

Effect of silanized silica nanofiller on tack and green strength of selected filled rubbers

Saeed Ostad Movahed,* Ali Ansarifar and Mo Song

Abstract

BACKGROUND: Tack and green strength of filled and gum (unfilled) natural rubber (NR), poly(styrene-co-butadiene) rubber (SBR), polybutadiene rubber (BR) and (SBR-BR) blend with different loadings of reinforcement agent, silanized silica nanofiller (Coupsil 8113), were studied and the results compared and discussed.

RESULTS: It was found that silica was fully dispersed in rubber matrix after 13 min of mixing. In addition, with some exceptions for NR and (SBR-BR) blend, filler loading decreased the tack strength of the studied filled rubbers. Green strength and Mooney viscosity increased with filler loading for all studied filled rubbers but with different rates and amounts. The optimum filler loadings for NR and (SBR-BR) filled blend were 30 and 10 phr, respectively. Tacks of NR filled rubbers were much higher than those of synthetic filled rubbers.

CONCLUSION: It was concluded that filler loading alters substantially the tack and green strength of the rubbers under investigation.

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Keywords: tack; green strength; rubber; silanized silica nanofiller

INTRODUCTION

The ability of two uncured rubber surfaces to resist separation after they are brought into contact for a short period of time under a light pressure is called tack. Two types of tack may be defined: autohesive tack where both materials are of the same chemical composition and heteroheasive (adhesive) tack where the materials have different compositions. A factor inherent in tack is compound green strength, the resistance to deformation and fracture of a rubber stock in the uncured state. The tack, or autohesion, and green strength of unvulcanized rubber compound components are of considerable importance in tyre manufacture. Tack properties must be optimized: too high a tack value will cause difficulties in positioning components during the building operation and may lead to trapped air between tyre parts giving after-cure defects; simultaneously, sufficient tack must be present so that the components of a green tyre will hold together until the curing process. In addition, to prevent creep with resultant component distortion, or tear occurring during moulding in the curing press, good green strength is required.

The principal theories that have been proposed to explain the mechanism of autohesion have been reviewed by Wake^{1,2} and Allen.³ The diffusion theory associated mainly with Voyutskii⁴ and Vasenin⁵ states that autohesive bonding takes place as a result of self-diffusion of polymer molecules across the interface between two similar polymer surfaces. The strength of the autohesive bond is controlled by self-diffusion due to the ability of the polymer chains to undergo micro-Brownian motion of the surface polymer molecules across the interface. Rhee and Andries,⁶ who investigated the factors influencing the autohesion of natural rubber (NR) and polystyrene-co-butadiene rubber (SBR), considered that combined diffusion-adsorption was operative.

It has been reported^{4,7-9} that the conditions that must be met by a rubber compound for exhibiting high tack are: (a) the two surfaces must come into intimate molecular contact, (b) diffusion of polymer chains across the interface must take place and (c) the bond thus formed should be capable of resisting high stress before rupture. The first two conditions describe bond formation and take place in sequence: molecular contact must always precede inter-diffusion of chain segments. When two surfaces are brought into contact, only a fraction of the total surface area comes in intimate contact due to surface asperities. The viscous flow of polymer due to contact load, generally referred to as contact flow, results in an increase of the contact area between the two surfaces with contact time. The inter-diffusion of polymer chains is facilitated upon achieving molecular contact. The third condition for high tack describes resistance to bond breaking and is dependent on both the green strength and tear strength of the polymer. It has been reported⁸⁻¹³ that diffusion of polymer chains across the interface is the major factor for bond formation. However, it has also been reported¹⁴⁻¹⁹ that an intimate molecular contact precedes the interfacial diffusion of polymer chains and thus it should be an important factor for bond formation. Hence, bond formation kinetics is influenced by both contact flow and inter-diffusion of polymer chains.²⁰ Although autohesion and adhesion of

* Correspondence to: Saeed Ostad Movahed, Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough LE11 3TU, UK. E-mail: S.Ostad-Movahed@lboro.ac.uk

Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough LE11 3TU, UK

carbon black-filled NR and SBR have been measured and studied previously by several authors under different conditions,^{6,7,21,22} these parameters have not been measured for rubbers filled with silanized silica nanofiller.

In the work reported in this paper, autohesion and green strength of several samples of NR, SBR, polybutadiene rubber (BR) and (SBR–BR) blends with different loadings of silanized silica nanofiller were studied and the results compared and discussed.

