

ELECTRICAL AND MECHANICAL PROPERTIES OF POLYANILINE-DBSA/SBR LATEX BLENDS

Chan-Young PARK,^a Young-Se OH,^{b*} Sang-Hyun BAEK,^b Tae-Young KIM^c and Soong-Hyuck SUH^d

^a Division of Applied Chemical Engineering, Pukyong National University,
Busan 608-810, Korea

^b Central Research Park, Kolon Industries Inc., Kumi 730-030, Korea

^c Engineering Research Institute, Chonnam National University,
Gwangju 500-757, Korea

^d Department of Chemical Engineering, Keimyung University,
Daegu 704-701, Korea

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The purpose of this study is to improve the mechanical and conductivity properties of SBR latex by adding small amounts of polyaniline(PANI)-dodecylbenzene sulfonic acid (DBSA) as conducting polymer. The conducting composites were prepared by the solution blending of PANI-DBSA and SBR latex in the aqueous medium. The composite films were prepared by the blended solution casting method. The PANI was protonated with DBSA. The morphological, dynamical mechanical, tensile, and electrical properties were measured as a function of the amount of PANI-DBSA complex content in the blends. Even though the electrical conductivity of the blends was shown the highest value at 1 wt% of PANI-DBSA complex content, the highest mechanical property was shown 2 wt% of PANI-DBSA complex content.

INTRODUCTION

The use of blends in the rubber industry has known to be important because it allows tailoring of the characteristics of a material by using two or more polymers with different properties in the composition. Conductive polymer blends became the most used way in fabricating conducting polymer materials. Intrinsically, conducting polymers, including polyaniline, polypyrrole, and polythiophene, have a potential utilization in a large number of applications: rechargeable batteries, conducting paints, conducting glues, anti-static formulations, electronic devices, etc. Especially, polyaniline (PANI) is one of the most studied conducting polymers due to its high electrical conductivity associated to good stability, facility of preparation and low cost of monomer. Under those conditions, their applications in PANI/polymer blends has been of great interest. However, the major problem in applying these polymers for basic materials is their poor morphological features due to the high van der Waals interaction of conducting polymers. Many methods were used to overcome this problem including N-substitutions¹⁻³ or ring substitutions^{4,5} of aniline by aliphatic large radicals, block copolymers⁶ and the doped PANI base with a functionalized protonic acid^{7,8}. In general, the solubility and electrical conductivity of the doped PANI increased with the longer alkyl chain length of dopants because the longer alkyl chain acted as a better surfactant and increased the free volume between polymer chains.^{9,10}

On the other hand, the initial particle size of the PANI base material was shown to affect the final conductivity of blends. Colloidal particles have the potential to be finely dispersed in a polymer medium due to their small size. Using colloidal particles of an intrinsically conducting polymer for blending of other

* To whom the correspondence should be addressed: email: ysoh@kolon.com

polymers, the high conductivity level may be realized at low PANI contents. For this reason, the preparation of colloidal particles¹¹⁻¹³ and their application in PANI/polymer blends¹⁴⁻¹⁸ have been paid much attention. Gospodinova *et al.*¹³ used colloidal polyaniline–dodecyl benzene sulfonic acid (DBSA) dispersion for the preparation of blends with both water soluble and water insoluble polymers. Beadle *et al.*¹⁵ obtained electrically conductive polyaniline/copolymer blends by polymerizing aniline in the presence of a chlorinated copolymer latex.

In this work we synthesized PANI–DBSA latex using a unique method of aniline polymerization⁸ in the presence of DBSA for the aqueous medium. Blends of styrene-butadiene rubber (SBR) and PANI-DBSA were prepared using the latex mixing method for manufacturing anti-static rubber materials, and the electrical, dynamic mechanical, and tensile properties of these blends of SBR/PANI-DBSA have been studied.

