

# Effect of Silica on Viscosity, Tack, and Shear Strength of Epoxidized Natural Rubber-Based Pressure-Sensitive Adhesives in the Presence of Coumarone-Indene Resin

Imran Khan, B. T. Poh

*School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia*

Received 13 January 2010; accepted 25 April 2010

DOI 10.1002/app.32686

Published online 14 July 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The viscosity, loop tack, and shear strength of silica-filled epoxidized natural rubber (ENR 25 and ENR 50 grade) adhesive were investigated using coumarone-indene as the tackifying resin. Silica loading was varied from 10–50 parts per hundred parts of rubber (phr), whereas the coumarone-indene concentration was fixed at 40 phr. Toluene was used as the solvent throughout the study. Polyethylene terephthalate substrate was coated at various adhesive coating thicknesses, i.e., 30, 60, 90, and 120  $\mu\text{m}$  using a SHEEN Hand Coater. Viscosity of the adhesive was determined by a HAAKE Rotary Viscometer whereas loop tack and shear strength were measured by a

Llyod Adhesion Tester operating at 30 cm/min. Result shows that viscosity of the adhesive increases gradually with increase of silica loading due to the concentration effect of the filler. Both loop tack and shear strength show maximum value at 40 phr silica for ENR 25. However, the respective values for ENR 50 are 20 and 40 phr of filler. This observation is attributed to the maximum wettability and compatibility of adhesive on the substrate at the respective silica loadings. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3439–3444, 2010

**Key words:** silica; viscosity; tack; shear strength; rubber

## INTRODUCTION

The structure of filled rubber compounds on a molecular scale, in particular when silica is used as filler, is not very well known. Silica has a number of hydroxyl groups on the surface, which results in strong filler–filler interactions and adsorption of polar materials by hydrogen bonds.<sup>1–3</sup> Mixing of silica with rubber is a challenge, as these materials are not very compatible in various aspects: surface energy, solubility, structure of the filler and viscoelastic properties. Silica has been used as an important reinforcing agent in a rubber compound together with carbon.<sup>1</sup>

Most pressure-sensitive adhesives (PSAs) are blends of rubbery polymers and oligomeric tackifier resins. PSA tapes can paste on various adherends under light pressure in very short time without heating or heavy pressure. The bonds formed are strong enough to use temporarily. However, PSAs sometimes need durability for a long time, especially the resistance to shear force. For example, PSAs are used for bookbinding, upholstery, and pasting papers on the wall.<sup>4</sup>

Epoxidized natural rubber (ENR) is prepared by peroxyacetic acid epoxidation of natural rubber (NR)

latex. The epoxidation reaction is a random process. The glass transition temperature of ENR 25 and ENR 50 is  $-45$  and  $-20^\circ\text{C}$ , respectively. ENR undergoes strain-induced crystallization. The curing characteristics and mechanical properties of epoxidized natural rubbers (ENR) have been widely studied.<sup>5–14</sup> Ishak and coworkers<sup>15</sup> has studied the curing characteristics and mechanical properties of ENR with filler silica and has reported that cure characteristics could be related not only to the fillers characteristics, i.e., particle size, structure, and aspect ratio, but also to the filler–rubber interaction. All these studies involve the bulk property of ENR. The solution property of ENR, especially its use in PSA was not widely reported. Recently, we have investigated the shear property of ENR-based adhesives<sup>16</sup> and the effect of zinc oxide, calcium carbonate, and rubber blends on the adhesion properties of ENR-based PSAs.<sup>17–19</sup> In view of the lack of scientific research in this field of interest, we have carried out a systematic research on the effect of silica on ENR on the viscosity, tack, and shear strength of the adhesive in the presence of coumarone-indene resins.

## EXPERIMENTAL

### Materials

Epoxidized natural rubber, ENR-25 and ENR-50 having 25 and 50 mol % of epoxidation, respectively

Correspondence to: B. T. Poh (btpoh@usm.my).