EXPERIMENTAL

Materials

The raw rubbers were standard Malaysian natural rubber grade L (98 wt% *cis*-1,4 content; SMRL), *cis*-butadiene rubber (BUNA CB 24; Bayer, UK) and styrene–butadiene copolymer (SBR-1712; Polimeri Europa UK Ltd).

The reinforcing filler was Coupsil 8113 (Degussa Ltd, Hanau, Germany). Coupsil 8113 is precipitated amorphous white silica, type ultrasil-VN3. The filler surfaces had been pre-treated with bis(3-triethoxysilylpropyl)tetrasulfane (TESPT). The filler contains 11.3% by weight TESPT and 2.5% by weight sulfur (included in TESPT), and has a 175 m² g⁻¹ surface area (measured by nitrogen adsorption) and a 20–54 nm particle size.

Sample preparation

The compounds were prepared in a Haake Rheocord 90 (Berlin, Germany), a small laboratory mixer with counter-rotating rotors. In these experiments, the Banbury rotors and the mixing chamber were maintained at ambient temperature (23 °C) for SBR and 50 °C for NR and BR. Earlier findings of the authors showed that dispersion of silica in rubber matrix at the above initial mixing temperatures was excellent.²³ In all cases the rotor speed was fixed at 45 rpm. The mixing time for all rubbers was 13 min and both rubber and filler were loaded in the mixer chamber in one stage.

For unfilled rubbers a total mastication time of 13 min was used. For (SBR–BR) blend preparation, filled individual SBR and BR (3 wt% SBR/BR) were loaded in the mixer chamber and allowed to mix for 7 min with initial mixing temperature of 90 °C. During mixing, the temperature rose to 105 °C due to heat generation by friction forces. In accordance with earlier findings of the authors,²⁴ the above mixing time and temperature were optimum for producing the best interphase characteristics (interphase amount and distribution of rubbers in the interphase) of (SBR–BR) blends.

For the determination of tack, rubber sheets (10 cm × 10 cm of 2 mm thickness) were prepared in a hydraulic press with nominal pressure of 12 MPa for 5 min at 100 °C between two smoothed sheets of aluminium foil. Subsequently the aluminium cover of one side was replaced with a latex-treated backing fabric (Henkel Consumer Adhesives, Winsford, Cheshire, UK). Without this backing fabric, measurement of tack strength was impractical using a peeling test machine because samples were fractioned before test completion. Test samples (2 cm × 9 cm) were cut from sheets and the other aluminium foil removed. Fresh rubber surfaces were allowed to come into intimate contact under a dead pressure (2 kg) and ambient temperature (23 °C) for NR and 50 °C for SBR, BR and (SBR–BR) blend for different contact times as variable parameter. The real contact area was 2 cm × 8 cm (Fig. 1).

For green strength measurements, dumbbell-shaped samples with width, gauge length, total test length and thickness of 3.6, 25, 75 and 2 mm, respectively, were cut from the same sheets.

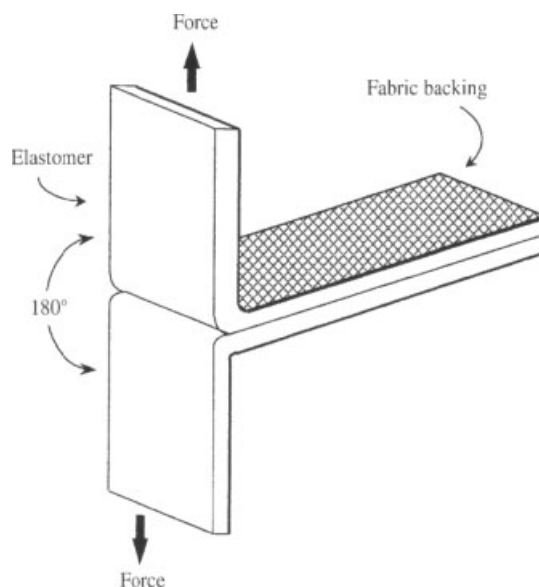


Figure 1. Peel test.

