polymer communications

Electrically conductive polymer composites: polymerization of acetylene in polyethylene

Mary E. Galvin and Gary E. Wnek

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

Composites of low density polyethylene, LDPE, and polyacetylene, $(CH)_x$, were prepared by polymerization of acetylene in LDPE films impregnated with a $Ti(OBu)_4/Et_3Al$ Ziegler–Natta catalyst. LDPE films were immersed in a toluene solution of this catalyst at 70°C to accomplish impregnation. Polymerization of acetylene in the LDPE films was carried out at 100°–110°C. The resulting composite films remain flexible and tough upon prolonged air exposure and those containing $<ca.$ 5 wt.% $(CH)_x$ soften upon heating to 120°–160°C. The films can be rendered conductive upon exposure to a 2 wt%. solution of I_2 in pentane. Ultimate conductivities of $ca.$ $10\,\Omega^{-1}\,cm^{-1}$ can be obtained. The conductivities of the doped composites decay more slowly as compared with I_2-doped $(CH)_x$ films. The synthetic approach, with some simple modifications, can be used in the construction of many electrically conductive, all-polymer composites having a combination of desirable physical, mechanical and electrical properties.

Introduction

The demonstration that organic polymers can be rendered highly conductive through chemical doping has generated considerable interest since many applications can be envisioned for electroactive materials which possess the high conductivity of metals and the light weight, flexibility and processability common to plastics[1]. Polyacetylene, $(CH)_x$, has been the focus of attention since it was the first organic polymer to display high conductivity upon doping and its relatively simple polyene structure affords a useful model for both theoretical and experimental studies. Recent work concerning the use of $(CH)_x$ electrodes in the fabrication of light-weight, efficient batteries[2] clearly indicates its technological potential. Unfortunately, $(CH)_x$ is unstable in air, becoming brittle after only a few days exposure with a concomitant decrease in conductivity. The intractability of $(CH)_x$ precludes fabrication using conventional methods. Other conductive polymers[3–7] are plagued with at least one undesirable characteristic such as environmental instability, improcessability and/or poor physical properties.

Traditionally, a useful approach for the modification of polymer properties has been the synthesis of hybrids, i.e., copolymers and blends. Copolymers of acetylene and methylacetylene have been prepared[8] which are swellable in organic solvents but which display somewhat lower conductivities upon doping and greater oxidative instability compared with $(CH)_x$. Copolymers of acetylene and l-hexyne have been prepared although electrical properties were not investigated[9]. Thermolysis of bromine-doped $(CH)_x$ has afforded partial substitution of bromine for hydrogen on the $(CH)_x$ backbone[10]. However, the full potential of this system and conductive copolymers in general has yet to be exploited. This communication describes the preparation of blends of $(CH)_x$ and low density polyethylene (LDPE) with the aim of obtaining novel and useful conductive composites. Although composites could be prepared by simply dispersing $(CH)_x$ particles in a polymer matrix, our interest has been directed toward the synthesis of composites which may possess intimate mixing at the molecular level. Thus, we have polymerized acetylene in solid LDPE which was impregnated with a Ziegler–Natta catalyst. This matrix was chosen since it is readily obtained as a film and it is economical, flexible and tough. Also, the hydrocarbon structure of LDPE renders it an inert 'solvent' for Ziegler–Natta polymerization.

Experimental

The $Ti(OBu)_4/Et_3Al$ system, which is the preferred catalyst for the preparation of $(CH)_x$ films[11], was used in this study. In a typical experiment, a 0.3 mm thick, commercial LDPE film which has been soaked in dry toluene for 24 h to remove additives is immersed in a freshly-prepared solution containing dry toluene (60 ml), $Ti(OBu)_4$ (3.75 ml) and Et_3Al (6 ml) in a Schlenk tube under argon. The tube is heated to *ca.* 70°C under a slow stream of argon for *ca.* 1.5 h to impregnate the film with the catalyst. After cooling to room temperature, the catalyst solution is removed with a syringe and the orange-brown LDPE film is washed with fresh toluene to remove surface catalyst residues. The Schlenk tube is then connected to a high vacuum line and the toluene is removed by pumping. Next, the film is allowed to contact acetylene gas (initial pressure *ca.* 700 torr) for various periods of time. Polymerizations have been carried out at temperatures between $-78°$ and 110°C. The high temperature polymerization is preferred since the polymerization rate is maximized without excessive melting of the matrix. During the high temperature polymerizations, the orange-brown catalyst impregnated LDPE film turns from blue to black as the acetylene diffuses into the film and polymerizes at the catalyst sites. Samples containing $>ca.$ 5 wt% $(CH)_x$ have a dull golden luster.