EXPERIMENTAL

Materials and Preparation of Samples

Styrene-butadiene rubber (SBR) latex was donated by Myeong Kwang Chemical Co. The composition of styrene to butadiene was 60 to 40 wt. %, and the solid content of SBR latex was measured to be 55 wt. %. Polyaniline–dodecyl benzene sulfonic acid complex (PANI–DBSA) was prepared by the following procedure described elsewhere⁸. Aniline (3 g, Junsei Co.) was mixed with DBSA (10.8 g, Aldrich Co.) in demineralized water (600 g) for 3 hours to form the homogeneous white dispersion complex. The dispersion was cooled about to 0°C, and an initiator solution of ammonium peroxydisulfate (APS) (15 g dissolved in 50 g water) was added as drop-wise. The polymerization reaction was carried out at 0°C for 7 hours in the glass reactor with stirring. The dispersion color was changed from white through blue to dark green with reaction, and the stable PANI–DBSA dispersion was obtained. From this dispersion, PANI–DBSA solid complex of 1.1 wt. % was measured by the complete precipitation with methanol.

Using a homomixer, SBR latex of the matrix polymer was mixed with the aqueous PANI–DBSA dispersion to prepare the aqueous emulsion blends. These emulsion blends were casted on a glass plate and evaporated at 35°C for 2 days, following by drying at 80°C for 1 day to prepare clear blend sheets.

Tests

Morphologies were studied using the cryogenically fractured surface of samples, sputtered with gold before viewing under a scanning electron microscope (SEM, JSM 9400). Dynamic mechanical properties of the cast sheets were measured on a rheovibron (Orientec DDV-01EP) at 11 Hz, and -50–80°C, with liquid N₂ purging. Tensile properties at room temperature were measured by following the standard procedure in ASTM D-412 with type C specimen using the universal test machine (Hounsfield) operated at 500 mm/min. Electric resistance of blends was measured by Wheatstone Bridge type L-3c (Yokogawa Electric Work Ltd.) with 40 mm(L) x 6.5 mm(W) x 1.5 mm(H) specimen. Electric conductivity was calculated from the following equation,

$$\text{Electric conductivity [S/cm]} = L/(R \times A) \quad (1)$$

where R is the real electric resistance [Ω] of the sample measured by Wheatstone Bridge, A is the cross-sectional area of sample [cm^2], and L is the distance between two electrodes on Wheatstone Bridge [cm]. Anti-static properties of blend sheets were studied using the static honestometer type S-4104 (Shisheido Co.), which was composed with disk-rotating 1000 rpm with the sample specimen of 32 mm(W) x 32 mm(L), electrode discharging 10 kV, and another electrode receiving electric charge on the sample surface. The static-charge of samples rapidly increased with running tester, and reached the constant value indicating the anti-static level. The lifetime of static charge was evaluated by measuring the required time until the charge reaches to the half value of full charge.

RESULTS AND DISCUSSION

Morphologies

SEM micrographs of the fractured surface of SBR/ PANI-DBSA blends were shown on Fig.1. As can be seen in this figure, the resulting morphology does significantly vary with PANI-DBSA component changes. By increasing the concentration of PANI-DBSA, the morphology of the fractured surface of matrix

polymers totally changed from smooth to very rough. At very low concentration, PANI-DBSA polymer particles were irregularly dispersed in the lamella rubber matrix. For more than 2 wt% of PANI-DBSA polymer, however, better dispersions were progressed to some extents of unable to finding PANI-DBSA particles, whereas the fractured surface is rougher, and agglomerated structure is displayed in matrix. This change of morphology may possibly suggest better dispersions for PANI components within the matrix, due to the action of the DBSA unit as a surfactant. Therefore, the agglomerated structure shown in the fractured surface of blends should be responsible for the high level of conductivity in blends due to an infinite-link formation.

