Increasing coating thickness causes the shift from cohesive to adhesive failure [17,18]. However, adhesive thickness does not affect the peel force at low peel rates when the failure is cohesive [10]. For a fixed coating thickness, the adhesive containing gum rosin consistently shows the highest peel strength compared with coumarone-indene resin and petro resin. This observation is attributed to the nature of the tackifying resin. Gum rosin consists of oleoresin, a natural product, whereas coumarone-indene resin and petro resin are synthetic resins from polymerization products. We speculate that

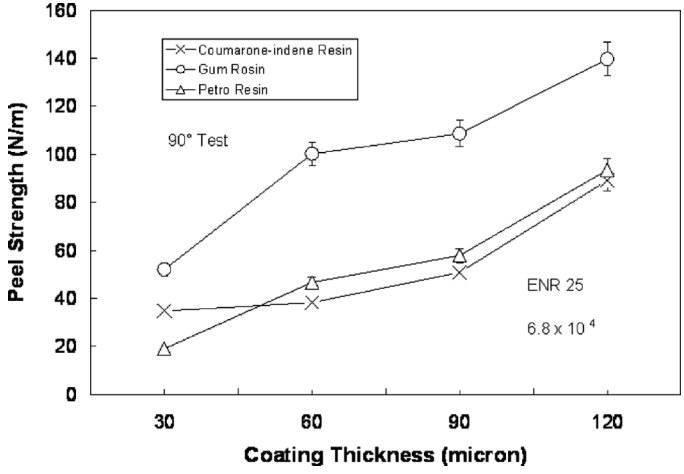

FIGURE 9 Dependence of peel strength of ENR 25-based adhesive on coating thickness for various tackifier systems.

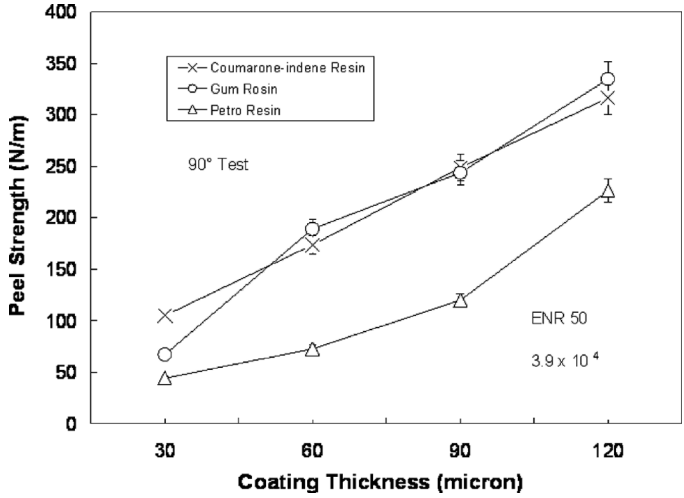

FIGURE 10 Dependence of peel strength of ENR 50-based adhesive on coating thickness for various tackifier systems.

the higher peel strength of the ENR 25/gum rosin adhesive system is associated with the better compatibility and wettability between ENR 25 and gum rosin. On the other hand, poorer compatibility between ENR 25 and the synthetic resin results in lower peel strength as shown in Fig. 9. The dependence of peel strength on coating thickness for ENR 50-based adhesives is illustrated in Fig. 10. The plot also shows that peel strength increases with increasing coating thickness, an observation which is ascribed to the enhancement of wettability due to the presence of more rubber component. Adhesives containing gum rosin and coumarone-indene resin exhibit similar peel strength, a phenomenon which is attributed to the better interaction between the polar ENR 50 and the tackifiying resins. This means that better compatibility occurs in the two adhesive systems which are reflected by the high peel strength as indicated in Fig. 10. Conversely, petro resin being a hydrophobic hydrocarbon tackifier is not so compatible with ENR 50, hence lower peel strength is observed in the ENR 50/petro resin system.

CONCLUSIONS

From this study, the following conclusions can be drawn.

1. Maximum peel strength occurs at a molecular weight of 6.8×10^4 and 3.9×10^4 for ENR 25 and ENR 50, respectively, after which

it decreases with further increase in molecular weight of the rubber. This observation is attributed to the combined effects of wettability and mechanical strength of rubber at the respective optimum molecular weights of ENR. Peel strength decreases beyond the optimum molecular weight due to the effect of chain entanglement of rubber molecules. The lower optimum molecular weight exhibited by ENR 50 is attributed to the higher degree of epoxidation compared with ENR 25. The optimum molecular weight to achieve maximum peel adhesion for ENR 25 and ENR 50 is independent of the tackifier system.

2. Peel strength of ENR-based adhesives increases with coating thickness for the three tackifiers studied. This observation is, we believe, is due to the increasing amount of rubber component which enhances the adhesion of the adhesive. Adhesive containing gum rosin consistently exhibits the highest peel strength due to better compatibility between the rubber and gum rosin. However, in the case of ENR 50, adhesives containing gum rosin and coumarone-indene resin exhibit similar peel strength for all coating thickness investigated, an observation which is ascribed to better interaction between polar ENR 50 and the two tackifying resins.

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REFERENCES

[1] Poh, B. T. and Kwo, H. K., *J. Appl. Polym. Sci.* **105**, 680–684 (2007).
[2] Poh, B. T. and Chow, S. K., *J. Appl. Polym. Sci.* **106**, 333–337 (2007).
[3] Poh, B. T. and Lim, A. L., *J. Appl. Polym. Sci.* **109**, 115–119 (2008).
[4] Poh, B. T. and Yong, A. T., *J. Macromol. Sci. Part A* **46**, 97–103 (2009).
[5] Poh, B. T., Yee, K. W., and Lim, H. B., *J. Appl. Polym. Sci.* **110**, 4079–4083 (2008).
[6] Billmeyer, F. W. Jr., *Textbook of Polymer Science,* 3rd ed. (Wiley, New York, 1984), Ch. 8, pp. 208–210.
[7] Bateman, L., Ed., *The Chemistry and Physics of Rubber-Like Substances*, (Maclaren, London, 1963), Ch. 6, p. 149.
[8] Sperling, L. H., *Introduction to Physical Polymer Science*, (Wiley, New York, 1986). Ch. 1, p. 6.
[9] Bahadur, P. and Sastry, N. V., *Principles of Polymer Science*, (Alpha Science International, Oxford, 2006), Ch. 5, p. 203.
[10] Satas, D., Ed., *Handbook of Pressure-Sensitive Adhesive Technology*, (Van Nostrand Reinhold, New York, 1982), Ch. 4, p. 54, pp. 63–64.
[11] Davies, C. K. L., Wolfe, S. V., Gelling, I. R., and Thomas, A. G., *Polymer* **24**, 107–113 (1983).
[12] Poh, B. T., Ismail, H., and Quah, E. H., *Polym. Test.* **20**, 389–394 (2001).

[13] Skeist, I., Ed., *Handbook of Adhesives,* 3rd ed. (Van Nostrand Reinhold, New York, 1990), Ch. 3, p. 65.
[14] Gardon, J. L., *J. Appl. Polym. Sci.* **7**, 625–641 (1963).
[15] Gardon, J. L., *J. Appl. Polym. Sci.* **7**, 643–665 (1963).
[16] Leong, Y. C., Lee, L. M. S., and Gan, S. N., *J. Appl. Polym. Sci.* **88**, 2118–2123 (2003).
[17] Poh, B. T. and Chee, C. L., *Int. J. Polym. Mater.* **56**, 247–255 (2007).
[18] Fukuzawa, K., *J. Adhesion Soc. Japan.* **5**, 294 (1969).