No attempt was made to remove catalyst residues from

the films. The samples were stored in a Schlenk tube under argon.

The amount of $(CH)_x$ in the blends was determined by acetylene uptake during polymerization and elemental analysis of the resulting materials, which typically contain *ca.* 0.15 wt% and 0.20 wt% of Ti and Al, respectively. The results from both methods were generally in good agreement.

Results

Visible absorption spectra of thin films prepared at 110°C are consistent with the presence of the *trans* $(CH)_x$ isomer[1,2]. The films remain flexible and tough indefinitely. Samples containing $<ca.$ 5 wt% $(CH)_x$ soften between 120°–150°C, although samples with *ca.* 6–10 wt% $(CH)_x$ do not soften up to 210°C. This is apparently due to entanglements of rigid $(CH)_x$ and LDPE chains and/or the presence of a lightly crosslinked $(CH)_x$ network within the LDPE matrix. Optical microscopy of composites sectioned through the film thickness indicate that $(CH)_x$ is present within the entire film with slightly higher concentrations (as indicated by the intensity of the blue colouration due to *trans* $(CH)_x$) near the film surfaces. The microscopic homogeneity of the composites is presently under investigation. However, the optical microscopy results in conjunction with preliminary studies of mechanical and thermal properties indicate that these materials are not simply LDPE films 'coated' with $(CH)_x$.

Exposure of the films to a 2% solution of I_2 in pentane for 24–48 h results in ultimate conductivities (four probe method) of *ca.* 5–10 Ω^{-1} cm^{-1}. Preliminary results concerning the dependence of conductivity on $(CH)_x$ content of the I_2-doped blends are shown in *Figure 1*. It is interesting to note that a reasonably high conductivity is achieved at only 2 wt% $(CH)_x$. That the conductivity is not due to solely surface-confined $(CH)_x$ is demonstrated by mounting the four platinum wires used for the conductivity measurements on the same side of the film and in another experiment mounting the pairs of wires on opposite sides. The results are essentially identical. Also excessive scraping of the surface with a razor blade preceding the conductivity measurement does not significantly change the result.
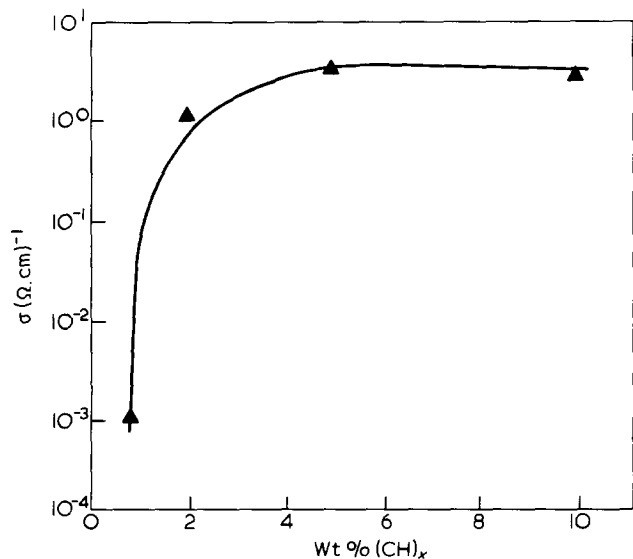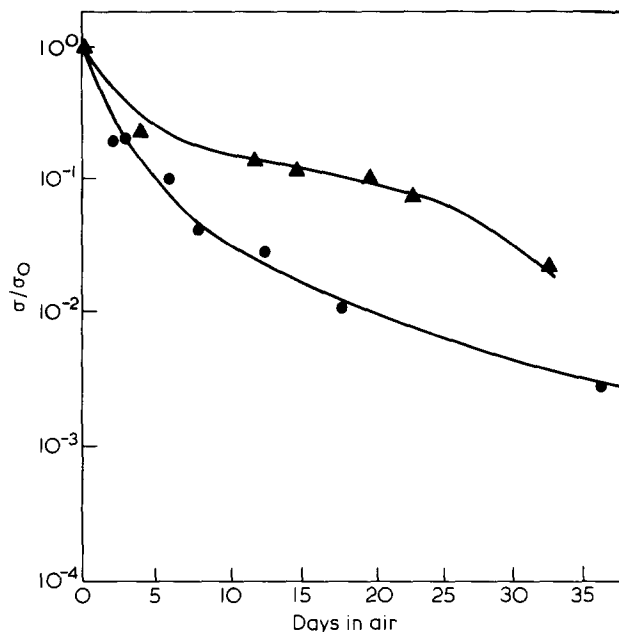

