A Conducting Composite of Polypyrrole with Ultrahigh Molecular Weight Polyethylene Foam

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ABSTRACT: Through a chemical polymerization of pyrrole inside ultrahigh molecular weight polyethylene (UHMWPE) foam, a conducting polymer composite was obtained. To produce conductive polymer foams, successive imbibiting of reactives, $FeCl_3$ and pyrrole in tetrahydrofuran solutions, were carried out. The conductive polymeric materials were characterized by FTIR, DSC, and SEM. Mechanical property measurements were carried out on the films prepared by the compression molding of the conductive foam polymers. These films showed rather high tensile strength compared to pure UHMWPE. Conductivity determined by a two-probe technique showed that it increased with the pyrrole content in the UHMWPE foam matrix. The compression molding, however, resulted in a considerable reduction in the conductivities. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1843–1850, 1999

Key words: polypyrrole; foam ultrahigh molecular weight PE; conductive composite

INTRODUCTION

It is well known that most of the organic compounds, including polymers, are insulators. In fact, polymers have been used as excellent insulating materials in electrical engineering. However, after the discovery of electrical conducting polymers, polymers of this kind have drawn as much attention as possible as potential substitutes for conventional metallic conductors or semiconductors in a wide variety of electrical and electronic devices and other industries.¹⁻⁶ In particular, the improvement of their mechanical properties by the synthesis of hybrids, such as copolymers and polymer composites, has increased their potential for commercial applications.^{3,5,6} Potential advantages of conducting or semiconducting polymers lie in their light weight and in their versatility with which their synthesis can be accomplished.^{4,7–9}

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Most plastic materials are produced and used because of desirable mechanical, optical, thermal, and electrical properties in addition to their chemical stability, ease of processing, light weight, and low cost. These properties are considered to be the most important of all physical and chemical characteristics of polymers. On the other hand, conducting polymers have at least one of the following undesirable characteristics: (1) poor mechanical properties; (2) poor processability; or (3) very low environmental stability. In the last decade, a considerable number of studies on conducting polymers have been carried out to overcome these shortcomings by incorporating conducting polymer with other conventional polymers by various methods.^{10–27}

One of the most common monomer pyrrole, besides thiophene and aniline, has been polymerized mainly by electrochemical methods on an inert electrode surface to make a conductive polymer. Chemical methods based on oxidation for pyrrole have also been known and applied in various ways for years. However, polypyrrole (PPy), both films produced by electrochemically or powders obtained by oxidative chemical reactions, are difficult handle and this, hence, restricts its potential applications. Low elongation and the brittleness of PPy films, though it has high electrical conductivity and ambient stability, are one of the major weaknesses of pure PPy.

The difficulties in the improvement of mechanical properties of PPy was usually overcome by preparing composites of PPy with a polymer having better mechanical properties through electrochemical and oxidative polymerization. In the electrochemical method, PPy can be electrochemically impregnated into the host polymer, which coats the electrode.⁷⁻¹⁹ There are, however, limitations regarding the practical applications of such composites in this method. Indeed, uniform thin films of the host polymers are necessary for this process and, therefore, it becomes very difficult to apply in a large scale. Chemical methods, on the other hand, compared to the electrochemical method, produce less conductive PPy, but it has the advantage of easier mass production in a shorter time.^{13,14,18,20–24} Polymer composites produced by chemical methods are found to be more attractive. Among these conductive composites, the host polymers used are PVC,¹⁰⁻¹⁷ porous crosslinked PS,² PV alcohol,¹⁵ fluorine-vinylidiene polymers and its copolymers,¹⁶ polyimide,¹⁸ poly(phenylene terephthalamide),¹⁹ PMMA and its copolymers,²⁰ UHMWPE fibers and gels,^{21–23} cellulosic materials,^{24,25} and Polycarbonate.²⁶ The samples produced by the chemical oxidation polymerization of pyrrole with powder PE, PP, and also PMMA showed better conductivity than the blends prepared by mechanical mixing.²⁷

However, the penetration of the monomer resulting in a conductive polymer upon chemical processing is always found to be lower in a nonporous host polymer matrix than that of the porous host polymers like filter paper,²⁴ porouscrosslinked PS,² or a nucleopore membrane.²⁶ The general procedure of chemical polymerization in these porous matrix studies is that first the material is imbibed with the oxidant solution, followed by partial drying, and then the monomer solution makes contact with the material. The monomer is expected to polymerize inside the host polymer.

