**Effect of Silica Filler on Viscosity and Adhesion Properties of Natural Rubber Based Adhesive**

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Viscosity, tack, peel strength and shear strength of natural rubber-silica composite-based adhesive were studied using gum rosin as the tackifying resin. The silica content varied from 0–50 phr. Toluene and poly(ethylene terephthalate) (PET) were used as the solvent and coating substrate respectively. Viscosity of the adhesive was measured by a Brookfield Viscometer whereas tack, peel strength and shear strength were determined by a Lloyd Adhesion Tester operating at 30 cm/min. Results indicate that viscosity increases steadily with silica loading due to the concentration effect of the filler. However, tack, peel strength and shear strength increase with silica content up to 20 phr silica loading, after which the adhesion properties decrease with further addition of silica. This observation is attributed to the culmination of wettability and cohesive strength at 20 phr of silica loading. **In all cases, tack, peel strength and shear strength increase with coating thickness of the adhesive.**

**Keywords:** Natural rubber; silica; adhesive; peel; shear

Several studies on the adhesion properties of natural rubber (NR)-based adhesives have been carried out. Fujita *et al.*1–2 studied the effects of miscibility and viscoelasticity on tack and shear creep resistance of NR-based pressure-sensitive adhesives. It was found that tack values of immiscible adhesives were much smaller than those of the miscible ones. The holding time of miscible NR-based adhesives tended to decrease as the tackifier content was increased, whereas for the immiscible adhesives, the effect of tackifier content on holding time was different from tackifier to tackifier. Hamed and Preechatiwong3 reported on the effect of crosslinking on the rate and temperature response on peel adhesion of NR bonded to PET. On the other hand, Leong *et al.*4 investigated the viscoelastic properties of NR pressure-sensitive adhesive using acrylic resin as a tackifier. It was observed that for a good pressure-sensitive adhesive, the ratio storage modulus at high frequencies to low frequencies should be high. The modelling of peel performance of NR-based pressure-sensitive adhesives at different rates of testing was also proposed5–6. With regard to filled adhesives, Bahattab *et al.*7 and Donate-Robles *et al.*8 have studied the adhesion properties of polyurethane adhesives containing nanosilicas and precipitated calcium carbonate, respectively. The thermal and lap shear characteristics of epoxy adhesive filled with metallic and non-metallic particles were also reported by Ghosh *et al.*9 Recently,

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we have also published a few studies on the effects of magnesium oxide, zinc oxide and kaolin on the adhesion properties of natural rubber adhesives\textsuperscript{10–12}. Results indicate that viscosity increases with filler loading. Generally, the adhesion property passed through a maximum value at an optimum filler loading. Owing to the scarcity of research on filled rubber adhesive, it is thus the objective of this paper to discuss our results on the viscosity and adhesion properties of silica-filled NR composite adhesive.

**EXPERIMENTAL**

**Materials**

SMRL was used as the elastomer for the preparation of rubber-based adhesive. It was supplied by Rubber Research Institute of Malaysia. Silica with a surface area of 50 m\(^2\)/g and specific gravity of 2.0 was chosen as the filler. Gum rosin, toluene and PET were used as the tackifier, solvent and coating substrate respectively in this research. All the materials were freshly supplied commercial grades and no purification was carried out prior to use.

**Preparation of Adhesives**

NR was masticated on a two roll-mill for 10 minutes. The rubber sample size was 2 cm \(\times\) 5 cm \(\times\) 8 cm. Nip setting was 1 mm and fraction ratio of the two-roll mill was set at 1.2. In order to facilitate easy dissolution in 30 mL of toluene, 5g of the masticated rubber was shredded. The rubber solution was then closed and kept overnight at 30°C. Meanwhile, 2g - corresponding to 40 phr of tackifier - of pulverised gum rosin was slowly added into the rubber solution with constant stirring. The rubber adhesive formed was kept for 2 h before the addition of silica filler. Five different loadings of silica, \textit{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 were used in this study. For comparison purposes, one control sample without silica loading was also prepared.

**Measurements**

**Viscosity.** A Brookfield viscometer fitted with spindle (CPE-51) and metal cup (CPE-44Y) was used to measure the viscosity of the silica-filled NR adhesive with a testing speed of 1 rpm. The platform and spindle head were cleaned with isopropyl alcohol to ensure no traces of contaminants. A drop of adhesive was then gently placed at the middle of the platform and measurement was started for one minute. The average viscosity was calculated from at least five readings recorded.