Contract grant sponsor: Universiti Sains Malaysia (FRGS).

were used as the elastomer for the preparation of the pressure-sensitive adhesive. The rubbers were supplied by Rubber Research Institute of Malaysia. Coumarone-indene resin is used as the tackifier. It is a chemically inert hydrocarbon resin and shows low reactivity property and resistant to alkalis, acids, and moisture. The molecular weight of the resin is 1000–3000. Its specific gravity and softening point is 1.08 and 112°C, respectively. Silica which has a surface area of 50 m<sup>2</sup>/g and specific gravity of 2.0 was used as the filler in this study. Toluene and polyethylene terephthalate (PET) film were chosen as the solvent and substrate, respectively. All the materials used in this experiment were freshly supplied commercial grades. No purification was carried out prior to use.

### Preparation of adhesive

After mastication of rubber on a two-roll mill for 10 min, 5 g of the masticated rubber were shredded into small pieces and dissolved in 20 mL of toluene. The rubber solution was then left overnight to ensure complete dissolution. With constant stirring, 2 g of pulverized coumarone-indene resin that corresponded to 40 phr of tackifying resin was slowly put into the rubber solution. This was followed by the addition of silica filler into the adhesive solution. Five different loadings of silica, i.e., 0.5, 1.0, 1.5, 2.0, and 2.5 g corresponding to 10, 20, 30, 40, and 50 phr of filler and one control sample without silica were prepared.

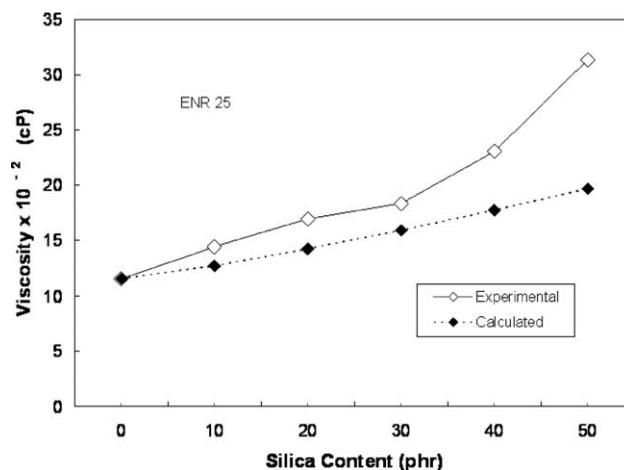
### Measurement

#### Viscosity

A HAAKE rotary viscometer (Model PK 100) was used to measure the viscosity of the adhesives. The platform was cleaned with acetone and then raised up to touch the spindle head. A few drops of adhesives were put at the middle of platform, and testing was carried out for one minute or ten rounds of spinning. The average viscosity was computed from at least five readings recorded.

#### Tack

Loop tack is essentially a peel test involving low contact pressure and short application time.<sup>20</sup> PET substrate with dimension of 4 cm × 25 cm was coated at the center of the film (4 cm × 4 cm) at various coating thickness i.e., 30, 60, 90, and 120 μm using SHEEN Hand Coater. The coated sample was conditioned at room temperature for 24 h before testing. The adhesive-coated area was gently brought into contact with a glass plate. The debonding force from the glass plate was determined by a Lloyd Adhesion Tester (Model LRXPlus with NEXYGEN software) operating at a testing rate of 30 cm/min. The



**Figure 1** Variation of viscosity of ENR 25-based adhesive with silica loading.

three highest peaks from the load-propagation graph were used to calculate the average debonding force. The loop tack was expressed as the debonding force per area of contact with the glass plate (N/m<sup>2</sup>).

