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Electrically Conductive Thermoplastic Elastomer/Polyacetylene Blends

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SUMMARY

Three different types of thermoplastic elastomers, styrene-butadiene-styrene, styrene-isoprene-styrene, and styrene-ethylenebutylene-styrene triblock copolymers have been blended with polyacetylene utilizing various blending techniques. In one method, acetylene gas was polymerized with the Ziegler-Natta catalyst in the presence of either the thermoplastic elastomer film or a hydrocarbon solution of the thermoplastic elastomer. The resulting polyacetylene/thermoplastic elastomer blend has been characterized with infrared spectroscopy, X-ray diffraction and electron microscopy. Upon doping with either iodine or ferric chloride, the ultimate conductivities of the blends were found to be 60-100 Ω^{-1} cm^{-1}.

INTRODUCTION

Polyacetylene, being a highly conjugated polymer, is difficult to fabricate into a desirable shape. Furthermore, because it contains high concentrations of unsaturated sites which can be easily attacked by ozone and UV light, polyacetylene is very unstable to the environment. In order to overcome serious obstacles of instability and improcessability of the material, some workers (CHIEN et al. 1981) (DEITS et al. 1982) attempted to copolymerize acetylenes with substituted acetylenes in the hope that such an approach might lead to soluble, processable conducting polymers. But it was found that conductivities of such copolymers were not as high as those of polyacetylenes.

Recently, an alternative attempt has been made to obtain processable polyacetylene by GALVIN and WNEK (1982); a composite of polyacetylene and low density polyethylene has been prepared by polymerizing acetylene in the presence of low density polyethylene film. In order to introduce polyacetylene into the polyethylene matrix, they employed a high polymerization temperature (100°-110°C) to break the crystallinity of polyethylene. Such high polymerization temperature might lead to side reactions, such as crosslinking and chain scission. Furthermore, in certain applications, the blend of polyethylene and polyacetylene is still a rigid material because the host polyethylene is partially crystalline. In this connection, we have prepared a number of elastomer/polyacetylene blends in order to impart flexibility into the polyacetylene blend (LEE and JOPSON 1983). However, most conventional elastomers such as polybutadiene, butyl rubber (copolymer of polyisobutylene and polyisoprene), ethylene-propylene-diene rubber, etc., may not be good host polymers for polyacetylene due to the fact that such polymers need postcuring subsequent to blend preparation. The heat and harsh chemicals associated with the curing process would cause scission and/or crosslinking of the highly conjugated double bonds of the polyacetylene. For these various reasons, we have prepared a highly conducting blend of the styrene/diene triblock copolymer and polyacetylene.

EXPERIMENTAL

Three different types of Kraton® (a trade name of Shell Chemical Co.) thermoplastic elastomers, Kraton 1107 (styrene-isoprene-styrene triblock copolymer), Kraton 1101 (styrene-butadiene-styrene) and Kraton 4609 (styrene-ethylene butylene-styrene) were obtained from Shell Chemical Co. The polymers were purified by dissolving in toluene and precipitating in methanol. The typical experimental procedure for the preparation of the polyacetylene/styrene-diene triblock polymer blend is as follows:

Two grams of Kraton were dissolved in 80 ml of freshly distilled toluene. Two ml of Shirakawa catalyst ($Ti(OBu)_4/AlEt_3$) (ITO et al. 1974) were added to the Kraton®/toluene solution. The solvent was removed with the aid of vacuum to form the film on the wall of the flask. Subsequently, acetylene gas was introduced into the flask. The polymerization of acetylene was evident from the color change of the film (brown → black). The flask was left closed and filled with acetylene overnight at room temperature. The reaction flask was flushed with argon to remove monomer residue. The film was washed with freshly degassed heptane at low temperature. Subsequently, the film was dried under vacuum and doped with iodine vapor overnight. The conductivity of the film, which was measured using standard four-point probe techniques, was found to be $60\Omega^{-1}cm^{-1}$.