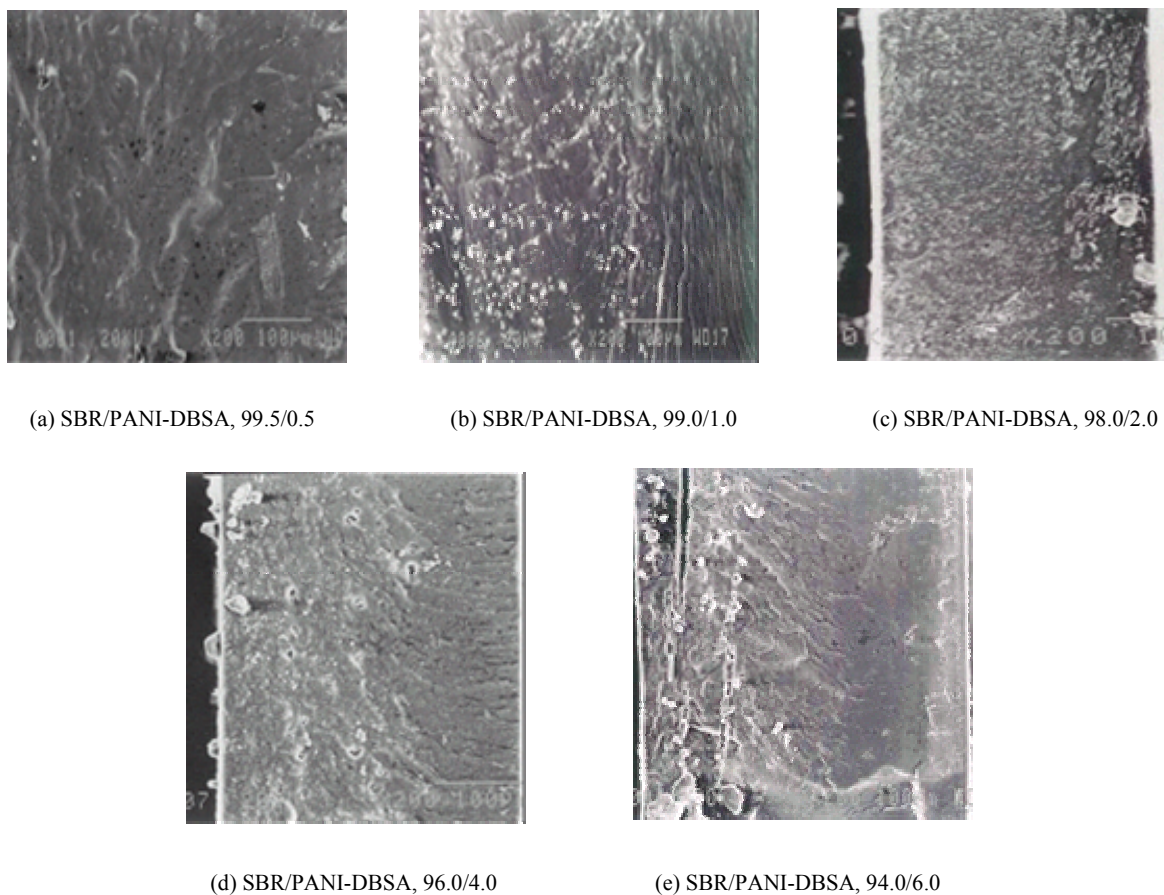


Fig.1 – SEM micrographs of PANI-DBSA/SBR latex blends.

Dynamic mechanical properties

Dynamic mechanical analyses give information about storage modulus (E'), loss modulus (E''), and $\tan \delta$. Fig. 2 illustrates the storage modulus curves for the SBR / PANI-DBSA blends as a function of temperature. Regardless of blend compositions, the storage modulus rapidly decreased at round 18°C , showing a damping. However, with an increase of PANI-DBSA content, the storage modulus of elastic regions at $40\text{--}60^\circ\text{C}$ was increased, especially showing the tiny plateau region in the blends of more than 4 wt% for PANI-DBSA. This implies that SBR phase was reinforced by PANI-DBSA particles at the elastic region.

Fig. 3 shows $\tan \delta$ curves as a function of temperature. The glass transition temperature (T_g) of SBR phase was clearly observed at 33°C . The correct value for the glass transition temperature of PANI-DBSA has not yet been confirmed although there were some papers to explain such transitional effects based on the

molecular relaxation of the chains²⁰. As shown in Fig. 3, the Tg of SBR was very slightly shifted to higher temperature with increasing the PANI-DBSA content. This result qualitatively indicates that, although there is no significant variation in the Tg of SBR phase, *i.e.*, blends are miscible, there is the structural interaction between the PANI-DBSA particle and SBR, as indicated in Fig. 1.