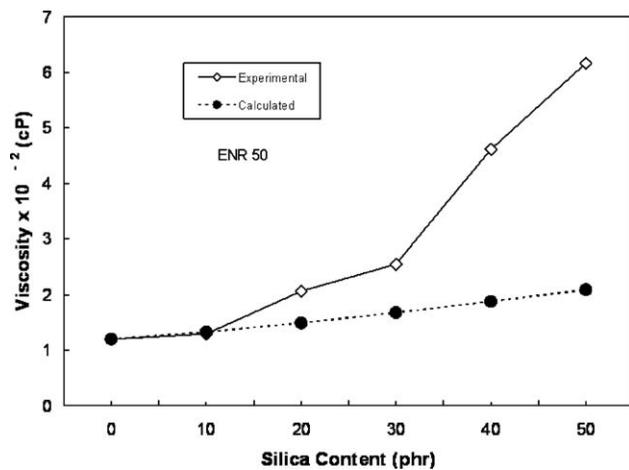
#### Shear strength

The dimension of the PET film was 15 cm × 2.5 cm. A SHEEN Hand Coater was used to coat the adhesive from the end of the substrate with 5 cm × 2.5 cm dimension at 30, 60, 90, and 120 μm coating thicknesses. It was then conditioned at room temperature for 24 h before testing on a Lloyd Adhesion Tester operating at 30 cm/min. The testing distance was 5 cm which corresponded to the length of the coated area. Shear strength was expressed as the shear force per unit area of testing (N/m<sup>2</sup>).

## RESULTS AND DISCUSSION

### Viscosity

The effect of silica on the viscosity of ENR 25 and ENR 50-based PSA in the presence of coumarone-indene resin is shown in Figures 1 and 2, respectively. From the plot, it is obvious that viscosity of the adhesive increases with increase in silica content. This observation is attributed to the interaction between silica and ENR, both of which are polar in nature. An examination of Figures 1 and 2 also reveals that there is rapid increase in viscosity after 30 phr silica loading for both ENR 25 and ENR 50 adhesives. This is explained by the increase in thickening effect of silica which acts as a filler in the adhesive formulation.<sup>21</sup> Our previous report on the effect of zinc oxide<sup>17</sup> and kaolin<sup>22</sup> on the viscosity of ENR-25 based pressure-sensitive adhesive also show increase in viscosity of adhesive with increase in filler content. A predicted viscosity value ( $\eta$ ) based the



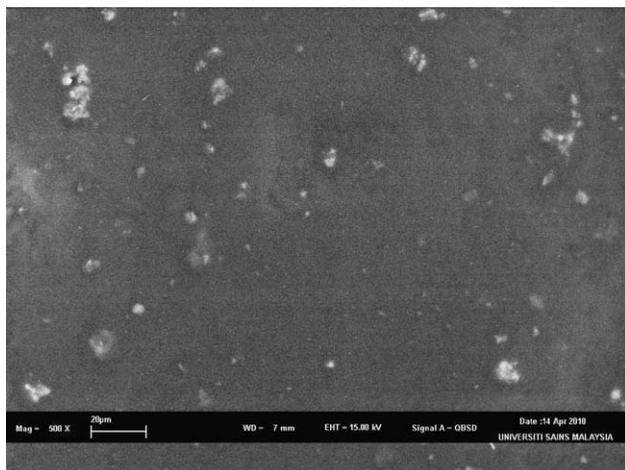
**Figure 2** Variation of viscosity of ENR 50-based adhesive with silica loading.

composite material theory for rubber was carried out<sup>23</sup> using eq. (1) below.

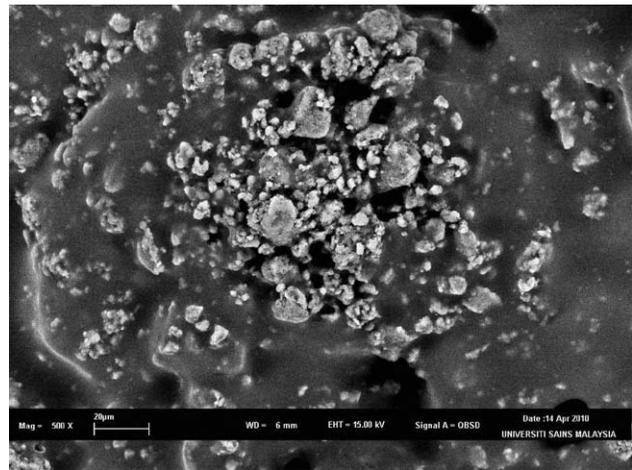
$$\eta = \eta_0(1 + 2.5\phi + 14.1\phi^2), \quad (1)$$

where  $\eta_0$ ,  $\eta$  is the viscosity of unfilled and filled adhesive.  $\phi$  is the volume fraction of filler in the adhesive.

