Change of Conductivity of Polyaniline/(Styrene–Butadiene–Styrene) Triblock Copolymer Composites During Mechanical Deformation

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ABSTRACT: A measuring method for a conductivity change through a current change during extension deformation or compression deformation of conductive elastomeric composites composed of a polyaniline (PAn)/styrene–butadiene–styrene (SBS) triblock copolymer was established. The composites were prepared by *in situ* emulsion polymerization of aniline in the presence of SBS using dodecylbenzene sulfonic acid (DBSA) as an emulsifier and a dopant. The product was melt-processed (MP), solution-processed (SP), or secondary doped with *m*-cresol (SSP). The results for measurement of the conductivity change of the composites processed by the three different methods showed that for the MP and SP samples conductivity increases with extension, whereas for the SSP sample when the PAn content is lower than the percolation threshold, conductivity diminishes with increasing extension, but when the PAn content exceeds the percolation threshold value, conductivity followed an empirical equation with a maximum value. During compression, the conductivities of most of the MP, SP, and SSP samples exhibited a maximum value with change of the compression force, except the MP sample with a higher PAn content, the conductivity of which increased with the compression force. All the differences are related to their different morphological structures. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2156–2164, 2000

Key words: mechanical deformation; polyaniline; composite; thermoplastic elastomer; conductivity

INTRODUCTION

Conductive elastomers are generally made by two ways: One is to add conductive particles, such as metal powder, carbon black powder, or fine conductive fibers to an elastomer; the other is to make composites containing a conductive polymer and elastomer. The latter is now paid much attention by researchers, because the elastomer molecules as a matrix can be mixed with the conductive component molecules more thoroughly than in the former method. Hassan et al.[1] studied the effect of tensile deformation on the electrical

conductivity of SRF black-loaded styrene–butadiene rubber and showed that the equilibrium value of the electrical conductivity increased with deformation up to an elongation of 110% and then decreased with further increase of the extension. Radhakrishnan and Saini[2] studied the dependence of the electrical resistivity (ρ) of polypyrrole (PPy)/styrene–butadiene–styrene (SBS) on mechanical deformations both in compression and extension modes and indicated that the dependence followed a power law of the type $\rho = \rho_0 (\Delta L/L)^{\beta}$, where L is the length of the sample and β is an exponent, which has a value of 4 for the PPy/SBS composite and only 1.5 for the carbon/SBS blend. Recently, we[3] reported the preparation of PAn/SBS composites via *in situ* emulsion polymerization of aniline in the presence of SBS

using dodecylbenzene sulfonic acid (DBSA) as both the emulsifier and the dopant and showed that the composites behave like a conductive thermoplastic elastomer. The composites can be processed by the melt method or the solution method. The conductivity and morphology of the composites are different for different processing methods. Secondary doping[4] for the solution-processed composite enhanced, obviously, the conducivity of the composite and changed its morphology.

This article deals with the conductivity change during extension deformation and compression deformation of PAn/SBS composites processed by three methods, namely, melt processing (MP), solution processing (SP), and secondary doping (SSP), in order to determine their electrical behavior during application.

EXPERIMENTAL

Materials

Aniline was distilled under reduced pressure and stored in a refrigerator. SBS was supplied by the YueYang Petroleum Chemical Co. with a styrene content of about 30% and an M_n of 1.2×10^5. DBSA with a sulfonic acid content of 0.31 mol/100 g was purified by treatment with concentrated hydrochloric acid and extraction with toluene followed by drying. All the other chemicals used were chemically pure.

Preparation and Processing of PAn/SBS Composites

The conductive PAn/SBS composite was prepared via *in situ* emulsion polymerization of aniline in the presence of SBS using DBSA as an emulsifier and ammonium persulfate as an oxidant, as follows: SBS, 93 g, was dissolved in 600 mL xylene with stirring, followed by adding 18.1 mL aniline dropwise. Then, a 200-mL xylene solution of 97.6 g DBSA was added slowly. After mixing with a 100 mL distilled water with vigorous stirring to form an emulsion, a 100 mL aqueous solution of 22.7 g ammonium persulfate was added dropwise into the emulsion with stirring at room temperature. The polymerization lasted for 12 h.

MP Method

After polymerization, the emulsion of PAn/SBS was precipitated by pouring it into acetone. The dark green sediment was filtered and washed with acetone and water, then vacuum-dried for 48 h. The composite was pressed at 130°C for 7 min.

SP Method

The resulting emulsion was deemulsified and washed five times with an acetone–water (1:1) mixture in a separating funnel to remove excess DBSA and ammonium sulfate. A green solution of the PAn/SBS composite in xylene was obtained, which was stable at room temperature during storage. The film of the composite was obtained by casting the solution onto glass and then dried under an infrared lamp and under a vacuum at 40°C.