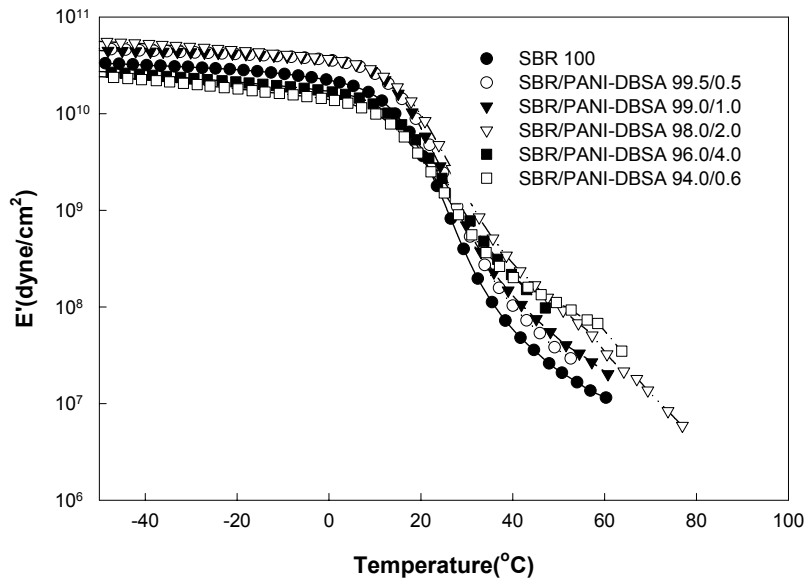


Fig. 2 – Storage modulus (E') of PANI-DBSA/SBR latex blends.

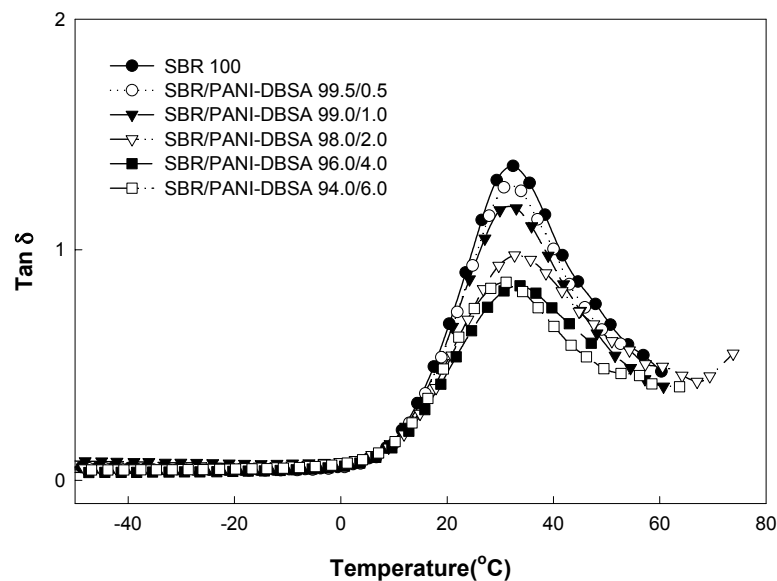


Fig. 3 – $\text{Tan } \delta$ of PANI-DBSA/SBR latex blends.

To evaluate the effect of DBSA in PANI blends, we prepared the free DBSA blend, SBR/PANI (96/4) blend, with the same procedure. The dynamic properties of the free DBSA blend were compared with that of SBR/PANI-DBSA (96/4) in Fig. 4. The storage modulus of the glass region was the same level in both blends; however, the higher storage modulus of elastic region was observed in the PANI-DBSA blend. This result may be derived from the possible formation of physical cross-linking through the chain inter-linking of PANI-DBSA with SBR matrix. Consequently, high conductivity is pronounced by these chain inter-linkings.