UHMWPE fibers and films were made conductive by incorporating them with a thiophene derivative,²¹ aniline,²² and pyrrole-2-carboxylic acid.²⁴ In the former two, monomers were added into the UHMWPE gels in solution, and fibers were drawn from the gel. This process was followed by chemical oxidation polymerization of the monomers. The mechanical properties were found to vary with the amount of conductive polymer, and the conductivity reached useful levels. The composite produced from microporous UHMWPE and pyrrole derivative was found to result in tough and flexible films with varying conductivities.²³ It was also seen that microfibrils of UHM-WPE was coated with a continuous network of PPy.

In this work, highly porous UHMWPE foams²⁸ were made conductive through chemical oxidation of monomer pyrrole. The coating of PPy on the surface of the foams and inside of the foams were found to be homogenous. The conductivities were measured with a two-probe technique rather than a four-probe because of the difficulties raised from highly porous foams. The conductive composites were further characterized by DSC, FTIR, SEM, and also the films obtained by hot compression molding tested mechanically.

EXPERIMENTAL

The preparation and characterization of UHM-WPE foams were already described in our previous work.²⁸ They were labeled as GUR 412 and GUR 415 according to the producer company Hoechst, where the molecular weights are 4×10^6 and 6×10^6 , respectively. UHMWPE foams were machined in cylindrical shape (r = 5 mm and h = 3 mm) at liquid nitrogen temperature in order not to destroy the surface pores of foams. These foams were made by a conducting composite in two steps by imbibing an oxidant solution followed by a pyrrole solution.

The foams of both kind, GUR 412 and GUR 415, were left in 24% w/v FeCl₃·6H₂O–Tetrahydrofuran solution (Fe-THF) for 12 h. Then they were partially dried at room temperature for 30 min. The foams containing oxidant solution were contacted with various concentrations of Pyrrole-Tetrahydrofuran solutions (Py–THF) for 2 h to obtain different weight percentages of Polypyrrole (PPy). Pyrrole was expected to polymerize inside the foam. The conducting composites were left at ambient conditions for a day, and FeCl₂ was removed from the samples by using an ultrasound bath at room temperature. To increase the amount of PPy deposited inside the foam this process was repeated twice or more, depending on the required percentages of PPy in the composite. Finally, the samples were dried at 50°C in an oven for 12 h. All chemicals used in the procedure were supplied from Merck, and used without any further purification.

Compression-molded films were obtained from the conducting composite foams, and used particularly for mechanical testing. Compression molding was achieved between steel plates at 200°C and 340 atm, and followed by shock cooling to an ambient temperature.

The thickness of the films varied from 80 to 310 μ m, depending on the amount of PPy in the composite. The compression molding of the foam composites usually failed to give proper films for tensile testing in both of the UHMWPE-PPy composites. This is partly due to the inherent difficulty in processing of UHMWPE, and also due to the involvement PPy into the UHMWPE foam matrix. The films that had no defects and irregularities were, therefore, used for mechanical testing. Tensile testing were carried out with Instron Tensile Testing Machine, Model TM 1102. The mechanical tests were made on dog bone-shaped samples of a gage length of 3.0 cm, with a drawing rate of 5 cm/min to evaluate the ultimate tensile properties at room temperature.

No further doping was done on the conductive composites. Because of the difficulty in finding flat regions on the foam structure, conductivity measurements of both foam samples—surface and inside—and films were carried out by using two probe measurements at room temperature and represented in terms of kOhm.

Thermal properties of the conductive samples having various weight percentages of PPy were analyzed by DSC, a Perkin-Elmer Model 4, on 5.0 \pm 0.1 mg samples with a heating and cooling rate of 10°C/min from room temperature to 200°C. FTIR spectra of compression-molded films of pure UHMWPE film obtained from the foam UHM-WPE and pure PPy and conductive composites of foam–PPy after grinding to a fine powder at liquid nitrogen dispersed in KBr pellets were examined by a Nicolet DX-5 FTIR spectrometer. Scanning Electron Microscope (SEM) studies of fractured surfaces of both the pure foam and conductive composites were made at various magnifications with a JEOL JSM.6400 SEM after protective gold coating on the samples.