From the plot, close agreement is exhibited at lower silica content, especially for ENR 50 system. However, for higher silica loading, the experimental data consistently indicates higher values than the predicted viscosity. For silica loading less than 30 phr, silica structure can be represented by a spherical filler model where eq. (1) was derived. However, for higher silica loading greater than 30 phr, the filler begins to form a percolated structure and eq. (1) is no longer valid to predict the viscosity at high silica loadings. To demonstrate the silica structure at different loadings, Scanning Electron Microscopy (SEM) method was used. Figures 3 and 4 show the micro-



**Figure 3** SEM micrograph of ENR 25-based adhesive containing 10 phr silica at 500X magnification.

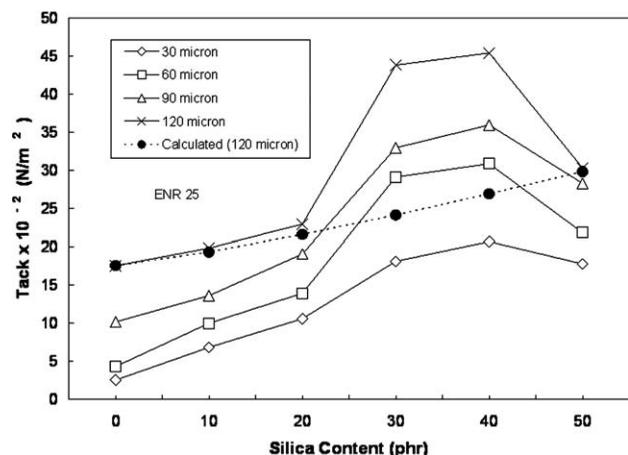


**Figure 4** SEM micrograph of ENR 25-based adhesive containing 50 phr silica at 500X magnification.

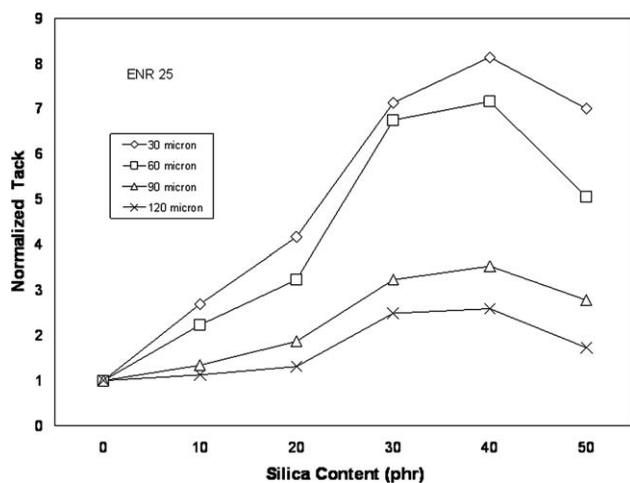
graphs of ENR 25-based adhesive containing 10 and 50 phr silica loading, respectively. At low silica loading e.g., 10 phr silica, the filler is well dispersed in the adhesive matrix. On the other hand, at higher silica loading, the filler is not well dispersed and agglomerate into a percolated structure as shown in Figure 4 for adhesive containing 50 phr silica content.

#### Tack

Tack can be described as the adhesion property whereby adhesives will adhere tenaciously to any surface when it comes in contact with only a pressure which is not more than finger pressure. Figure 5 shows the dependence of loop tack on silica loading for the ENR 25-based adhesive. The increase in tack with increasing silica loading is attributed to the increasing wettability and compatibility of adhesive on the substrate where maximum tack value occurs at 40 phr silica content. At this optimum silica loading, the adhesive conforms to the irregularities of