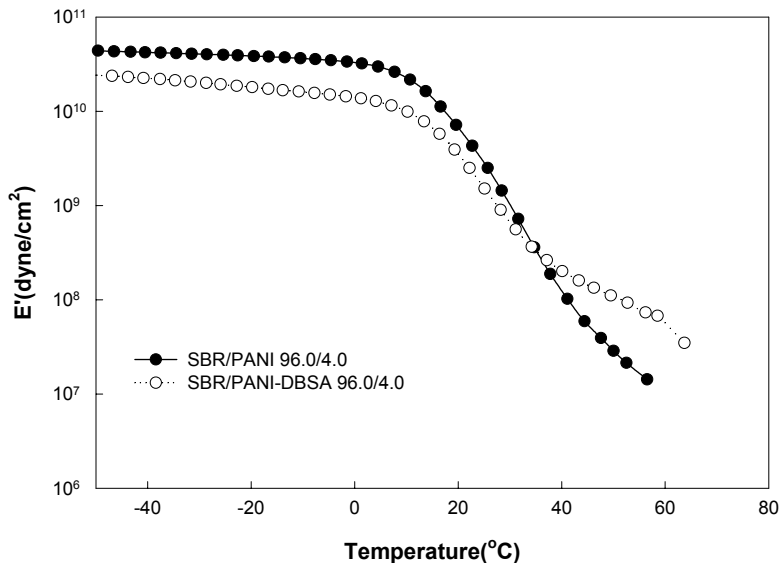


Fig. 4 – Storage modulus of PANI/SBR latex blends and PANI-DBSA/SBR latex blends at 96/4 composition.

Tensile properties

Fig. 5 shows the tensile strength of SBR at the breaking point as a function of PANI-DBSA contents. There is an initial increment of the strength at break for 1 wt% of PANI-DBSA, followed by a pronounced decrease to 6 wt% of PANI-DBSA. Elongation at break (Fig. 6) shows slight increasing to 1 wt% of PANI-DBSA, and there is an abrupt decrease between 1 and 2 wt% of PANI-DBSA, followed by slight decreasing to 6 wt% PANI-DBSA. The initial modulus (Fig. 7) shows an abrupt increase between 0.5 and 1 wt% PANI-DBSA and a constant in a slightly lower level to 6 wt% PANI-DBSA as shown in the storage modulus behavior at the glass region (Fig. 3). This effect is assigned to the rigidity of PANI-DBSA particles, acting as reinforcing filler and changing the viscoelastic behavior of the rubber to a rigid material. PANI-DBSA also contributes to increase the rubber cross-link density.

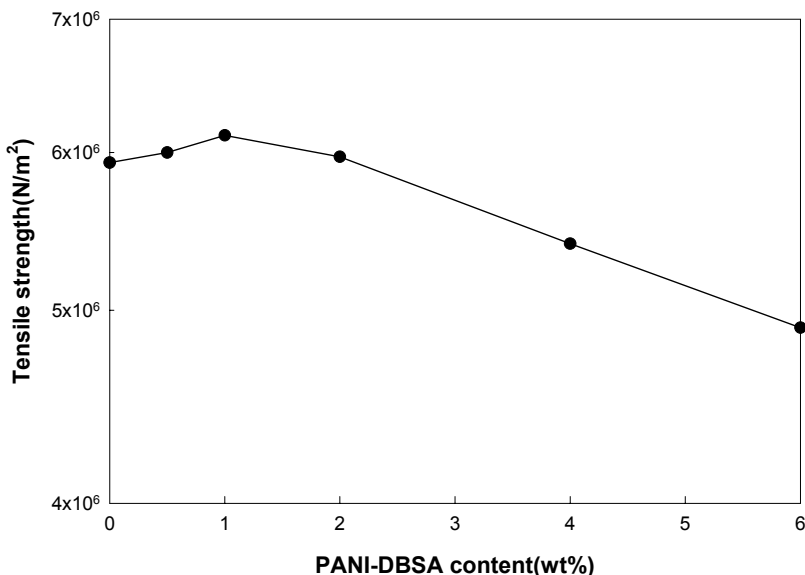


Fig. 5 – Tensile strength of PANI-DBSA/SBR latex blends.