RESULTS AND DISCUSSION

Foams of UHMWPE have already been shown to absorb liquids more than three times of their own weight.²⁸ For the preparation of thick and large conducting objects, the host polymer, in our case foam UHMWPE, must be able to be appreciably



Figure 1 Variation of % deposition of PPy (by weight) in UHMWPE foams with respect to Pyrrole–THF solution application where \bigcirc and \triangle are for GUR 412 and GUR 415 foams, respectively.

imbibed by both the monomer and the oxidant solution. The chemical oxidative polymerization employed in this work is considered to occur within the foam structure. As described in the Experimental part, the successive processes of the $FeCl_3$ -THF solution followed by the Py-THF solution swelling is to produce a uniform coating and deposition of PPy in the foam. Hence, an enhanced conductivity is expected in the conductive composites, depending on the amount of PPy involved into the host polymer.

FTIR, DSC, and SEM Characterization of Composites

Due to the nature of the polymerization technique, it is strongly believed that PPy is polymerized through a combination of radical-cation reactions or a formation polaron, as described in various works.^{14,23} Therefore, the conductive composites produced require some further characterizations to evaluate the changes in the host polymer and PPy formed by chemical oxidative polymerization.

The variation of deposition of PPy on the surface and inside the foam with respect to the concentration of the PPy–THF solution applied is shown in Figure 1. An almost linear increase of PPy deposited with the change of the PPy–THF solution is observed. However, it should be kept in mind that in some cases two or three successive imbibing processes were applied to observe this



Figure 2 FTIR spectra of (a) pure PPy, (b) pure UHMWPE film from compression molding of UHMWPE foam, GUR 415, and (c) GUR 412–PPy conducting composite film prepared from the foam composite by compression molding. The development of carbonyl peak around 1725 cm⁻¹ is due to the thermal oxidation in molding process.



Figure 3 Variation of T_{mp} and T_{cp} temperatures of GUR 412–PPy and GUR 415–PPy conducting composites, (a) foams, and (b) films. Symbols are $\triangle -\blacktriangle$ for GUR 412–PPy and $\bigcirc - \odot$ for GUR 415–PPy, where unfilled symbols are for T_{mp} and filled symbols correspond to T_{cp} .

effect. But at low concentrations of the PPy–THF solution one could hardly get enough deposition of PPy in the foam.

FTIR spectra of the pure polymers and the composites between regions of 2000 and 400 cm⁻¹ are given in Figure 2(a), (b), and (c), where (a) and (b) are for pure polymers of powder PPy in the KBr pellet and compression-molded foam UHM-WPE, respectively, and the final spectrum (c) is for the conducting foam composite. This was prepared by grinding the foam into fine powder at the liquid nitrogen and then pelletized into the KBr. The characteristics peaks of the individual polymers also appeared in the FTIR spectrum of the conducting composite, as indicated in the corresponding figures. There exists no specific IR absorption indicating a chemical interaction between the polymers.

Thermal characterization of conducting foams and films obtained from those foams are pre-



(a)



(b)

Figure 4 Morphology of (a) GUR 412 foam, and (b) 46% PPy containing GUR 412–PPy composite.



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(a)

(b)

Figure 5 Morphology of (a) GUR 415 foam, and (b) 44% PPy containing GUR 415–PPy composite.

sented in Figure 3. The melting and cooling maximum peak temperatures, referred as T_{mp} and T_{cp} , for both GUR 412 and GUR 415 UHMWPE foam-PPy-conducting composites revealed that no appreciable change in the melting point of the host polymer. This strongly suggests that the radical-cation polymerization of pyrrole does not alter the structure of UHMWPE. However, we observe that there is a slight increase in the crystallization temperature, T_{cp} , at low PPy content, and it becomes larger at the highest PPy content as shown in Figure 3(a). The melting point of the peak temperatures of the films, because they have already passed through a temperature treatment during compression molding, show lower T_{mp} (2) or $3^{\circ}\mathrm{C})$ than that of the corresponding foam composites. The lowest T_{mp} is observed in the 60% PPy–UHMWPE film composite, as seen in Figure 3(b). The cooling peak temperatures of the film composites showed almost a similar trend as that observed in the foam composites.



Figure 6 Stress-strain curves of the compression-molded films: (a) For GUR 412 composites, and (b) GUR 415 composites with various compositions as indicated in the figure.

The morphology of the foams and the conducting foams are given in Figures 4 and 5. In both cases PPy content was about 45%. The conducting foams show that PPy coats the UHMWPE fibers in the foam structure, and the pore size of the foams becomes smaller. In the higher magnification [Fig. 5(b)], it was observed that there still existed uncoated UHMWPE fibers, and that PPy was localized at certain points.