Method of SSP

The SP film was fully immersed in *m*-cresol, becoming semiswollen, and taken out and dried under infrared light and under a vacuum at 40°C to a constant weight.

Characterization and Testing

The morphology of broken sections of different processing samples was examined on a JSM-35C scanning electron microscope. The PAn content was determined by elemental analysis performed on a Carlo–Erba MOD 1106 apparatus. The conductivity of the composites with different PAn contents at a static state was measured by the four-probe method for higher conductivity and by the high-impedance method for lower conductivity.

Principle for Measurement of Conductivity Change via Current Change During Mechanical Deformation

The relationship between electric conductivity (σ), electric current (I), voltage (V), length (l), and volume (Z) is expressed as

$$I = \sigma VZ/l^2$$

where Z is assumed to be a constant, since the volume change of an elastomer during deformation is less than 1%.[5] Under the condition of the constant potential V, the change of electric current from the original state (I_0) to an extended state (I) may be expressed as follows (the subscript 0 is for the original state):

$$I_0/I = (\sigma VZ/l^2)/(\sigma_0 VZ/l_0^2) = \sigma l_0^2(\sigma_0 l^2)$$

Since the elongation $\kappa = (l - l_0)/l_0$, then

$$\sigma/\sigma_0 = (1 + \kappa)^2 I/I_0 \qquad (1)$$

According to the above equation, when the ratio of an electric current at a certain extension to the original electric current is measured, then the conductivity change can be obtained.

Method for Measuring Conductivity Change Versus Extension

Samples of 2-mm thickness were cut into a rectangular shape, the ends of which were uniformly coated with silver paste and used as electrodes and connected with two copper wires using an adhesive. Polytetrafluoroethylene film was sandwiched between the sample and clamps of the XL-2500 tensile tester. The copper wires were connected with a TD-3690 potentiostat and a 3086X–Y recorder. The sample was extended by the tensile tester with an extension rate of 200 mm/min. The electric potential was kept at low voltage (5 V) to prevent a joule thermal effect.

Method for Measuring Conductivity Change Versus Compression

Samples were made into circular shapes. Two sides of the sample were coated uniformly with silver paste, which were used as electrodes and connected with two copper wires using an adhesive. The copper wires were connected to a TD-3690 potentiostat and a 3086X–Y recorder. The sample was insulated with a polytetrafluoroethylene bag and sandwiched in a mold, on which was applied a compression force gradually using a XL-2500 tensile tester. The electric current change during compression was recorded on the X–Y recorder.

RESULTS AND DISCUSSION

Conductivity and Morphology of PAn/SBS Composites Processed by Different Methods

Figure 1 shows that conductivity of the PAn/SBS composites increase quickly at first and then slowly with increase of the PAn content. The abrupt increase of conductivity at a certain content of a conductive component is defined as the percolation threshold, which implies that certain conductive routes are formed in the insulating matrix. The percolation threshold value can be obtained by intersecting two tangent lines on the
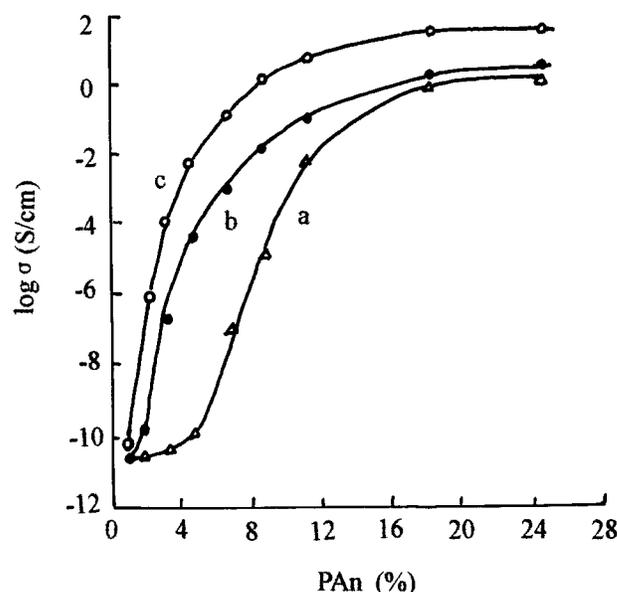

Figure 1   Conductivity as a function of PAn content in PAn/SBS composites, processed by different methods: (a) MP sample; (b) SP sample; (c) SSP sample.

curve, one for the quick-change section and the other for the slow-change section. Different processing methods affect the conductivity of the PAn/SBS composites. At the same PAn content, the room-temperature conductivity increases in the following order: MP < SP < SSP. The percolation threshold values for SSP, SP, and MP are 3.8, 7.0, and 10%, respectively. SSP is most favorable to the formation of a conductive route by the self-assembly of the conductive component, and solution processing is better than melt processing for the conductive PAn chains to form a conductive route.