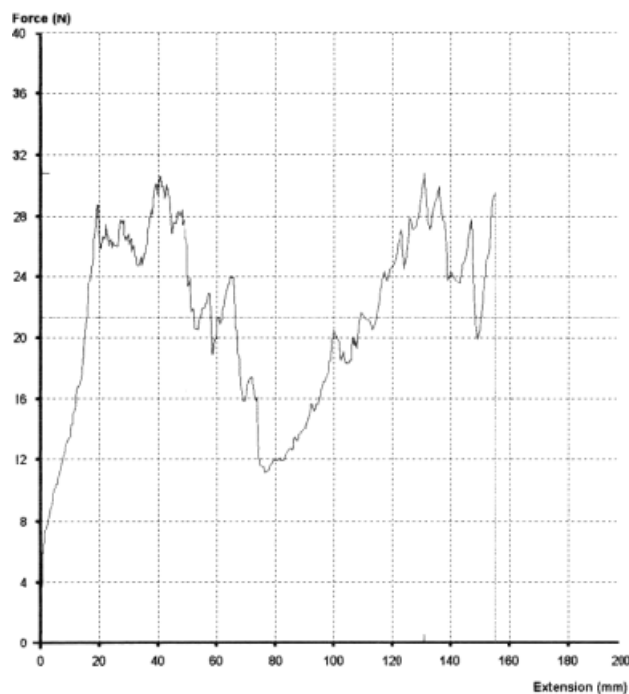


Figure 2. Typical force–extension graph for peeling test.

Measurement of tack and green strength

Peeling tests were performed at 180° (Fig. 1) using a Lloyd mechanical testing machine at ambient temperature (23 °C) and at a crosshead speed of 50 mm min⁻¹. Lloyd DAPMAT computer software was used to store and process the data. A 500 N load cell was installed on the Lloyd instrument. Figure 2 shows a typical force–extension curve for a peeling test for which the average value of force was measured and the corresponding tack strength (N m⁻¹) was calculated using the following equation:

$$\text{Tack strength} = \frac{2F}{\omega} \quad (1)$$

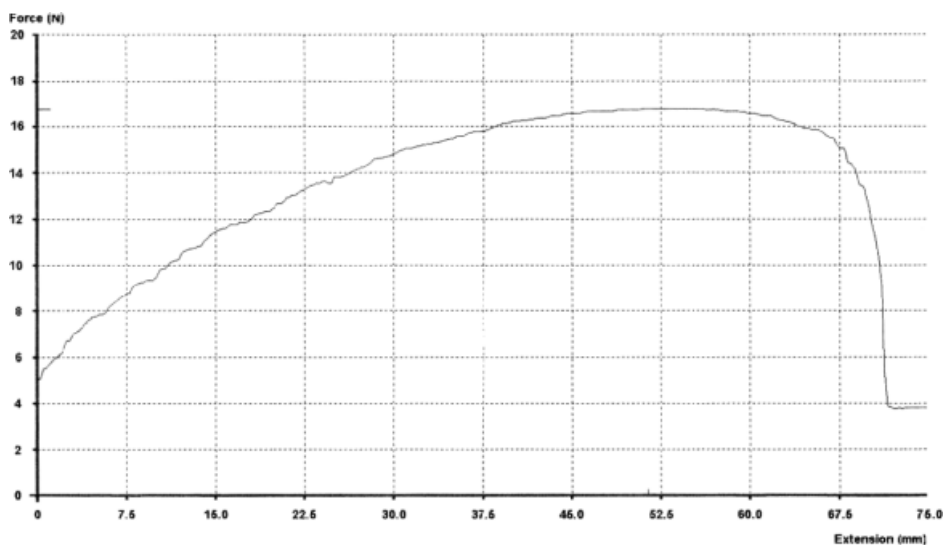


Figure 3. Typical force–extension graph for green strength test.

where F is the average peeling test force (N) and ω is the width of the sample (m). Reported tack values are the mean value for five tested samples.

For green strength measurements, the same Lloyd machine was employed and the green strength was taken as the maximum stress in the stress–strain plot (Fig. 3). The tests were carried out at ambient temperature (23 °C). Reported green strength values are the mean value for five tested samples.

Mooney viscosity measurements

The viscosity of the rubber compounds was measured (in ML: Mooney units with large rotor, 1 + 4 min) at 100 °C using a single-speed rotational Mooney viscometer supplied by Wallace Instruments, Surrey, UK. In accordance with the relevant British standard,²⁵ the torque necessary to rotate a metal disc (here a large rotor, 38.1 mm in diameter) in a cylindrical chamber filled with un compounded or compounded rubber was measured. The Mooney viscosity number is proportional to the value of this torque.