As an alternative procedure, the polymerization of acetylene was also carried out by bubbling acetylene gas into the toluene solution of Kraton® rubber. In this way, the gel form of the polyacetylene/Kraton® rubber blend was produced. After evaporating toluene under vacuum, the gel was pressed and dried under vacuum. Highly elastic films resulted. Upon doping with either I_2 or $FeCl_3$ in nitromethane, conductivities of the material were found to be the same as in the case of the film preparation.

RESULTS AND DISCUSSION

In general, all of the resulting polyacetylene/Kraton® thermo-

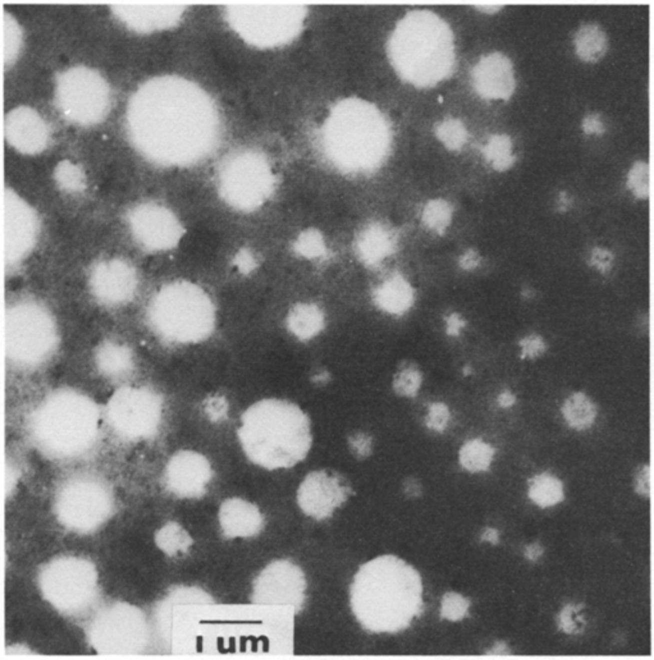

Figure 1. Transmission electron micrograph of the OsO_4-stained polyacetylene/SBS blend

TABLE I

Effect of I_2 Doping on the Elongation of SBS Triblock Copolymer/Polyacetylene Blends*

Time Doped (minutes)	Conductivities $(\Omega^{-1}cm^{-1})$	Elongation (%)	% I_2 Uptake
0	--	1127	--
15	0.95	335	14.8
30	0.54	314	15
60	2.49	300	24.3
120	2.35	255	29.3
180	3.00	167	29.5

* SBS Triblock Copolymer used was Kraton D1101.

plastic elastomer blends were found to be quite flexible metallic-looking films. The infrared spectrum of the blend indicated that the material contains both Kraton® and polyacetylene moieties. Polyacetylene was present in the predominantly trans-configuration as evidenced by a characteristic infrared absorption band at 1015 cm^{-1}. Examination of X-ray data clearly indicated the polyacetylene moieties in the blend retain high crystallinity.

In order to investigate the detailed morphology of the blend, a considerable amount of time has been devoted to electron microscopic studies. It is well known that, in the ABA-type triblock copolymer, the outer glassy A blocks form spherical domains while the central rubbery blocks are dispersed as the matrix. As shown in Figure 1, the polyacetylene is incorporated into the rubbery matrix rather than the glassy polystyrene domain. Since the polymerization of acetylene in the presence of the triblock polymer was carried out below the glass transition temperature of the polystyrene block, the above result appears to be quite reasonable. Thus, as in the case of the polyacetylene/elastomer blends, the polyacetylene/Kraton® blends become less elastic with increasing polyacetylene content. Work is in progress to incorporate polyacetylene in the polystyrene domain of the Kraton® polymer.

We have also studied the elongation of the blend upon doping. As shown in Table I, the undoped blend was found to be extremely elastic and can be stretched up to 1100% of its original length. However, upon doping with iodine, the elongation was considerably reduced. This corroborates the electon microscopic result that polyacetylene moieties indeed incorporate into the rubbery region of the triblock polymer.

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