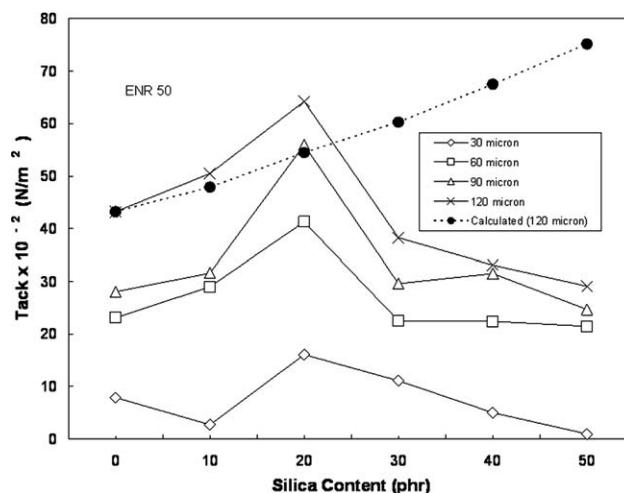


**Figure 5** Variation of tack of ENR 25-based adhesive with silica loading for various coating thickness.



**Figure 6** Variation of normalized tack of ENR 25-based adhesive with silica loading for various coating thickness.

the substrate, i.e., low surface energy condition is observed.<sup>19</sup> However, as the silica loading is further increased beyond 40 phr, wettability and compatibility decreases due to the increasing dilution effect of the silica. Figure 5 also shows that for a fixed silica loading, 120  $\mu\text{m}$  coated sample consistently indicates highest tack value than the other lower coating thickness. This observation is attributed to the higher amount of adhesive in the system as the coating thickness is increased. This means that more adhesive is available to enhance wettability on the substrate, thus giving rise to higher tack. As in the viscosity study, a predicted tack based on the composite material theory for rubber was calculated using a modified eq. (1) where  $\eta_0$  is replaced by the measured tack in an unfilled adhesive. For comparison purposes, the tack at 120  $\mu\text{m}$  coating thickness was used as shown by the dotted line in Figure 5. For low silica content, experimental data agrees well with calculated values. However, for silica content exceeds 20 phr, experimental data shows positive deviation from the predicted values. One possible explanation for this deviation is that composite material theory predicts bulk properties of the rubber composite whereas tack behavior involves surface phenomenon, namely wettability and compatibility. Nevertheless, the predicted tack value using the modified eq. (1) gives an indication on the dependence of tack on silica loading since bulk property to some extent affects the adhesion property of rubber adhesives. Figure 6 is a normalized plot based on the tack value at 0 phr silica content. The trend is similar between original and normalized graphs, i.e., both plots show increased tack with increasing silica content until optimum silica loading is reached. For fixed silica content, the original plot indicates that tack increases with coating thickness. However, for the normalized plot, the reverse behavior is obtained. This observation is due

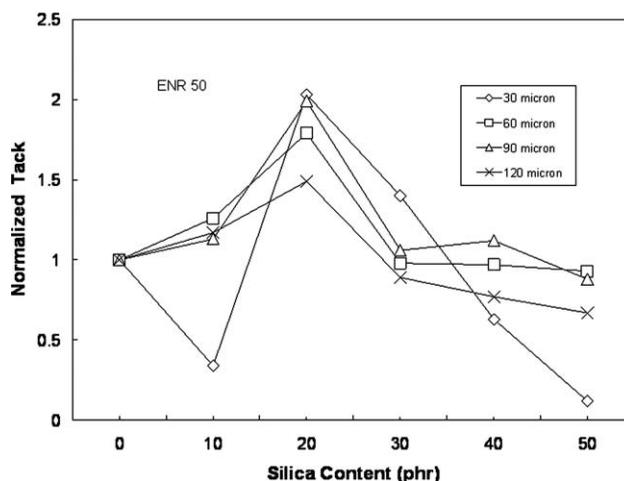


**Figure 7** Variation of tack of ENR 50-based adhesive with silica loading for various coating thickness.

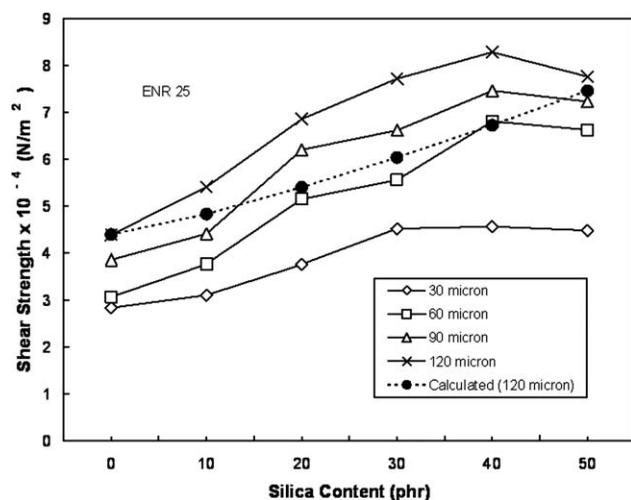
to nonlinear dependence of tack on coating thickness. Similar tack behavior is also observed for the ENR 50-based adhesive as shown in Figures 7 and 8 for original and normalized plots, respectively. In this case, peak tack value occurs at lower silica content, i.e., 20 phr silica loading.