Assessment of silica dispersion in the rubbers

Twenty-four hours after mixing ended, the rubbers were examined using SEM to assess the filler dispersion. Dispersion of the silica particles in the rubbers was assessed using a LEO 1530 VP field emission gun SEM instrument. Small pieces of the uncured rubber were placed in liquid nitrogen for 3 min and then fractured to create two fresh surfaces. The samples, 60 mm² in area and 5 mm thick, were coated with gold, and then examined and imaged using SEM.

RESULTS AND DISCUSSION

When two pieces of rubber are brought in intimate contact, polymer chains diffuse through the interface (contact flow) to form new polymer–polymer and/or polymer–filler physical bonds (bond formation). A stronger bond formation results in higher tack strength.

The nature of the rubber and filler and their ability to construct strong bonds are key factors in tack strength determination.⁷

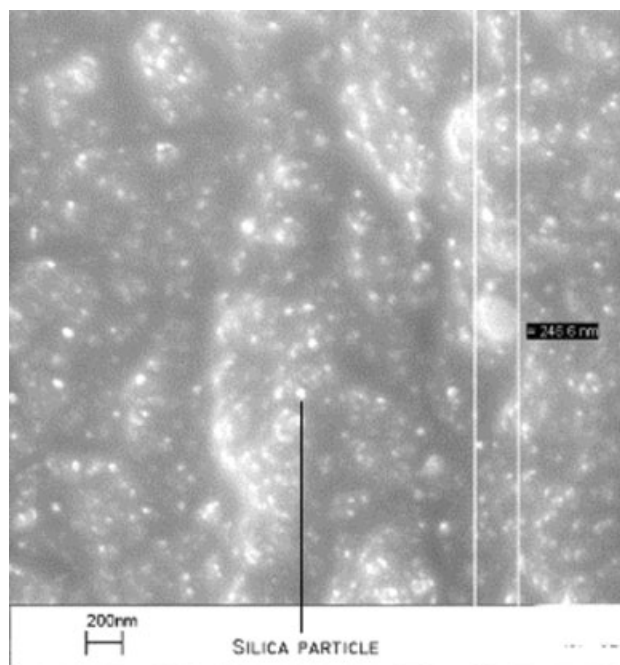


Figure 4. SEM image showing the dispersion of silica particles in the rubber matrix. Specimen: NR loaded with 60 phr Coupsil 8113. Mixing time: 13 min with good dispersion.

If the rubber is capable of forming strong bonds (regardless of decreasing contact flow due to the existence of filler particles in the rubber matrix and consequent restriction of polymer chain mobility) tack strength will be increased. Tack enhancement of NR with 40 phr carbon black loading is an example of this mechanism.²¹ In contrast, if the rubber cannot make strong bonds and in conjunction the contact flow is reduced due to filler loading then tack strength will be decreased. Reduction of SBR tack strength with 40 phr carbon black loading is an example of this mechanism.⁷

In some cases, depending upon the amount of filler loading, either the first or second mechanism may be applicable in the

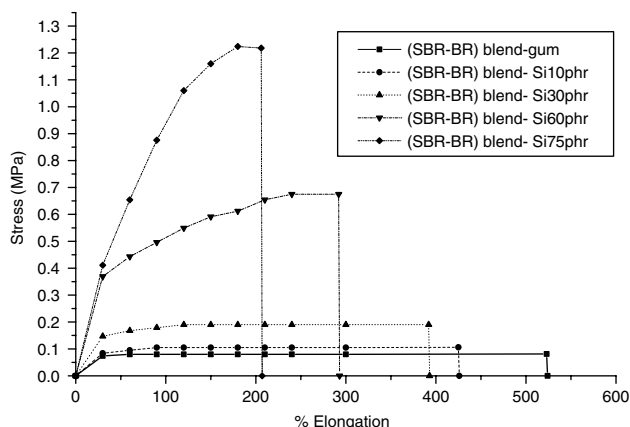


Figure 5. Stress versus percentage elongation for (SBR-BR) blend (75-25 phr) for different loadings of silanized silica nanofiller.

same system. Here an optimum filler loading exists for maximum tack strength.²²

Silica dispersion assessment

Figure 4 shows a full dispersion of silica particles in NR matrix for an optimum mixing time of 13 min. Large silica aggregates were seen in the rubber matrix after short mixing times.²⁴ In addition, Fig. 4 shows that the size of particles was down to about 60 nm. This was similar to the actual particle size of the filler, 20–54 nm, before mixing with the rubber. The same situation was seen for the rest of the BR, SBR and (SBR-BR) blend filled rubbers.