The morphology of the broken sections of the three samples all with 11.0% PAn content is shown in Figure 2(a–c). The broken section of the MP sample exhibits the brittle fracture character with microvoids of several micrometers size, which indicates aggregation of PAn chains into the microdomains, whereas that of the SP sample shows the ductile fracture feature such as hills and valleys without voids. This is because during solution casting the PAn molecules dispersed in the polystyrene domains reduced the strength of the physical crosslinkage due to the polystyrene domains, which was demonstrated by the fact that the mechanical strength of the SP composite was lowered at first with increase of the PAn content.[3] The broken section (c) of the SSP sample is smooth, which indicates that after SSP the coil-like PAn chains expand and self-assemble
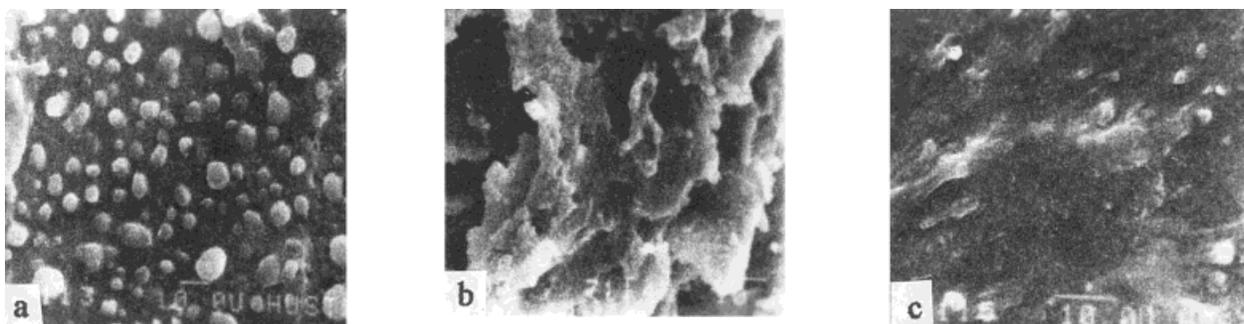
Figure 2 SEM photographs of broken section of PAn/SBS composite, processed by different methods: (a) MP sample; (b) SP sample; (c) SSP sample.

into conductive routes with a weak interaction. The expanded PAn chains are rigid and exhibited a crystalline structure, thus causing the composite to display the rigid character during deformation.

Figure 3 shows the WAXD curve of the SP sample (a) and the SSP sample (b) of the PAn/SBS composite after SSP. It can be seen that no peak occurs at a small angle for the SP sample, but a sharp peak appears at $2\theta = 2.4$ for the SSP sample, denoting that the SP sample, which has no crystallinity, exhibits a crystalline structure after SSP. This is attributed to the fact that SSP makes the coiled PAn chains expand and self-assemble into a crystalline structure. These results indicate that the processing method has a noticeable effect on the dispersion behavior of the conductive component in the SBS matrix, which directly decides the formation of the conductive route.

Change of Conductivity with Extension for MP and SP Samples of PAn/SBS Composites

Figure 4 shows that for the MP sample with 11.0% PAn content the electric current dimin-
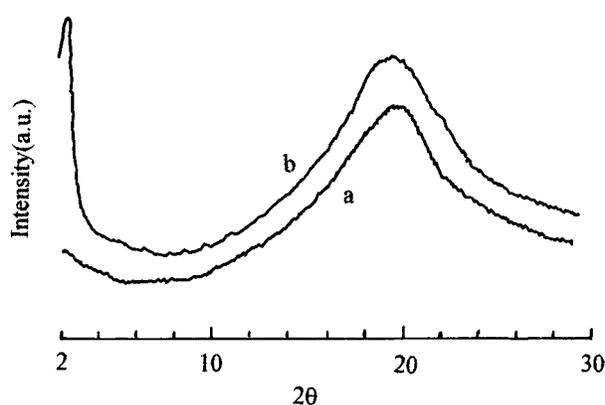
ishes with increasing extension. But when the elongation exceeds 200%, the electric current increases with the extension. After conversion of the electric current into conductivity according to eq. (1), the change of conductivity versus extension is also illustrated in Figure 4. The result shows that conductivity increases with extension first slowly and then quickly. When the elongation reaches 450%, the ratio of $\sigma/\sigma_0 = 15.6$.