#### Shear strength

The effect of the silica loading on the shear strength of ENR 25-based PSA is shown in Figure 9 for various coating thicknesses at fixed 40 phr coumarone-indene concentration. The graph shows that for all coating thicknesses, the lowest shear strength is exhibited by the control sample i.e., at zero concentration of the filler. In general, the shear strength increases gradually with increasing silica content up to 40 phr silica content before a slight drop in shear strength is observed. This observation may be attributable to the increase in the cohesive strength

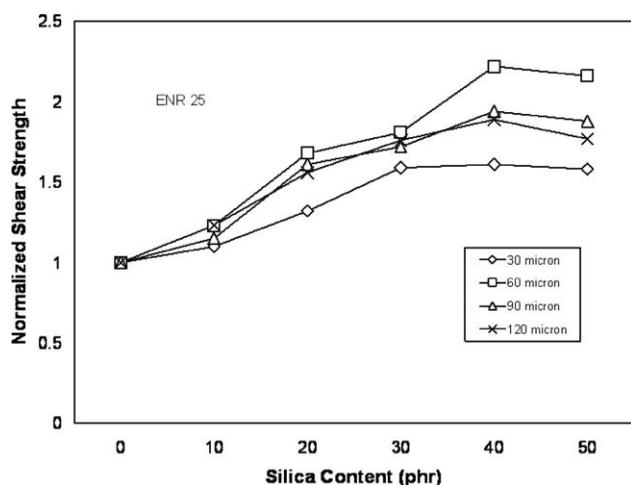


**Figure 8** Variation of normalized tack of ENR 50-based adhesive with silica loading for various coating thickness.

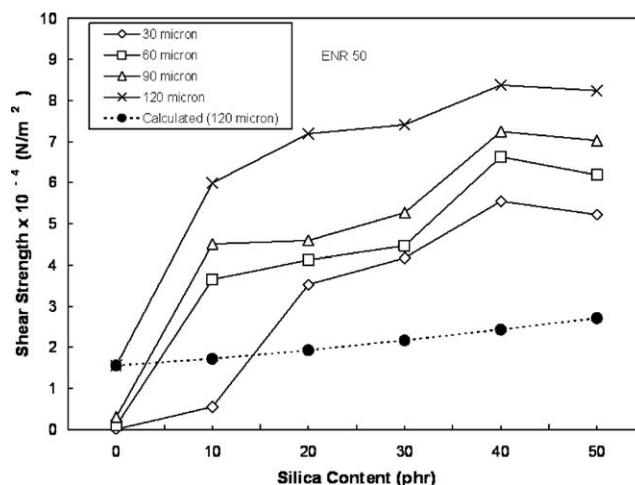


**Figure 9** Variation of shear strength of ENR 25-based adhesive with silica loading for various coating thickness.

between the ENR and the silica. The shear strength increases with increase in silica content due to increasing interaction between silica and rubber, i.e., greater filler reinforcement occurs. The rubber, which acts as the binder in the adhesive system, will enhance its holding power as the silica content is increased as illustrated by the increase in shear strength in Figure 9. The slight decrease in shear strength after 40 phr silica loading is primarily due to the dilution effect of silica as filler. The plots also show that shear strength increases with the increasing coating thickness. This may be associated with the increase in the amount of adhesive at higher coating thickness which enhances the resistance to shearing action. As discussed earlier for viscosity and tack, a predicted shear strength based on the composite material theory for rubber was also calculated using a modified eq. (1). The calculated data at

