Design and Synthesis of Conducting Secondary Crosslinked Interpenetrating Polymer Network

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SYNOPSIS

A new conducting composite of a secondary crosslinked interpenetrating polymer network (IPN) was first designed and synthesized by chemically incorporating a rigid conducting polymer within the flexible crosslinked network and forming the link between them. The new conducting composite produced with a low content of polypyrrole exhibited unusually good conductivity, processability, and mechanical properties, and the conductivity was not influenced by the formation of an IPN. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Recently, a considerable amount of investigation has been focused on the improvement of the stability,[1] processability,[2,3] and physical properties[4,5] of a conducting polymer. Conducting polyheterocyclic polymers, e.g., polypyrrole,[6] and polythiophene,[7] have drawn considerable attention because of their good environmental stability.[6-8] It has long been recognized that rigid conjugated polymers tend to be insoluble and infusible. Thus, several strategies have been explored for the improvement of their processability and mechanical properties,[9-12] such as the synthesis of a copolymer (e.g., a copolymer of styrene and pyrrole)[9] and the blend of a highly porous matrix/conducting polymer.[12]

Frisch et al.[13-15] reported conductive interpenetrating polymer networks (IPNs) with one of the components from nonconjugated polymers such as natural rubber. The IPN can be an electrical conductor only after suitable doping, and the conductivity depends mainly on the structure of the doped IPN. In contrast to this conductive IPN, a new conductive IPN based on rigid conjugated polymers and flexible insulating polymers was synthesized. Within

IPNs, conjugated polymers can be used as reinforcing elements just as can rigid-rod polymers in molecular composites[16] and to enhance conductivity. On the other hand, flexible polymers are able to enhance good processability. The entanglement involving a chemical/physical link or strong interaction within IPNs was designed to reduce the phase separation. This new kind of conducting secondary crosslinked IPN was designed and synthesized (Fig. 1).

The copolymers (1) can be easily obtained via functional vinyl monomers copolymerizing with many commercially available vinyl-type monomers and combinations of these monomers,[17] whose structures can readily be controlled to provide the well-defined properties. The flexible crosslinked network (2) can be formed via the functional copolymer reacting with a crosslinker, whose properties can also be modified by varying either the ratios of the various constitutes or their chemically attached manners. The conducting polymers such as polyheterocyclic polymer and polyaniline are grafted onto the flexible crosslinked network by crosslinking or interacting with the unreacted functional group and interpenetrated with the flexible crosslinked network, forming a chemical and physical link to increase their degree of mixing to achieve a combination of good processability and mechanical and electrical properties. It is clear that a large variety of the conductive IPNs should be obtainable by

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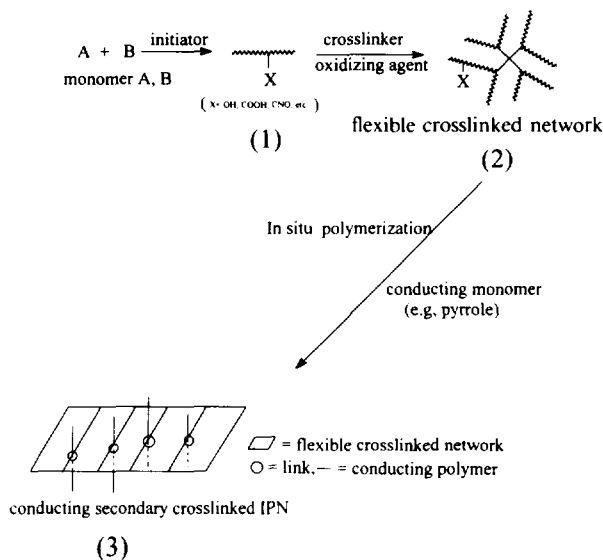† Present address: Institute of Chemistry, Academia Sinica.

Figure 1 Formation of conducting secondary cross-linked IPN.

varying the nature, number, and ratios of the vinyl monomers used and the nature of the conductive component. We report here on the design and synthesis of a poly(methyl acrylate-co-acrylic acid) (PMAA)/polypyrrole conductive secondary crosslinked IPN system.

PMAA (**1**) was synthesized as described earlier.[18] PMAA (M_n, 1×10^4; the molar ratio of $COOCH_3/COOH$ is $6 : 1$) was crosslinked with tetraethyl orthosilicate (TEOS)[16] in the ratios of $100 : 0$, $95 : 5$, and $80 : 20$, respectively, using dodecyl benzene sulfonic (DBSA) as a catalyst (0.1%). With the addition of 0.1% H_2O, the reaction was allowed to proceed for 1 h at the reflux in tetrahydrofuran (THF). To terminate the reaction, $FeCl_3$ was added into the solution (30%) and then the film was cast, placed in air for 24 h at room temperature, and cured in bake oven at 80°C for another 1 h. The preparation of free-standing conductive IPN films was carried out at −8°C by exposing crosslinked PMAA films containing $FeCl_3$ to pyrrole vapor for 24 h, washing several times with methanol until the solvent remained colorless, and then pressing with a glass plate and drying *in vacuo* for more than 12 h.