For the SP samples with 11.0 and 8.6% PAn content, the conductivity also increases with extension, but the change seems smaller than that for the MP sample (Fig. 5). At an elongation of 500%, the conductivity ratio $\sigma/\sigma_0 = 5.2$. This result indicates that, for the MP sample, the conductivity that increased due to the extension and orientation of the conductive PAn chains is larger than that for the SP sample. The difference is related to the phase separation of PAn in the composite. Since PAn chains are more rigid than the SBS chains, extension of the composite affects
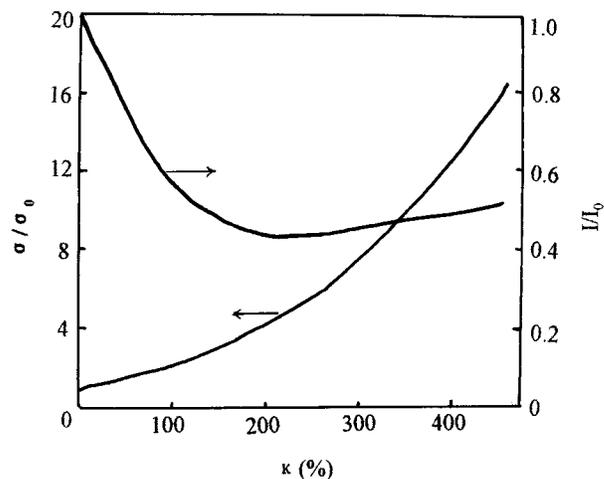

Figure 3 WAXD curves of (a) SP sample and (b) SSP sample of PAn/SBS composites.

Figure 4 Change of conductivity and electric current during extension of PAn/SBS MP sample with PAn content of 11.0%.
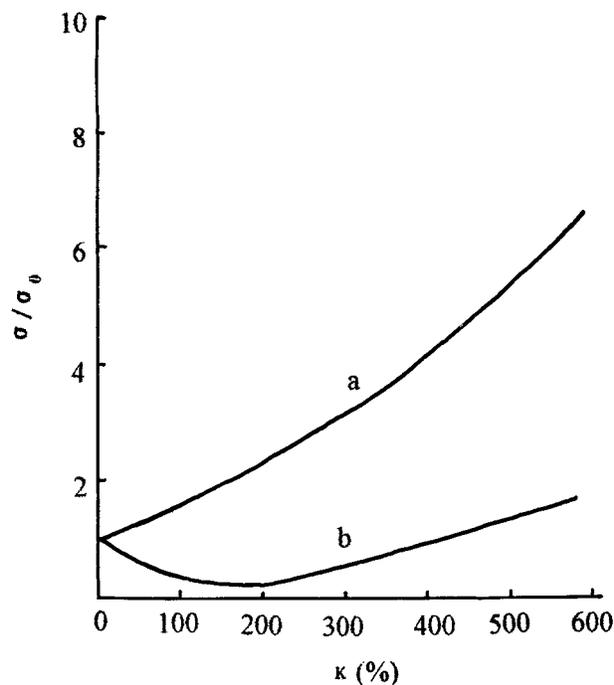
Figure 5 Change of conductivity during extension of PAn/SBS SP samples with PAn content of (a) 11.0% and (b) 8.6%.

mainly the deformation of the SBS matrix and the orientation of the PAn chains. The larger the conductive aggregates, the greater the probability for contact of the aggregates during extension and the greater is the sensitivity for the change of conductivity. At the same PAn content, the conductivity increase is greater for the MP sample than for the SP sample due to the larger conductive aggregates in the MP sample.

The conductivity change of the composite containing 8.6% PAn differs from that containing 11.0% PAn. The former PAn content approaches that of the percolation threshold of the SP composites. At the beginning of the extension, the relative displacement of the PAn chains lowers the contact probability between the conductive components, resulting in a decrease of conductivity. When the elongation exceeds 150%, the conductivity begins to increase, probably because the contraction effect of the cross section of the sample becomes predominant during further extension; thus, the contact probability between the conductive components begins to increase with the extension.

Relation Between Conductivity and Extension for PAn/SBS Composites with SSP

Figures 6 and 7 show the change of electric conductivity with the extension for PAn/SBS samples

with different PAn contents after SSP. For the sample containing 4.6% PAn, the conductivity decreases quickly with increase of the extension and decreases almost one order of magnitude at 100% elongation, probably because when the conductive content approaches the percolation threshold of the SSP sample the conductive routes were quickly destroyed by the extension. With increasing conductive content, the change of the conductivity with the extension for the SSP samples is different from that with the lower PAn content. During extension, the conductivity increases at first and then decreases. This phenomenon may be attributed to two factors: During the extension process, the orientation of the expanded PAn chains was enhanced and the stretching of soft segments reduces partially the hindrance of the soft segments to the conductive components, thus increasing the contact between the conductive components, resulting in increasing conductivity. On the other hand, relative displacement of the conductive chains during the extension process increases the distance between the conductive components, thus decreasing the contact probability and conductivity. At the beginning of the extension, the former factor plays the main role. After a certain extension, the latter factor plays the main role. The extent of change is related to
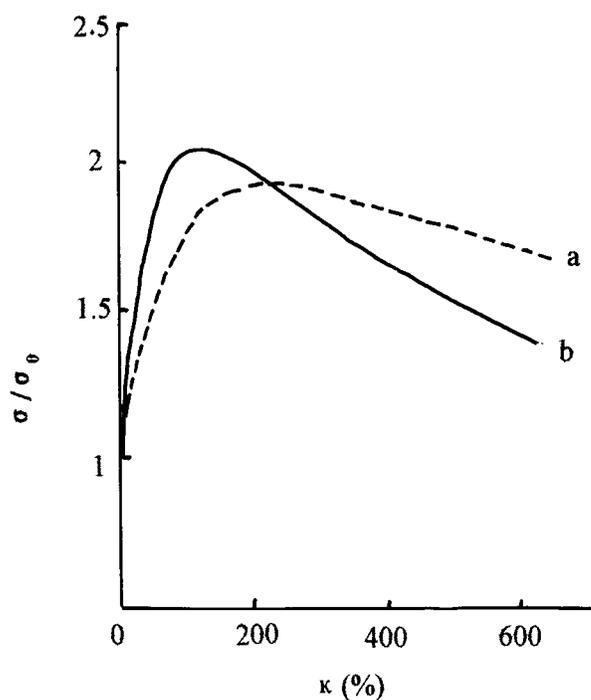