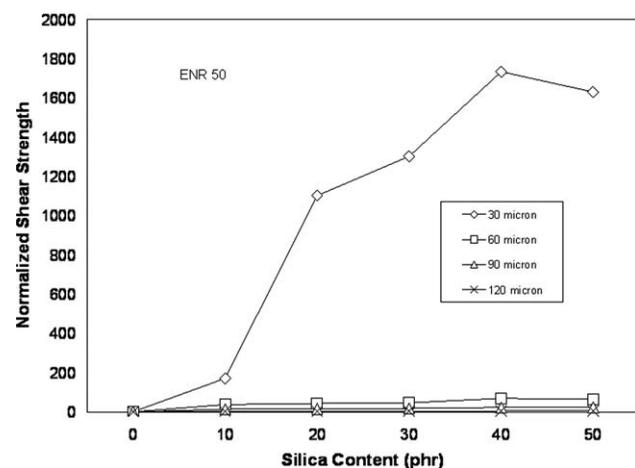


**Figure 10** Variation of normalized shear strength of ENR 25-based adhesive with silica loading for various coating thickness.

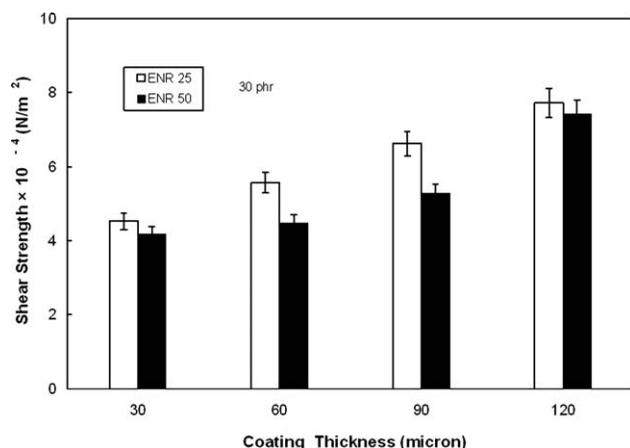


**Figure 11** Variation of shear strength of ENR 50-based adhesive with silica loading for various coating thickness.

120  $\mu\text{m}$  coating thickness is shown by the dotted line in Figure 9. Again, experimental data exhibits positive deviation from the predicted value, an observation which is ascribed to the surface phenomenon of shear test when compared to the bulk properties of the rubber composite from the predicted value. Figure 10 shows the normalized graph of shear strength based on 0 phr silica content. Both original and normalized plots indicate similar dependence on the silica content where optimum shear strength is obtained at 40 phr silica loading. However, original plot shows different dependence of shear strength on coating thickness compared to normalized graph. This difference is due to nonlinear relationship between coating thickness and shear strength as mentioned previously for the tack study. Figures 11 and 12 indicate the variation of shear strength of ENR 50-based adhesive with silica content for original and normalized plots, respectively. For



**Figure 12** Variation of normalized shear strength of ENR 50-based adhesive with silica loading for various coating thickness.



**Figure 13** Comparison of shear strength between ENR 25 and ENR 50-based adhesives at 30 phr silica loading for various coating thickness.

the original plot, experimental data also shows positive deviation from the predicted value at 120  $\mu\text{m}$  coating thickness. As mentioned previously in the tack study, the predicted value provides an indication on the dependence of shear strength on silica loading since shearing action is a combination of bulk and surface properties. For the normalized plot, the 30  $\mu\text{m}$  coated sample exhibits the highest value followed by 60, 90, and 120  $\mu\text{m}$  coating thicknesses. This observation is attributed to the extremely low shear strength at 0 phr silica content. Figure 13 shows the comparative study of the shear strength for adhesives prepared from ENR 25 and ENR 50 at 30 phr silica content. ENR 25-based adhesive consistently indicates higher shear strength than ENR 50. This observation is attributed to the flexibility and better strain-induced crystallizability of ENR 25 when subjected to shearing action. Also, better compatibility between ENR 25 and the silica may contribute to the higher shear strength. ENR 25 resists shear deformation better than ENR 50 especially at higher coating thickness where the effect of ENR 25 becomes more pronounced. A 5% error is estimated in the determination of shear strength. For 30 and 120  $\mu\text{m}$  coating, shear strength between ENR 25 and ENR 50 does not show significant differences. This may be attributed to the similar failure modes at both coating thicknesses.