**Loop Tack.** The dimension of PET substrate was 4 cm \(\times\) 25 cm. A Sheen hand coater was used to coat the adhesive at the centre of the substrate (4 cm \(\times\) 4 cm) at 60 \(\mu\)m and 120 \(\mu\)m coating thicknesses. The coated sample was conditioned at 30°C for 24 h to remove the solvent before testing. A loop was then formed and the outside coated area was slowly brought into contact with a clean glass plate without any force other than the pushing force on the loop sample. A Lloyd Adhesion Tester operating at 30 cm min\(^{-1}\) was used to determine the debonding force. The average debonding force was computed from the three highest peaks displayed. Loop tack was defined as the debonding force per unit area of contact (Nm\(^{-2}\)).

**Peel Strength.** PET film was used as the coating substrate. Peel strength was determined using T-, 90° and 180° peel tests where the respective dimensions are shown in Table 1. For all the modes of peel testing, a Sheen hand coater was used to coat the adhesive from the end of a base stock at a coating area of 10 cm \(\times\) 4 cm at 60 \(\mu\)m and...
120 μm coating thicknesses. The face stock was carefully placed on the coated base stock to form the test specimen which was then conditioned at 30°C for 24 h to remove the solvent. A Lloyd Adhesion Tester operating at 30 cm min$^{-1}$ was used to measure the peel strength of the samples. The average peel force was computed from the three highest peaks displayed from the load-propagation plot. 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).

**Shear Strength.** The dimension of PET substrate was of 20 cm × 4 cm. A Sheen hand coater was used to coat the adhesive on the base stock from the end of the substrate at a coated area of 10 cm × 4 cm at 60 μm and 120 μm coating thicknesses. One end of the face stock (uncoated substrate) was then gently laid on the coated area of the base stock. The testing distance was 10 cm which corresponded to the coated length. The test specimen was then conditioned at 30°C for 24 h to remove the solvent before testing on a Lloyd Adhesion Tester operating at 30 cm min$^{-1}$. Shear strength was defined as the shear force per unit area of testing (N m$^{-2}$).

### RESULTS AND DISCUSSION

The effects of silica loading on the viscosity and adhesion properties of the silica-filled NR adhesive are systematically discussed below.

#### Viscosity

The effect of silica loading on the viscosity of SMRL-based adhesive is shown in Figure 1. The plot shows that viscosity of adhesive increases steadily with silica loading, the rate of increase of viscosity is faster at higher silica loading. This observation is consistent with our previous study whereby viscosity of SMR10-based pressure-sensitive adhesive increases with addition of sodium sulphates.$^{13}$ The increase in viscosity can be attributed to the molecular interaction between silica and rubber molecules. The higher the concentration of silica, the greater is the interaction between the filler and rubber chains, i.e. concentration effect of filler is observed. Figure 1 also shows that viscosity of adhesive does not increase linearly with silica concentration. This observation is associated with the nonlinear dependence of molecular interaction between silica and rubber as the filler loading is increased, thus suggesting that rubber-silica composite is not an ideal mixture.

#### Tack

Tack is defined as the property of a material to form a bond of measurable strength immediately upon contact with another surface, usually with low applied pressure.$^{14}$ Figure 2 shows the variation of tack with silica concentration at 60 μm and 120 μm coating thicknesses. The graph shows that tack increases with silica loading up to 20 phr of the filler for both coating thicknesses. The tack value then decreases with further
Figure 1. Variation of viscosity of NR-based adhesive with silica concentration.

Figure 2. Variation of loop tack with silica concentration at 60 μm and 120 μm coating thicknesses.
addition of the silica filler. This observation is attributed to the increase in wettability of adhesive which culminates at an optimum silica loading of 20 phr where lowering of surface tension to provide the proper flow and wetting characteristics is achieved\textsuperscript{15}. However, at higher silica concentration, the increase in viscosity as shown in Figure 1 decreases the viscous component of the adhesive due to the reduction of rubber chain mobility. This in turn decreases the wettability of adhesive as reflected by the lower tack value at higher silica loading. Figure 2 also indicates that the 120 μm coated sample consistently shows higher tack value than that of 60 μm coating thickness. This phenomenon is ascribed to the presence of higher amount of adhesive in 120 μm coated sample which enhances the viscoelastic response of the adhesive\textsuperscript{4}. This finding is in agreement with the general beliefs that peel force increases with increasing adhesive thickness up to a certain limit\textsuperscript{16}.