Figure 6 Change of conductivity during extension of PAn/SBS SSP samples with PAn content of (a) 11.0% and (b) 6.2%.
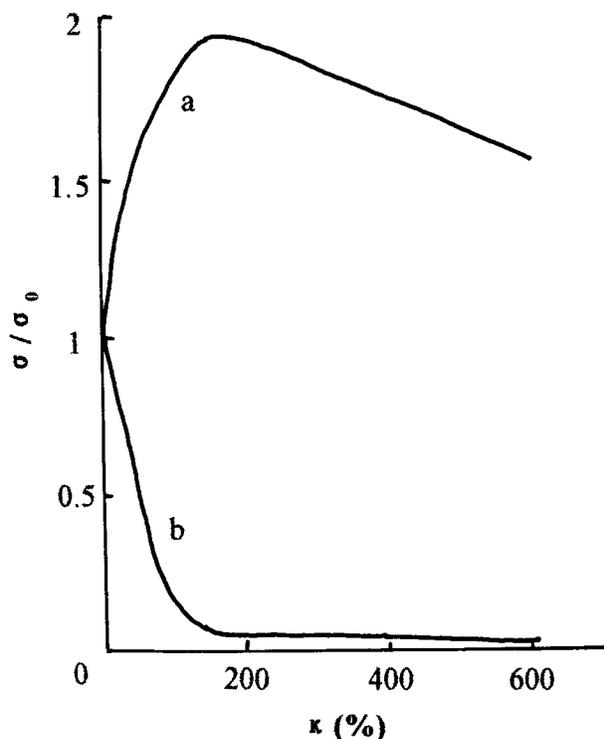
Figure 7 Change of conductivity during extension of PAn/SBS SSP samples with PAn content of (a) 8.6% and (b) 4.6%.

Table I Relative Parameters Between Conductivity and Elongation for the SSP Samples of PAn/SBS Composite

PAn (%)	a	b
6.2	0.670	0.320
8.6	0.967	0.271
11.0	1.219	0.211

factor for increasing the conductivity plays the main role, whereas the factor for decreasing conductivity plays the smaller role. Figure 8 compares the calculated curve based on the empirical equation with the experimental data. It is interesting to note that the empirical curve can represent the change of conductivity with the extension in most cases, especially for the composites containing a lower PAn content such as 6.2% PAn.
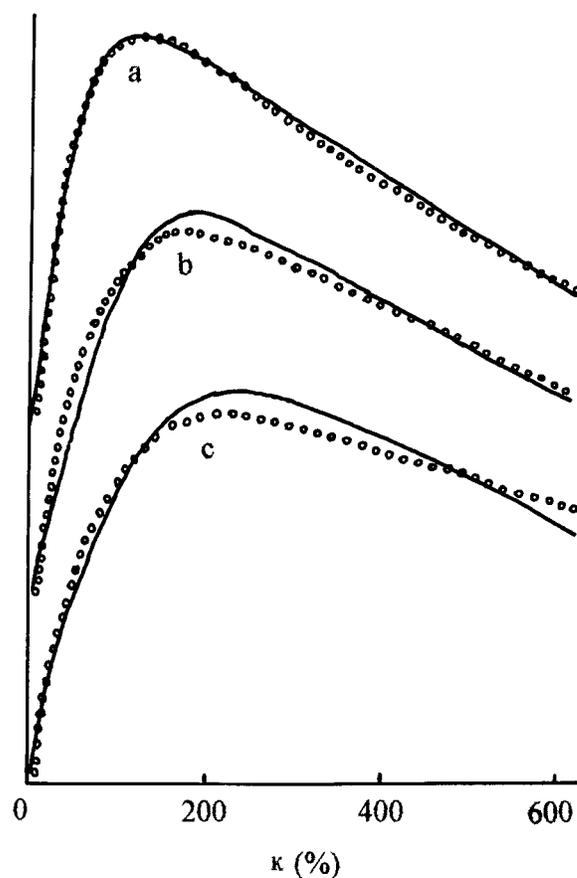
the conductive routes formed. Based on the above analysis, the relation between extension and conductivity can be established as the following equation:

$$\Delta\sigma/\sigma_0 = 1/(a/\kappa + b\kappa)$$

where the physical meaning of a/κ is that with increasing extension the conductivity increases due to increase of the contact probability between the conductive components, whereas the physical meaning of $b\,\kappa$ is that the conductivity decreases with increasing extension due to the relative displacement.