Figure 2 Normalized conductivity vs. days of ambient air exposure for I_2-doped *trans* $(CH)_x$ film and an I_2-doped, $(CH)_x$/LDPE blend containing *ca.* 5 wt % $(CH)_x$. ●, $(CH)_x$; ▲, $(CH)_x$ in $(CH_2)_n$

It is found that the conductivities of the I_2-doped blends decay somewhat more slowly upon air exposure compared with I_2-doped, *trans* $(CH)_x$ film. In *Figure 2* we plot the normalized conductivity vs. time for an I_2-doped blend containing *ca.* 5 wt% $(CH)_x$ and an I_2-doped, *trans* $(CH)_x$ film. The increase in stability is marginal at best and probably reflects the poor oxygen barrier properties of polyethylene. It is anticipated that further enhancement of environmental stability can be obtained through judicious selection of the matrix.

Preliminary experiments have examined the generality of the synthetic approach to obtain conductive composites. It is found that composites of $(CH)_x$ and materials which are soluble in the catalyst solution (e.g., polystyrene, polybutadiene) can be prepared by casting catalyst-impregnated films in a dry-box followed by exposure to acetylene gas. Our experiments suggest that many polymer matrices may be employed provided that they are devoid of functional groups which may render the catalyst inactive.

Conclusions

In summary, a method for the preparation of novel conductive composites has been described. Composites of $(CH)_x$ and LDPE have reasonably high conductivities upon doping with iodine (*ca.* 5–10 Ω^{-1} cm^{-1}) at a relatively low $(CH)_x$ concentration (*ca.* 2 wt%). The composites soften on heating in the range of 120°–150°C provided that the $(CH)_x$ content is less than *ca.* 5 wt%. A small improvement in the environmental stability of the doped $(CH)_x$ component is observed. The materials remain flexible and tough essentially indefinitely. The synthetic approach described herein is useful in the construction of electrically conductive, all-polymer composites having a combination of desirable physical, mechanical and electrical properties.

Figure 1 Conductivity of I_2-doped $(CH)_x$/LDPE blends as a function of $(CH)_x$ content

References

1   MacDiarmid, A. G. and Heeger, A. J. *Synth. Metals* 1979/80, **1**, 101
2   MacInnes, Jr., D., Druy, M. A., Nigrey, P. J., Nairns, D. P., MacDiarmid, A. G. and Heeger, A. J. *Chem. Comm.* 1981, **317**
3   Shacklette, L. W., Chance, R. R., Ivory, D. M., Miller, G. G. and Baughman, R. H. *Synth. Metals* 1979/80, **1**, 307