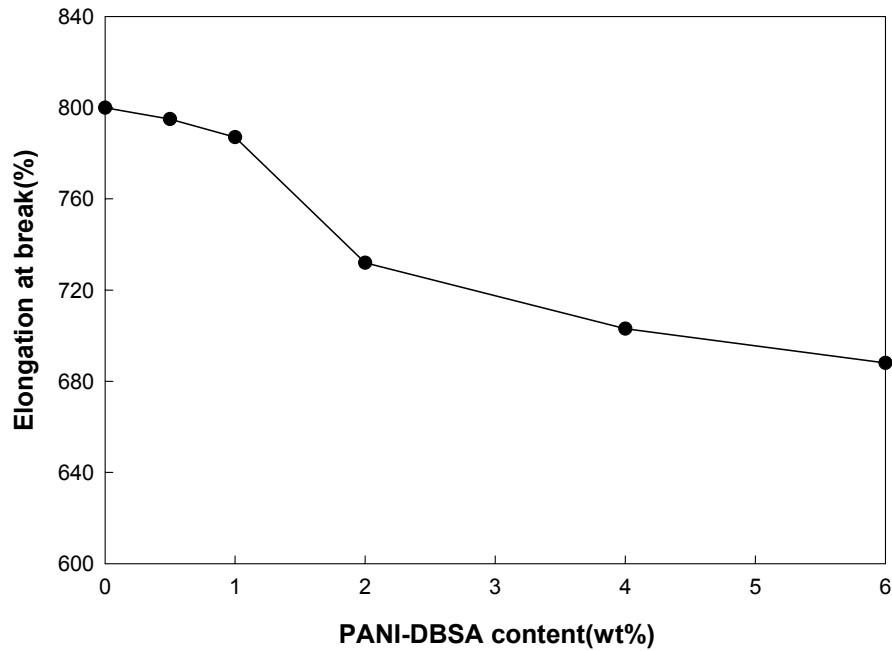


Fig. 6 – Elongation at break of PANI-DBSA/SBR latex blends.

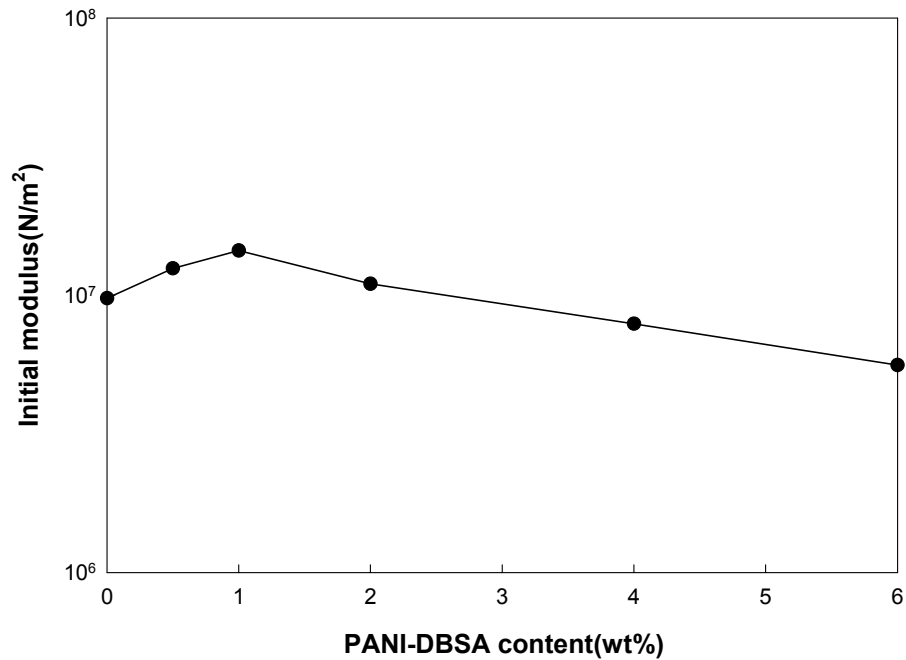


Fig. 7 – Initial modulus of PANI-DBSA/SBR latex blends.