Since $\sigma = \sigma_0 + \Delta\,\sigma$, then

$$\sigma/\sigma_0 = 1 + \kappa/(a + b\kappa^2) \qquad (2)$$

By means of nonlinear regression, the a and b constants can be calculated according to the κ and σ values. Table I lists the calculated values of a and b for the composite samples with different PAn contents. It can be seen that parameter a increases with the PAn content, whereas parameter b decreases with increasing PAn content. This implies that with increasing PAn content the

Figure 8 Comparison of conductivity change during extension of PAn/SBS SSP samples between calculated values based on (line) empirical equation and (circles) experiment data. The PAn contents are (a) 6.2%, (b) 8.6%, and (c) 11.0%.
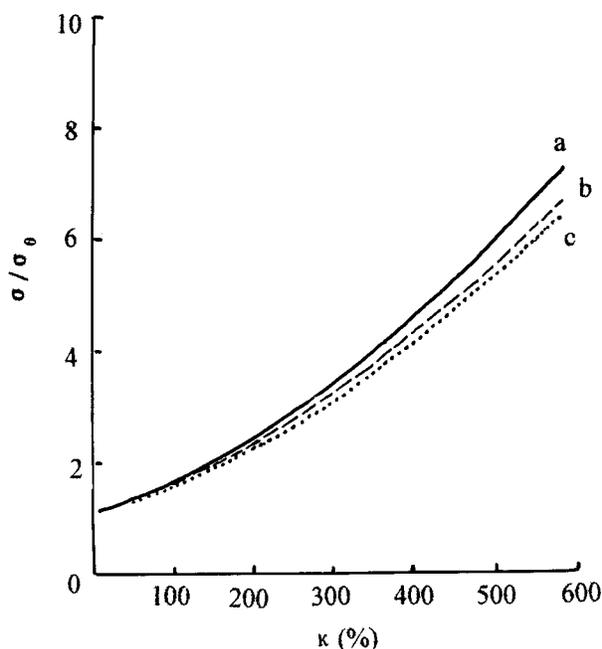
Figure 9   Influence of extension rate on the change of conductivity during extension of PAn/SBS SP sample: (a) 80 mm/min; (b) 200 mm/min; (c) 500 mm/min.

Effect of Extension Rate and Repeated Extension on the Relation Between Extension and Conductivity

Using an SP sample of the PAn/SBS composite containing 11.0% PAn, the effect of the extension rate on the relationship between the conductivity change and the extension is shown in Figure 9. It can be noted that the extension rate affects the relation between the conductivity change and the elongation only slightly in the range of 200–500 mm/min. But in the range of 80–200 mm/min, the lower the extension rate, the greater the conductivity change with the extension, probably due to the lower hysteresis and better orientation of the conductive components in the composite during extension.

Figures 10 and 11 show the effect of repeated extension on the change of the electric current, which represents the change of conductivity, for the SP and SSP samples containing 11.0% PAn content, respectively. The second extension is carried out after the first extension is stopped at a certain elongation and kept without stress for 1 h. It is interesting to note that the SP sample seems to have a memory effect for the last extension, as shown in Figure 10. When the next extension exceeds the first extension, the curve shows a deflection point near the last elongation of the last extension. For the SP sample, the electric

current or conductivity can nearly be recovered after repeated extension, whereas for SSP sample, the conductivity cannot be recovered. These results demonstrate that a certain type of processing makes the conductive components distribute in a certain state, and during extension, the conductive components are distributed again. For the SP sample, the conductive coiled PAn chains tend to orient during duplicate extensions, but they can be recovered after removal of stress. However, for the SSP sample, the conductive routes formed by self-assembly of expanded PAn chains into the crystalline structure due to weak interaction were destroyed during the extension. When the strain is recovered, the crystalline structure of expanded PAn chains cannot be easily recovered. Thus, the conductivity of the SSP sample is lowered.