4   Chance, R. R., Shacklette, L. W., Miller, G. G., Ivory, D. M., Sowa, J. M., Elsenbaumer, R. L. and Baughman, R. H. *Chem. Comm.* 1980, **348**; Rabolt, J. F., Clarke, T. C., Kanazawa, K. K., Reynolds, J. R. and Street, G. B. *ibid* 1980, **347**
5   Kanazawa, K. K., Diaz, A. F., Geiss, R. H., Gill, W. D., Kwak, J. F., Logan, J. A., Rabolt, J. F. and Street, G. B. *ibid* 1979, **854**
6   Wnek, G. E., Chien, J. C. W., Karasz, F. E. and Lillya, C. P. *Polymer* 1979, **20**, 1441
7   Gibson, H. W., Bailey, F. C., Epstein, A. J., Rommelmann, H. and Pochan, J. M. *Chem. Comm.* 1980, **426**
8   Chien, J. C. W., Wnek, G. E., Karasz, F. E. and Hirsch, J. A. *Macromolecules* 1981, **14**, 479
9   Enkelman, V., Muller, H. and Wegner, G. *Synth. Metals* 1979/80, **1**, 185
10   Kletter, M. J., Woerner, T., Pron, A., MacDiarmid, A. G., Heeger, A. J. and Park, Y. W. *Chem. Comm.* 1980, **426**
11   Ito, T., Shirakawa, H. and Ikeda, S. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 11
12   Shirakawa, H., Ito, T. and Ikeda, S. *Polym. J.* 1973, **4** 460

Accuracy of fluorescence polarization measurements and discrimination of uniaxial deformation models

Manfred Hennecke and Jürgen Fuhrmann
Fachbereich Chemie, Universität Kaiserslautern, Postfach 3069, D-6750 Kaiserslautern, FRG
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The technique of fluorescence polarization is examined for the influence of measuring errors on the light intensities and the depolarization correction parameter p. It is shown how the accuracy of the received orientation coefficients depends on the measured quantities, especially on the absolute value of p, the latter restricting the polymer systems to which the method is suitable. The lowest accuracy needed to take advantage of the information on the fourth moment of the orientation distribution function is calculated as well as the considerable accuracy required to discriminate orientation models, e.g. the pseudoaffine model, from others.

Keywords Fluorescence polarization; deformation models; orientation distribution function; experimental accuracy requirement

Introduction

With the fluorescence polarization method (fpm), the 2nd and 4th moment of the orientational distribution function (odf) of the anisotropic chromophores are determined[1,2]. In the case of uniaxial symmetry of both the rigid anisotropic matrix (e.g. polymer films or fibres) and the fluorescent molecule, the angle θ, i.e. the angle between the orientation axis of the sample and the molecular orientation axis of the fluorescent molecule, is the only variable in the odf. In this case, with the fpm the moments $\langle \cos^2\theta \rangle$ and $\langle \cos^4\theta \rangle$ are obtained. Equivalent to the presentation of moments is the use of the 2nd and the 4th coefficient of the development of the odf in a series of Legendre polynomials. These two coefficients usually allow for an approximate graph of the odf[3].

In the aforementioned case of symmetry three polarized fluorescence components, e.g. I_{ZZ}, I_{ZY}, and I_{YY} (Z orientation axis of the sample, X optical beam axis of the apparatus; first subscript denotes the polarizer direction, second subscript the analyser direction) are independent[1]. These three light intensities must be measured. Additionally, the photophysical parameter p_m which indicates the optical anisotropy of the absorption tensor $a = (a_{ij})$ and the emission tensor $e = (e_{ij})$ must be known to determine $\langle \cos^2\theta \rangle$ and $\langle \cos^4\theta \rangle$. There is only one

parameter p_m under the condition of rotationellipsoidic anisotropy of absorption and emission transition moments relative to the uniaxial symmetry of the fluorescent molecule mentioned above.

$$p_m = \frac{2a_{22}}{2a_{22}+a_{33}} = \frac{2e_{22}}{2e_{22}+e_{33}} \tag{1}$$

The parameter p_m ($0 \leqslant p_m \leqslant 2/3$ for $a_{22} \leqslant a_{33}$; if $a_{22} > a_{33}$ the true p_m may be calculated by exchanging a_{22} and a_{33}) may be measured independently by means of a sample of known orientation, usually an isotropic sample. p_m is related to the fundamental fluorescence anisotropy r_0 by

$$p_m = 2/3 - 1/3\sqrt{10\,r_0} \tag{2}$$

where

$$r_0 = \left(\frac{I_{ZZ}-I_{ZY}}{I_{ZZ}+2I_{ZY}} \right)_{\text{isotropic}} \tag{3}$$

is measured with two polarized intensities in the isotropic state.