It was concluded that a minimum mixing time of 13 min was sufficient to fully disperse the silica particles in the rubbers, which helped to maximize the reinforcing effect of the filler on the mechanical properties of vulcanizates.

Long mixing times break down the rubber and cause a reduction in the molecular weight and viscosity. The reduction is due to chain scission or the mechanical rupture of the primary carbon-carbon bonds that are present along the backbone of the rubber chains. This is often compensated by the reinforcing effect of the filler resulting in Mooney viscosity increase.

Effect of different loadings of silanized silica nanofiller on green strength and Mooney viscosity of rubbers

To study the green strength of filled rubbers, it is useful to study their Mooney viscosities because filler loading increases both parameters.

Generally, on filler loading (Coupsil 8113), the green strength increases and elongation at break decreases. As an example, Figs 5 and 6 show a reduction of the elongation at break from 523 to 207% and green strength enhancement from 0.08 to 1.22 MPa for gum (unfilled) and 75 phr filler loaded (SBR-BR) blends, respectively.

Figure 6 also compares the green strength of different rubbers versus filler loading. The absolute values of this property for gum and loaded NR (0.235–3.56 MPa) were higher than those of other gum and filled rubbers. In addition, for lower filler loading (less than 40 phr), BR and (SBR-BR) blend had the lowest values. Unlike SBR and (SBR-BR) blend, for filler loading higher than 60 phr, NR and BR filled rubbers showed a sharp green strength enhancement.

Figure 7 compares Mooney viscosities (MU) of the different rubbers as a function of filler loading. As expected, the Mooney viscosities of all rubbers increased with filler loading but at different

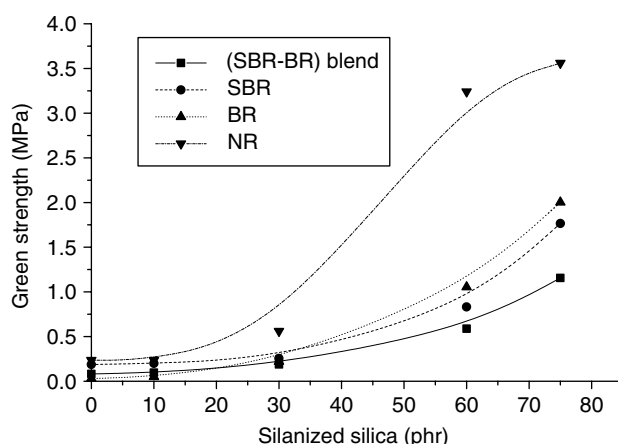


Figure 6. Green strength of different rubbers versus silanized silica nanofiller loading (test temperature 23 °C).

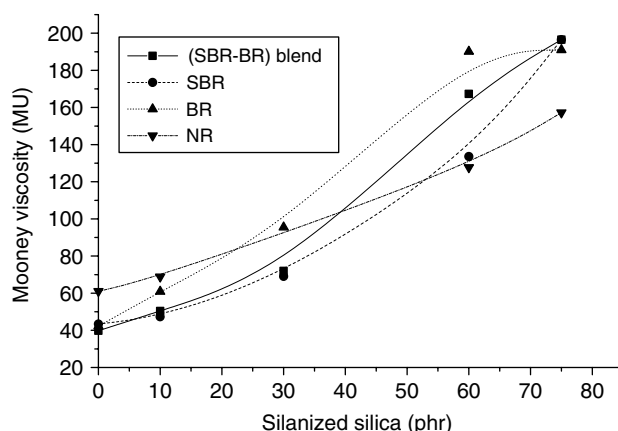


Figure 7. Mooney viscosity of different rubbers versus silanized silica nanofiller loading.