Conductivity Change of the Composite Samples During Compression

Figure 12 illustrates the change of the conductivity during compression of the MP samples with different PAn contents. For samples with higher PAn contents, the conductivity increases slowly at first and then quickly with increasing compression force, whereas for the sample with 11.0%
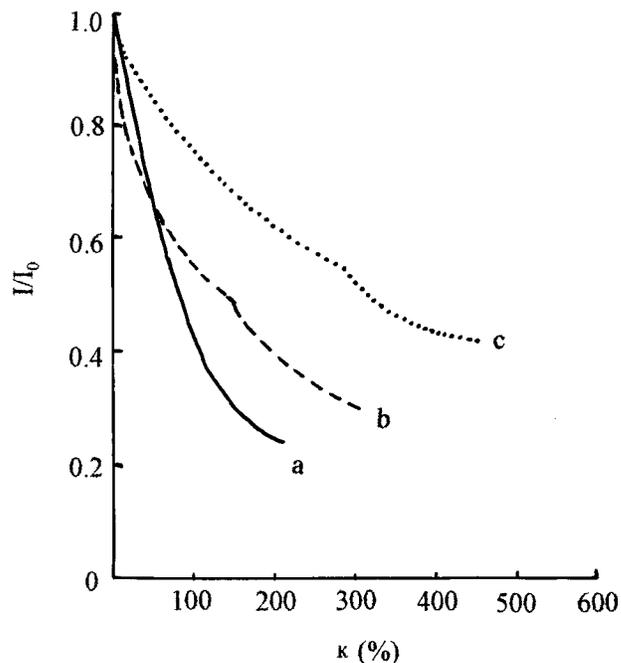

Figure 10   Influence of extension times on the change of electric current during extension of PAn/SBS SP sample with 11.0 % PAn content: (a) first time; (2) second time; (c) third time.
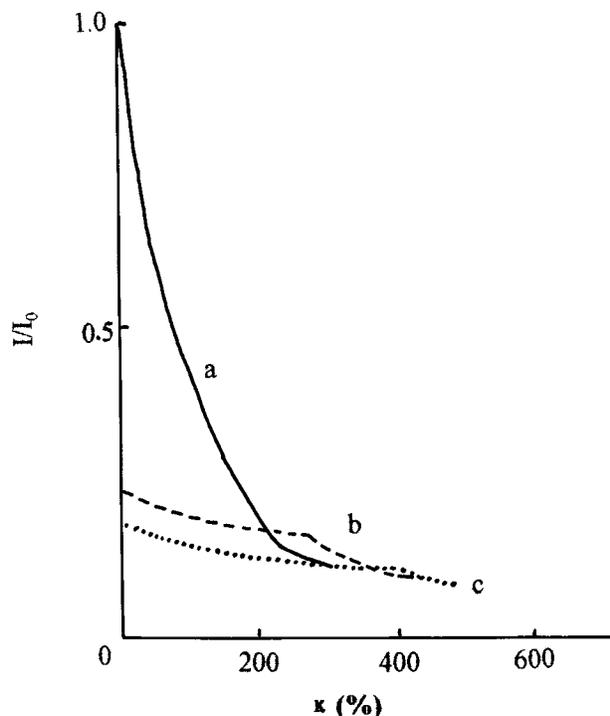
Figure 11   Influence of extension times on the change of electric current during extension of PAn/SBS SSP sample with (A) 11.0% PAn and (B) 8.6% PAn: (a) first time; (b) second time; (c) third time.

Figure 12   Change of conductivity during compression of PAn/SBS MP samples with PAn content of (a) 35.2%, (b) 21.o%, and (c) 11.0%.

Figure 13   Change of conductivity during compression of PAn/SBS SP samples with PAn content of (a) 21.0%, (b) 11.0%, (c) 8.6%, and (d) 6.2%.

PAn content, the conductivity increases at first and then decreases. Since compression can increase the contact between the co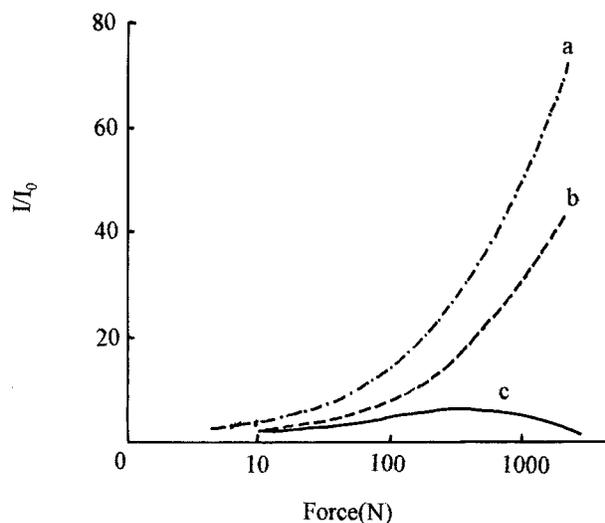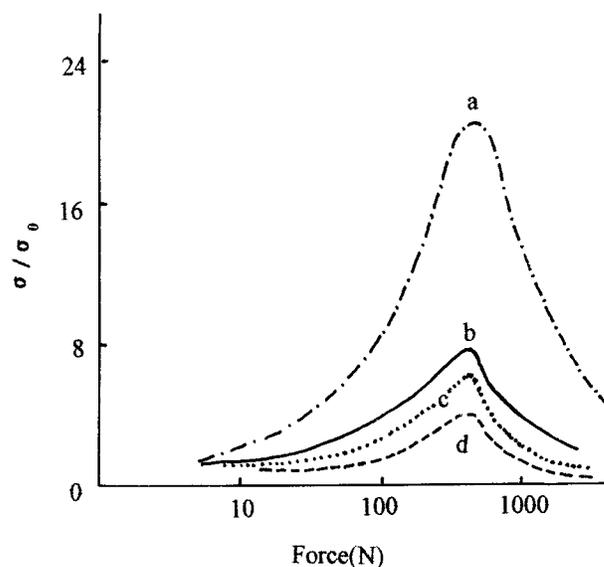nductive components, the conductivity can be enhanced. How-ever, when the content of the conductive component is not high, a high compression force can induce the extension of the sample perpendicular to the compression direction, thus enhancing the arrangement of the conductive component in the perpendicular direction, resulting in reduction of the conductivity along the compression direction.