**Peel Strength**

Figure 3 shows the variation of peel strength with silica loading for the T, 90º and 180º peel tests at 60 μm and 120 μm coating thicknesses. As in the case of loop tack, peel strength also increases with silica loading up to 20 phr for the three modes of peel tests. Peel strength decreases with further addition of silica filler as shown in the three plots in Figure 3 for both coating thicknesses. This observation is attributed to the initial increase in wettability which culminates at 20 phr of silica loading where mechanical interlocking and anchorage of the adhesive in pores and irregularities in the adherent is enhanced\textsuperscript{14,17}. However, at higher silica loading, wettability of adhesive decreases due to the increase in viscosity which restricts the chain mobility and hence, decreases the viscous component of adhesive as discussed earlier in the tack section. Maximum adhesion property also occurs between 30-40 phr of sodium sulphate loadings in the SMR10-based pressure-sensitive adhesive\textsuperscript{13}. Donate-Robles et al.\textsuperscript{8} observed that the addition of precipitated calcium carbonate filler to thermoplastic polyurethane adhesive produced a moderate increase in the rheology and viscoelastic properties of the adhesive due to poor dispersion of filler and the weak interactions between the filler nanoparticles and the polymer chains. The highest final adhesive strength was obtained with adhesive containing 10% filler. From Figure 3, it is observed that the 90º peel test indicates the highest peel strength compared to T- and 180º peel tests, an observation which is due to the angle of testing whereby higher peel force is needed in the 90º peel test. The rubber chains undergo more strain-induced crystallisation\textsuperscript{18–19} in 90º peel test compared to the other two peel tests as shown by the highest peel strength in the former peel test. For a fixed silica loading, the 120 μm coated sample consistently exhibits higher peel strength compared to that of 60 μm coating thickness for the three modes of peel tests. This observation is in line with the general beliefs that peel force increases with increasing adhesive thickness up to a certain limit\textsuperscript{16}. The presence of higher amount of adhesive in the 120 μm coated substrate enhances the viscoelastic response of the adhesive\textsuperscript{4} as shown by the higher peel strength in the thicker coated sample in Figure 3.

**Shear Strength**

The dependence of shear strength of NR-based adhesive on silica loading at 60 μm and 120 μm coating thicknesses is shown in Figure 4. The graph shows that the shear strength passes through a maximum value at 20 phr filler before decreasing with further addition of the filler. This observation is attributed to the continuous increase in the cohesive and adhesive strength up to the optimum filler.
Figure 3. Variation of peel strength with silica concentration at 60 μm and 120 μm coating thicknesses for the three modes of peel tests.
loading where maximum cohesive strength occurs. Cohesive strength is an indication of holding power of the adhesive. As the silica loading is further increased beyond the optimum value, the dilution effect of the filler weakens the adhesive to resist flow during shearing action\textsuperscript{11}. This means that the filler reduces the number of entanglements per unit volume and increases the long term compliance and flow\textsuperscript{15}. Therefore, the adhesive system loses its holding power as silica filler is increased beyond its optimum value of 20 phr as shown in Figure 4. Our recent study also shows that shear strength increases up to 20 phr zinc oxide and kaolin filler loading for SMRL-based pressure-sensitive adhesive\textsuperscript{11–12}. The rate of decrease of shear strength is greater in 120 μm coated sample than that of 60 μm coated sample. This observation suggests that the effect of filler dilution is more significant at higher coating thickness. Figure 4 also shows that for fixed silica loading, the shear strength of 120 μm coated sample consistently indicates higher shear strength compared to that of 60 μm coated sample. This observation is attributed to the additional shearing resistance. Hence, higher cohesive strength by higher amount of adhesive present in thicker coated sample.

**CONCLUSION**

The viscosity of NR-based adhesive increases with silica loading. This observation is attributed to the rubber-filler molecular interaction which increases with silica loading. Tack and peel strength passes through a maximum value at 20 phr of silica loading, an observation which is associated to the culmination of wettability at this optimum silica content. However, both adhesion properties decrease with further addition of silica filler due to the increase in viscosity which restricts the chain mobility and hence, decreases the wettability of adhesive. The
highest peel strength is exhibited by the 90º peel test, a phenomenon which is associated to the angle of testing whereby higher peel force is needed in the 90º peel test. For the shear strength, it also indicates a maximum value at the optimum silica loading of 20 phr. This observation is attributed to the maximum cohesive and adhesive strength occurring at this filler loading. However, the dilution effect of silica causes the decrease of shear strength at higher silica loading. In all cases, tack, peel strength and shear strength increase with coating thicknesses due to the higher amount of adhesive in thicker coated sample which enhances the viscoelastic response.

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