The conductive films of PMAA/TEOS in the ratios of $100 : 0$, $95 : 5$, and $80 : 20$ correspondingly marked P_1-F_0, $P_{2H}-F_0$, and $P_{4H}-F_0$ exhibited conductivities of 0.23, 0.16, and 0.27 S/cm, respectively. Element analyses of P_1-F_0, $P_{2H}-F_0$, and $P_{4H}-F_0$ indicated that these conductive IPN films contained ca. 1.7, 5.8, and 2.1% polypyrrole, respectively. There

is no great difference among P_1-F_0, $P_{2H}-F_0$, and $P_{4H}-F_0$. For P_1-F_0, poly(acrylic acid) in PMAA can function as a dopant,[19] but this function of poly(acrylic acid) should be not observed for $P_{2H}-F_0$ and $P_{4H}-F_0$ with or without fewer carboxyl groups,[16] indicating that the conductivity is not influenced by the formation of IPNs. Of course, DBSA in a pyrrole-containing system can function as a dopant.[20,21] Using DBSA as the dopant, in the literature,[21] the conducting composites produced with 10–50% also exhibited good conductivity (0.3 S/cm) and processability. To explore whether DBSA functioned as a dopant in this study, DBSA was replaced with volatile HCl in the preparation of $P_{2H}-F_0$, and the film produced with a conductivity of 0.16 S/cm remained essentially unchanged, denying the possibility of DBSA to lead to good conductivity. Therefore, it is suggested that the secondary crosslinked IPN with good conductivity has a similar conductive mechanism to that in polypyrrole prepared using $FeCl_3$ as the oxidizing agent.[22,23]

Soaking the conductive IPN films in a good solvent such as THF and acetone for crosslinked PMAA failed to extract any of the polymer, indicating that polypyrrole is chemically incorporated and interpenetrated in the matrix. Exposure in air at 40°C for 24 h also failed to change the conductivity, in agreement with the result that the conductive IPN films can be obtained via the above method. Scanning electron microscopy (Fig. 2) further indicated that polypyrrole was regularly linearly dispersed in the matrix, leading to high conductivity at a low content of polypyrrole.

The properties of these films strongly depend on the parameters, such as their compositions, structures, and synthetic conditions. The film of P_1-F_0 is so brittle that its mechanical properties are difficult to measure, while the $P_{2H}-F_0$ film has good flexibility and enough strength (elongation at the breakpoint, 16.5%; tensile strength 26.5 MPa; Young's modulus, 3.6×10^3 MPa), displaying greater improvement in mechanical properties comparable to that of P_{2H} (P_{2H} is the insulating crosslinked PMAA matrix of $P_{2H}-F_0$ (elongation at the breakpoint, 360%; tensile strength, 14.1 MPa; Young's modulus, 2.8×10^2 MPa). We believe that the conductive IPN film with good conductivity, processability, and mechanical properties could be extensively used in various electrical and electronic devices in the near future.

This conductive IPN system is only one of several that can be synthesized in a similar manner. For example, acrylic acid can be copolymerized with
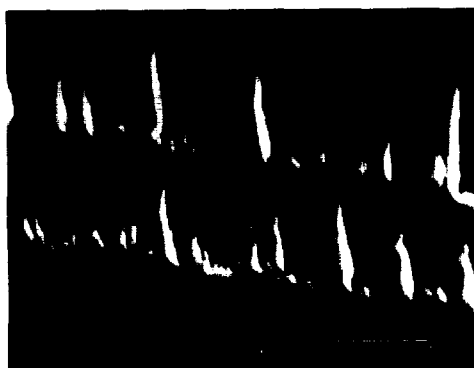
P_1-F_0
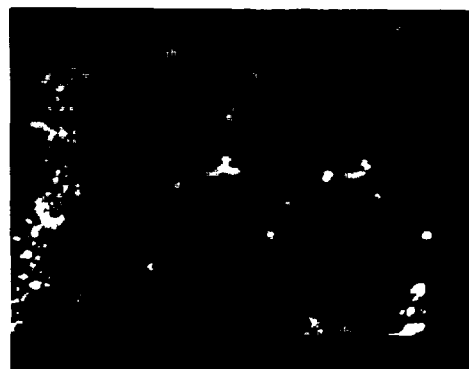
P_{2H}-F_0

P_{4H}-F_0

Figure 2   SEM of P_1-F_0, P_{2H}-F_0, and P_{4H}-F_0.

many commercially available vinyl-type monomers and combinations of these monomers and also can be replaced with other functional vinyl monomers, e.g., hydroxylethyl acrylate. Meanwhile, the conducting component can also be varied as the insulating matrix, e.g., pyrrole can be copolymerized with thiophene.[24] Therefore, a large variety of conductive IPNs could be obtained in the manner described above.
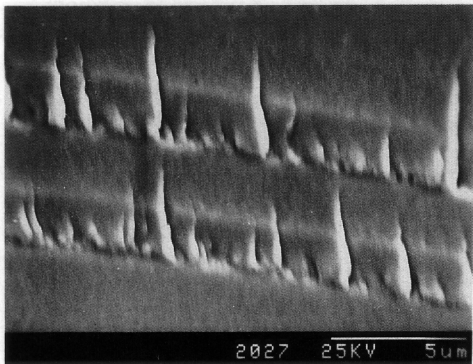
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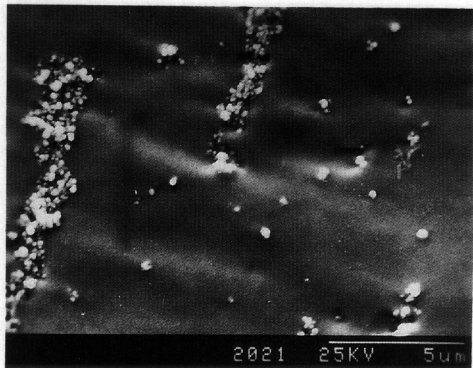12. E. Ruckenstein and J. S. Park, *J. Appl. Polym. Sci.*, **42**, 925 (1991).

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P_1-F_0

P_{2H}-F_0

P_{4H}-F_0

Figure 2 SEM of P_1–F_0, P_{2H}–F_0, and P_{4H}–F_0.