ELECTRICALLY CONDUCTIVE POLYMER-POLYMER COMPOSITES
M. Galvin, G. Wnek

To cite this version:

HAL Id: jpa-00222680
https://hal.archives-ouvertes.fr/jpa-00222680
Submitted on 1 Jan 1983

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
ELECTRICALLY CONDUCTIVE POLYMER-POLYMER COMPOSITES

M.E. Galvin and G.E. Wnek

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A.

Résumé - Des composites conducteurs ont été préparés par polymérisation de l'acétylène dans des films de polyéthylène suivie par un dopage à l'iode. L'obtention de conductivités élevées (5-10 S/cm) à faible concentration en (CH)\_x (3% poids) est expliquée à l'aide d'un modèle simple de percolation.

Abstract - Conductive composites have been prepared by polymerization of acetylene in polyethylene films followed by iodine doping. The attainment of high conductivity (5-10 S/cm) at low (CH)\_x concentrations (~3 wt%) is explained with a simple percolation model.

I - INTRODUCTION

The high level of interest in potential applications of polyacetylene, (CH)\_x, is tempered in many instances by the prospects of intractability and poor environmental and physical properties. In an attempt to mitigate such undesirable characteristics, we have prepared composites /1/ through the polymerization of acetylene in low density polyethylene (LDPE) impregnated with the Shirakawa /2/ catalyst. This approach may be potentially useful in that (1) in-situ polymerization could provide a more intimate molecular mixing of the components as compared with mechanically prepared dispersions, (2) a variety of matrices with desirable physical properties may be employed, (3) articles of the selected matrix material may be pre-fabricated to a desired structure followed by catalyst impregnation, polymerization and doping, and (4) (CH)\_x chains may be isolated in a matrix in order to study the influence of the local molecular environment (chemical composition, morphology, etc.) on, for example, soliton mobility. Recent studies concerning the (CH)\_x/LDPE system and preliminary results from syntheses employing ethylene/vinylacetate copolymers as matrices are presented in this report.

II - EXPERIMENTAL

The (CH)\_x/LDPE composites were prepared using the Ti(0Bu)\_4/Et\_3Al Ziegler-Watta catalyst system as previously described /1/. The highly amorphous EVA films (obtained from Ensign-Bickford Co.) allowed facile impregnation and acetylene polymerization at 25°C. The amount of (CH)\_x incorporated was determined by monitoring the acetylene uptake during the polymerization. Electrically conductive derivatives were prepared by immersion of the composites in a saturated I\_2/pentane solution for 24-48 hours. Electrical conductivities were measured by standard four-probe techniques.

III - RESULTS AND DISCUSSION

The relationship between the four-probe electrical conductivity, \( \sigma \), and the wt.% (CH)\_x in iodine-doped (CH)\_x/LDPE composites is shown in Figure 1. An apparent percolation threshold exists between 2-4 wt.% (CH)\_x. Many additional data points have been collected since our previous communication /1/ which show (as expected) a con-
FIGURE 1: CONDUCTIVITY OF 12-DOPED COMPOSITES VERSUS WT.% (CH)\textsubscript{x}.

FIGURE 2: CONDUCTIVITY OF 12-DOPED COMPOSITES VERSUS WT.% (CH)\textsubscript{x}, EXTRAPOLATED TO THE CONDUCTIVITY OF 12-DOPED, TRANS \((\text{CH})_2\).
continuous increase in $\sigma$ with (CH)$_x$ content beyond the "knee" in Figure 1. In Figure 2 we replot the data to include a value /3/ for $\sigma$ of 12-doped, trans (CH)$_x$; extrapolation of our data to this value affords a reasonable line. The apparent threshold at such a low loading is somewhat surprising although it is interesting that thresholds of ca. 4 vol.% carbon black in LDPE have been observed /4/. This has been rationalized as being due to a combination of particle size and wettability effects. It should be noted that the (CH)$_x$ entities (as revealed by transmission electron microscopy of thin films) in the composites are irregular in shape with sizes in the range of 600-2,000 Å. We find that (CH)$_x$ "powder" /2/ consists of much larger entities (hundreds of microns in size) and that simple dispersions of powdered (CH)$_x$ in LDPE (made by casting films from hot toluene in a dry box) of much higher loading levels (240 wt.%) generally fail to yield highly conductive materials upon I$_2$ doping. Thus, a virtue of the in-situ polymerization approach appears to be the ability to form much smaller (CH)$_x$ domains and is presumably responsible, at least in part, for the observed percolation threshold. It is possible that melt extrusion of LDPE/(CH)$_x$ particulate systems could afford materials having lower percolation thresholds (compared with solvent-cast systems) although we have not attempted to perform such experiments.

In an attempt to expand the scope of the in-situ method to include polar polymers, EVA matrices were employed. Acetylene polymerization proceeded rapidly at room temperature. Composites containing as much as 20 wt.% (CH)$_x$ were prepared but afforded conductivities of only 0.5 - 1.0 S/cm upon I$_2$ doping. The low conductivity may be due to microstructural constraints (perhaps enhanced phase separation because of the polarity difference between the two polymers) or to interactions between the polar vinylacetate groups and the doped (CH)$_x$ or I$_2$.

IV - ACKNOWLEDGEMENTS

We are grateful for support from the MIT Center for Materials Science and Engineering (NSF-MRL Core Fund DMR 78-24185), a DuPont Young Faculty Award (to G.E. Wnek) and a fellowship from Polaroid Corporation (to M.E. Galvin), and thank Dr. B. Skutnik of Ensign-Bickford Co. for the EVA samples.

V - REFERENCES