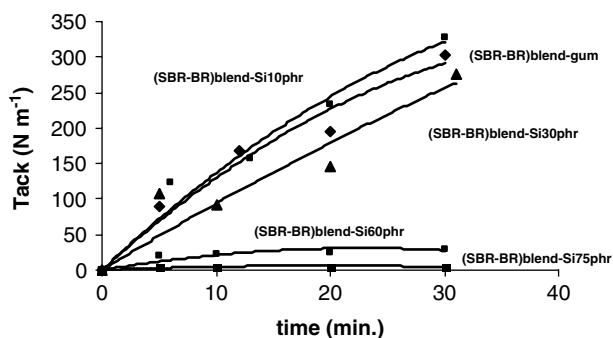


Figure 8. Tack of (SBR-BR) blend (75-25 phr) versus time for different silanized silica nanofiller loadings (test temperature 50 °C).

rates. For filler loading up to 50 phr, the Mooney viscosities of NR were higher, and beyond that loading were lower than those of the other rubbers. This means that the effect of filler loading was more important for smaller amounts in NR and for greater amounts in the other rubbers. In addition, the Mooney viscosities of (SBR-BR) blend (40–197 MU) lie between the values for BR (42–191 MU) and SBR (43–197 MU).

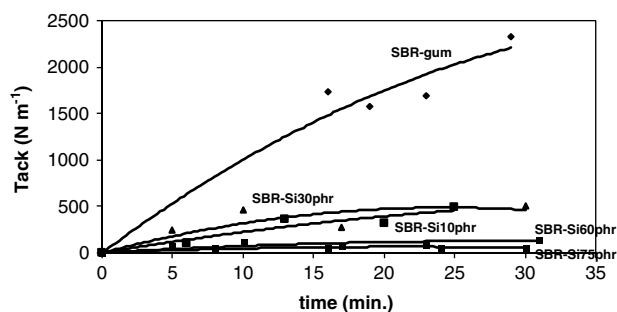


Figure 9. Tack of SBR versus time for different silanized silica nanofiller loadings (test temperature 50 °C).

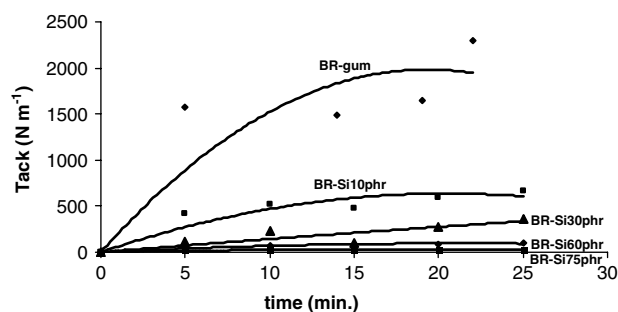


Figure 10. Tack of BR versus time for different silanized silica nanofiller loadings (test temperature 50 °C).

Effect of different loadings of silanized silica nanofiller on tack strength of (SBR–BR) blend

Figure 8 shows tack strength versus filler loading for the (SBR–BR) blend. It is clear that the tack of this rubber for low filler loading (10 and 30 phr) as well as the unfilled rubber was much higher than that for higher filler loading (60 and 75 phr).

Excepting the 10 phr filler loading, the tack of all (SBR–BR) filled rubbers was lower than for the gum rubber. This means the polymer chains are unable to form new polymer–polymer and/or polymer–filler physical bonds in conjunction with contact flow reduction. The existence of filler particles in the polymer matrix restricted polymer chain mobility, resulting in contact flow reduction.

It seems therefore that the optimum amount of filler loading for maximum tack enhancement is 10 phr. The tack for the blend filled with this amount of filler was higher than that for the gum rubber because polymer chains are able to disentangle and form new stronger physical bonds.

Effect of different loadings of silanized silica nanofiller on tack strength of SBR

Figure 9 shows tack strength versus filler loading for SBR. In this system the tack for all filled rubbers was lower than that for the gum rubber, but with some differences. Here, the inability of polymer chains to disentangle and pass through the interface (due to the existence of filler particles) is the reason for the reduction of tack with filler loading.

Practically, rubbers loaded with 60 and 75 phr filler did not have enough tack under the studied conditions. Interestingly, the rubber with 30 phr filler loading showed better tack strength than the other filled rubbers and was chosen as the optimum filler loading.

Although tack was still lower than that of the gum rubber, the present findings are in agreement with earlier findings for carbon black-filled SBR by Hamed.⁷ Hamed studied carbon black-filled SBR and found that the tack for all filled rubbers was lower than that for gum rubber. For example the tack of rubber loaded with 40 phr carbon black was about 30% of that of gum rubber. This ratio for a loading of 30 phr silica (Coupsil 8113) was 20% after 25 min contact time (Fig. 9). It seems that the silica under investigation reduces the tack of SBR more than does carbon black.