### CONCLUSION

In summary, the following conclusions can be drawn from this study:

1. Viscosity of ENR 25 and ENR 50-based adhesives increases steadily with increase in silica loading, an observation which is attributed to the interaction between silica and ENR, both of which are polar materials. Rapid increase in viscosity with silica content after 30 phr silica

loading is attributed to the increasing thickening effect of silica in the adhesive systems.

2. Loop tack exhibits maximum value at 20 and 40 phr silica loading for ENR 50 and ENR 25, respectively for all the coating thickness studied. This observation is attributed to maximum wettability and compatibility of adhesive on the substrate at the respective filler concentrations. However, loop tack decreases after the optimum silica loading for both ENR adhesives. Higher coating thickness consistently exhibits higher tack value due to the larger amount of adhesive to effect wettability of adhesive on the substrate.
3. Shear strength increases with increasing silica loading up to 40 phr filler content for all the coating thickness studied. This observation is attributed to the increase in the cohesive strength between the ENR and the silica which culminates at 40 phr filler loading. The shear strength of ENR 25 and ENR 50-based adhesives increases with the increasing coating thickness due to the presence of higher amount of adhesive which enhances the resistance to shearing action. ENR 25 exhibits higher shear strength than ENR 50 because of the greater flexibility and compatibility with filler in the former system.

### References

1. Wolff, S.; Wang, M.-J. *Rubber Chem Technol* 1992, 65, 329.
2. Boonstra, B. B.; Cochrane, H.; Dannenberg, E. M. *Rubber Chem Technol* 1975, 48, 558.
3. Voet, A.; Morawski, J. C.; Donnet, J. B. *Rubber Chem Technol* 1977, 50, 342.
4. Dahlquist, C. A. In *Pressure Sensitive Adhesive Technology*, 2nd ed.; Satas, D., Ed.; Van Nostrand Reinhold: New York, 1989; Chapter 20, p 97.
5. Poh, B. T.; Tan, B. K. *J Appl Polym Sci* 1991, 42, 1407.
6. Poh, B. T.; Tang, W. L. *J Appl Polym Sci* 1995, 55, 537.
7. Poh, B. T.; Kwok, C. P.; Lim, G. H. *Eur Polym J* 1995, 31, 223.
8. Poh, B. T.; Chen, M. F.; Ding, B. S. *J Appl Polym Sci* 1996, 60, 1569.
9. Sadequ, A. M.; Ishiaku, U. S.; Ismail, H.; Poh, B. T. *Eur Polym J* 1998, 34, 51.
10. Poh, B. T.; Razai, M. *J Polym-Plast Technol Eng* 1999, 38, 341.
11. Poh, B. T.; Khok, G. K. *Polym-Plast Technol Eng* 2000, 39, 151.
12. Poh, B. T.; Te, C. S. *J Appl Polym Sci* 2000, 77, 3234.
13. Ismail, H.; Poh, B. T. *Eur Polym Mater* 2000, 36, 2403.
14. Poh, B. T.; Tan, E. K. *J Appl Polym Sci* 2001, 82, 1352.
15. Teh, P. L.; MohdIshak, Z. A.; Hashim, A. S.; Karger-Kocsis, J.; Ishiaku, U. S. *J Appl Polym Sci* 2004, 94, 2438.
16. Poh, B. T.; Kwo, H. K. *J Appl Polym Sci* 2007, 105, 680.
17. Poh, B. T.; Chow, S. K. *J Appl Polym Sci* 2007, 106, 333.
18. Poh, B. T.; Lee, P. G.; Chuah, S. C. *eXPRESS Polym Lett* 2008, 2, 398.
19. Poh, B. T.; Lim, A. L. *J Appl Polym Sci* 2008, 109, 115.
20. Gierenz, G.; Karmann, W., Eds. *Adhesives and Adhesive Tapes*; Wiley-VCH: New York, 2001; p 103.
21. Skeist, I., Ed. *Handbook of Adhesives*; 3rd ed.; Van Nostrand Reinhold: New York, 1990; p 179.
22. Poh, B. T.; Chew, C. E. *J Elastomers and Plastics* 2009, 41, 447.
23. Mark, J. E.; Erman, B.; Eirich, F. R., Eds. *Science and Technology of Rubber*, 2nd ed.; Academic Press: New York, 1994; p 400.