Mechanical Properties Composites

The stress-strain curves of GUR 412 and GUR 415 foam-PPy compression-molded films are

given in Figure 6(a) and (b), respectively. The tensile strength increases and elongation at break decreases with the amount of PPy in the composites. We observed a very sharp increase in the tensile strength in GUR 412–PPy composites compared to GUR 415–PPy as given in Figure 7(a). The change in the elongation at break with PPy content showed a fast decrease in the strain in both composites [Fig. 7(b)]. The stress–strain curves also show that the elastic moduli of the composites become larger with PPy content.

As mentioned before, only a limited number of selected samples of UHMWPE–PPy compositions were prepared in the compression molding. The



Figure 7 Variation of ultimate mechanical properties with respect to PPy content in the conducting composites: (a) Stress at break for GUR 412–PPy, (\bigcirc) and for GUR 415–PPy, (\bigcirc), (b) strain at break for GUR 412–PPy, (\bigcirc), and for GUR 415–PPy, (\bigcirc), conducting composites obtained from the corresponding foams by compression molding.



Figure 8 Variation of surface resistance of foam composites, (a) GUR 412–PPy, (b) GUR 415–PPy.

formation of insoluble and infusible PPy and the restrictions of the processability of UHMWPE (flow properties in the processing) due to the inherent physical entanglements usually yielded low-quality films with defects and irregularities in the compression molding. Despite these difficulties, the enhancement in the mechanical properties appear to be very promising, and it also indicates a possible existence of interfacial interaction between these two polymers. Indeed, the high tensile strength (65 and 50 MPa for GUR 412 and 415 foams, respectively) and moduli at about 50% PPy content is a major result and interest of these measurements. These samples are found to keep their flexibility to a certain extent even at these low strains.



Figure 9 Variation of inside resistance of foams composites of GUR 412–PPy (\bigcirc) and GUR 415–PPy (\bigcirc).

Conductivity of Composites

The variation of the conductivities with respect to PPv for the foam composites are given in Figure 8(a) and (b) and also Figure 9. The conductivity measured on the surface of the foams as kOhm decrease well below 100 kOhm after 30% PPy in both of the UHMWPE foams. The fluctuations in conductivity measurements in near contents are basically due to the method of measurement, the two-probe technique, and also possible irregularities arising from the foam structure. The resistance decreases with slight variations in increasing PPy content. The resistance of foams with more than 30% PPy content was measured around 10 kOhm, regardless the type of UHM-WPE (Fig. 8). To follow the variation the conductivity inside of the foam, the foams were cut randomly after cooling to the liquid nitrogen temperature. The resistance inside of the foams indicated that again a threshold of 30% PPy is necessary for a better conduction. Indeed, a homogenous polymerization pyrrole is apparently achieved in this work if a comparison between surface and inside resistance measurements are considered. This percolation threshold was proven to be valuable for composites where two components are rather compatible with each other for several reasons, one of which can be H-bonding.²⁹ However, in Figure 9, such a case does not exist; that is, there is no threshold conductivity for the inside of the films. The need to go to high levels of PPv content to get lower values of resistance clearly shows that the polymerization

method leads to a big gradient in the structure. In addition to these results, the physical strength of these conductive composite foams remained the same as what we had in the pure foams. They still possess their original rigidity, and can be machined easily.

However, the compression molding caused the resistance to increases, particularly in low PPy containing foams. This increase in the resistance is due to the destruction of the linkages between PPy in the foam matrix as a consequence of hightemperature molding. Hence, the conductivity is apparently reduced compared to the foam composites. The highest PPy containing foams showed mostly 500 kOhm or higher resistance after compression molding, although these foam samples with 40% or more PPy content show very high tensile strength when they were converted into films and they lost their conductive property.

CONCLUSION

In this work, the homogenous oxidative polymerization of pyrrole in the foam matrix was achieved to reach even 50% PPy loadings. Despite the problems in measuring the conductivity due to the foam matrix, the enhanced conductivity variation with the content of polypyrrole with a big gradient in the structure due to the polymerization process was observed. The composite conductive foams appeared to maintain their properties like rigidity and solvent absorption capacity. The compression molding of these foams produced high tensile strength films where the elasticity is kept to a certain extent. These films showed a very high increase in the resistance, therefore, a decrease in conductivity, but the improved mechanical properties with that conductivity seems to be a promising composite material. Yet, the difficulty in obtaining good-quality films should be considered with care. Finally, the method that was described in this work—polymerization of a monomer yielding a conductive polymer in a foam matrix-appears to be a successful process compared to some methods, like melt blending or surface coating, to prepare conductive blends.

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