Effect of different loadings of silanized silica nanofiller on tack strength of BR

Figure 10 shows tack strength versus filler loading for BR. For all BR samples, with no exception, the tack strength decreased with filler loading. In this case, BR chains are unable to disentangle and

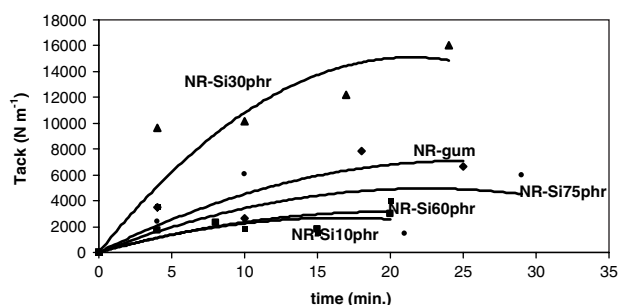


Figure 11. Tack of NR versus time for different silanized silica nanofiller loadings (test temperature 23 °C).

diffuse through the interface and form strong new physical bonds due to the existence of filler particles in the polymer matrix. Unlike the (SBR–BR) blend and SBR, in this system there is no optimum filler loading value.

Effect of different loadings of silanized silica nanofiller on tack strength of NR

Figure 11 shows tack strength versus filler loading for NR. The case of NR is more interesting than those of BR, SBR and (SBR–BR) synthetic rubbers. In this system, except rubber with 30 phr filler loading, the tack of all other filled rubbers was lower than that of the gum rubber. The rubber with 10 phr filler loading had the lowest tack and that with 30 phr filler loading the highest. It seems that the optimum filler loading was 30 phr. For this filled rubber, polymer chains in the presence of filler particles could disentangle and diffuse through the interface, thus making stronger physical bonds, better than those of gum rubber and of the other filled rubbers. These findings are in agreement with earlier findings for carbon black-filled NR.^{7,21} For example, Hamed⁷ found that 40 phr loading of carbon black in NR increased the tack by about 300% compared to gum NR. This ratio for NR filled with silica (Coupsil 8113) was 230% with 25 min contact time (Fig. 11).

The tack strength sequence (30 phr > gum > 75 phr > 60 phr > 10 phr) showed a severe competition between two mechanisms: the ability and tendency of polymer chains to disentangle and penetrate (diffuse) through the interface for new stronger physical bond formation; and the restriction of polymer chain mobility by filler particles.

Comparison of tack strength of different filled rubbers

Figure 12 compares the tack strength of the different filled rubbers (NR, SBR, BR and (SBR–BR) blend) for 10 phr filler loading. It is

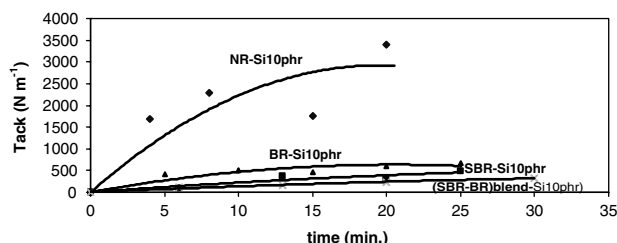


Figure 12. Tack of different rubbers versus time for 10 phr silanized silica nanofiller loading (test temperature 50 °C for all rubbers except NR which was 23 °C).

observed that the tack for NR filled rubbers was higher than that for BR, SBR and (SBR–BR) blend synthetic rubbers.

The lowest tack is shown by the (SBR–BR) blend, which – at least in part – stems from the partial miscibility of the two polymers, SBR and BR, resulting in diffusion of polymer chains through the interface which is even more difficult than in the case of the individual SBR and BR.

CONCLUSIONS

- Generally, with some exceptions for NR and (SBR–BR) blend, filler loading reduced the tack strength of the rubbers.
- Green strength and Mooney viscosities increased with filler loading for all filled rubbers but with different rates.
- For NR and SBR, the optimum filler loading was 30 phr; for (SBR–BR) blend, it was 10 phr.
- The tack of NR filled rubber was higher than that of the other synthetic rubbers.
- Silica particles were dispersed in rubber matrix at the nanoscale.

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