Electrical properties

The electrical conductivity of the SBR/PANI-DBSA blends vs. PANI-DBSA content is displayed in Fig. 8. The conductivity of blends gradually increases with PANI-DBSA contents without exhibiting a sharp percolative insulator-conductor transition. At 0.5 wt% PANI-DBSA, the conductivity is already above 10^{-1} S/cm and it tends to level off above 1 wt% PANI-DBSA.

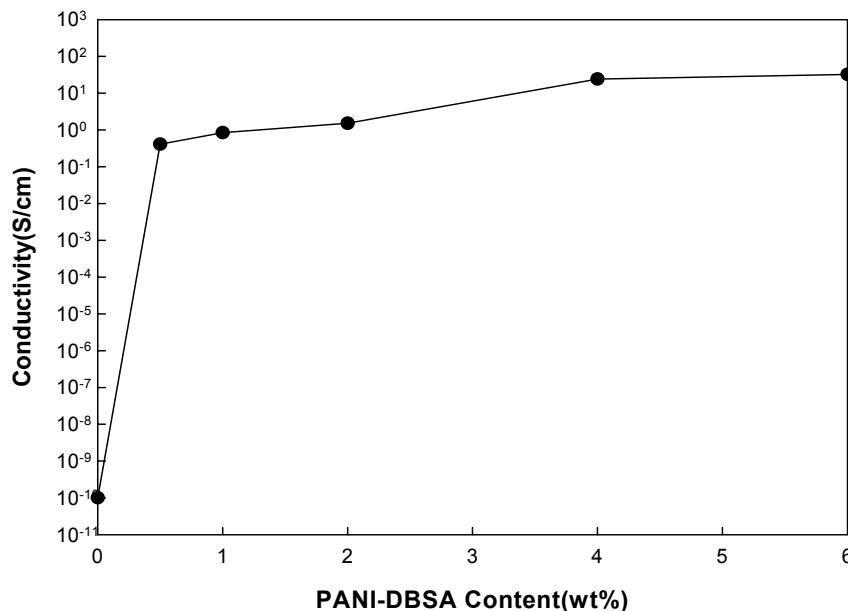


Fig. 8 – Conductivity of PANI-DBSA/SBR latex blends.

The gradual conductivity rise is observed, and the absence of a sharp percolative insulator-conductor transition in PANI blends is ascribed herein to a very significant and fast segregation process which is taking place already in the combined PANI-DBSA/polymer aqueous dispersions. This segregation stems from the different surface characteristics of the PANI-DBSA particles and the matrix polymer particles (refer to the different surfactants used to stabilize the particles, as given in the experimental part). It is also noted that segregation phenomenon in solution cast films, or within a polymer melt. Percolation threshold is defined as the minimum amount of conductive fillers that must be added to an insulator matrix to cause the onset of electrical conductivity. Theoretical studies for inorganic fillers show that the percolation threshold occurs when the filler represent 16% (v/v) in the mixtures.²¹ According to Fig. 8, the onset of conductivity increasing is reached with only 1 wt% of PANI-DBSA. This means that the percolation threshold is about 13 times smaller than the calculated by theoretical predictions. Other blends using conducting polymers also presented low percolation threshold, and this is explained by the formation of interpenetrating networks among the components of the mixture, which was observed by SEM measurements. The conductivity continuously increases with PANI-DBSA contents and seems to reach a plateau at 4 wt% PANI-DBSA.

CONCLUSION

In this work we prepared the elastomeric conductive blends of SBR and PANI-DBSA by obtaining stable PANI-DBSA aqueous dispersion and observed that PANI-DBSA composition affects mechanical and conductive properties of blends. SBR increases the elastic modulus from the glass region to the rubbery region using PANI-DBSA. Tensile properties of PANI-DBSA/SBR latex blends show the maximum value at 1 wt% PANI-DBSA. The conductivity of PANI-DBSA/SBR latex blends is already above 10^{-1} S/cm at 0.5 wt% PANI-DBSA and it tends to level off above 1 wt% PANI-DBSA. The conductivity slightly increases with PANI-DBSA contents and seems to reach a plateau at 4 wt% PANI-DBSA.

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