The conductivity change of the SP samples with the compression force is different from that of the MP sample. All the SP samples show a maximum value of conductivity at about 500 N (Fig. 13). The maximum value of σ/σ_0 increases with the PAn content, since the contact probability between the conductive components increases with the PAn content. At a compression force higher than 500 N, the conductivity ratio decreases with increasing compression force, probably because the aggregates of the conductive component of the SP sample are smaller than those of the MP sample, and at a higher PAn content, the arrangement of the conductive component perpendicular to the compression direction destroys the conductive route along the compression direction, resulting in a reduction of conductivity.

Figure 14 shows the effect of the compression on the conductivity of the SSP samples. In the range of a lower compression force, the conductivity also increases with the compression force, and in the range of a higher compression force, the conductivity decreases with an increasing compression force. However, the maximum conductiv-
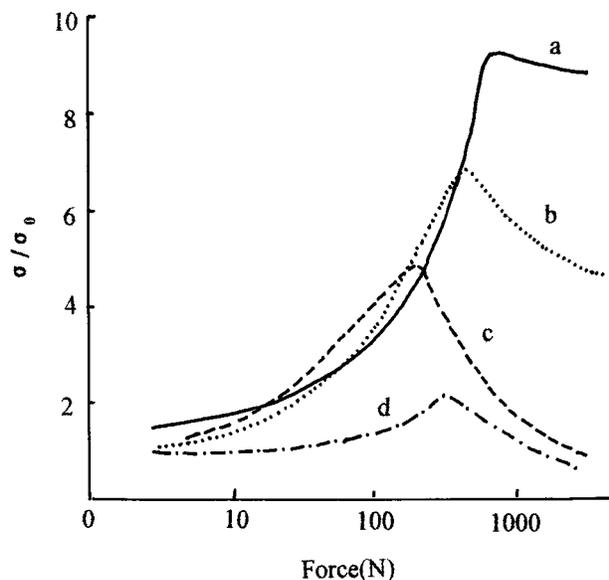
Figure 14 Change of conductivity during compression of PAn/SBS SSP samples with PAn content of (a) 11.0%, (b) 8.6%, (c) 6.2%, and (d) 4.6%.

ity occurs at different compression forces. The maximum conductivity value increases with the PAn content and the reduction of conductivity after the maximum value is slower with increasing PAn content. The increase of the conductivity with the compression force indicates that in the SSP sample the conductive routes formed by a weak interaction of expanded PAn chains can be strengthened by compression, but the ductile deformation of SBS along the direction perpendicular to compression at a higher compression force may destroy the conductive routes formed by a weak interaction between the expanded PAn chains. The higher the PAn content, the more difficult it is to destroy the conductive routes.

CONCLUSIONS

Measurement of the conductivity change of the composites processed by three different methods

through the current change showed that for the MP sample containing 11.0% PAn the conductivity increases obviously with the extension, and the conductivity at an elongation of 450% is 15.6 times that of the original. For the SP sample with the same PAn content, conductivity increases with the extension somewhat slowly and the conductivity at an elongation of 500% is 5.2 times that of the original. However, the conductivity change for the SSP sample is smaller. When the PAn content of the SSP composite approaches the percolation threshold, conductivity diminishes quickly with the extension. But when the PAn content exceeds the percolation threshold, the conductivity of the SSP sample follows an empirical equation with a maximum value. During compression, conductivity of the MP sample with a higher PAn content increases markedly with the compression force, but that with a lower PAn content showed a maximum value at a compression force higher than 500 N. All the SP samples showed a maximum conductivity at a compression force about 500 N, which increases with the PAn content. All the SSP samples also exhibited maximum conductivities but at different compression forces, both of which increase with the PAn content. All the differences are related to the morphological structure of the composites processed by different methods.

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