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ScienceDirect
Materials Letters 61 (2007) 1333 – 1336
materials letters
www.elsevier.com/locate/matlet

Focused ion beam milling and scanning electron microscopy characterization of polymer + metal hybrids

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Received 6 June 2006; accepted 9 July 2006
Available online 26 July 2006

Abstract

Hybrid materials were prepared by mixing commercial polymers with micrometric metal powders. The polymer matrix used was low density polyethylene (LDPE). We have used aluminum spheres with the average diameter of 1 μm. The particle concentration in the matrix was varied from 0.5 wt.% to 10 wt.%. Scanning electron microscopy (SEM) was used to investigate the particle dispersion on the surfaces of the microhybrids. Focus ion beam (FIB) milling was used to create a transversal cut in the material. SEM imaging was performed before, during and after ion milling to investigate the milling process. The hybrid surfaces are better characterized by backscattered electrons than by the secondary electrons; in the former case a higher contrast difference between the matrix and the dispersed phase allows us to identify the positions of the metal particles inside the matrix. Our SEM + FIB technique combination is useful for hybrids based on polymer matrices. Transversal cross-sections made with the ion beam allowed us to observe the dispersion of the metal particles inside the polymer. Although there can be certain problems during milling, such as heating provoking damage in the material, it is possible to optimize the experimental parameters so as to eliminate the problems. Our microhybrids have a uniform dispersion of the Al powder throughout the material.

Keywords: Composite materials; Microstructure; Polymers

1. Introduction

The scanning electron microscopy (SEM) is a technique that allows the observation of the surface in a wide variety of materials [1–5]. It is very popular for the reason that it is capable of creating 3D-like images in the micrometer to nanometer scale [6]. The sample preparation is relatively easy. Focused ion beam (FIB) technique has been used for milling or deposition in the surface of materials in well defined patterns in the micrometer and nanometer scale (micro- and nanoprinting) [7–11]. The combination of these two techniques has been used to prepare transmission electron microscopy (TEM) samples to an advantage [11] as well as to investigate cross-sections of a variety of materials [12–14].

There has been little work in the use of FIB in polymeric materials, and that focused mainly on the determination of the thickness of polymer thin films [12,14]. The purpose of the present work is to demonstrate the usefulness of the SEM/FIB combination to study hybrid materials composed of metallic particles in the micrometer scale immersed in a polymeric matrix. Polymer + metal hybrids exhibit interesting tribological and mechanical properties [15,16]. The present study includes both surface and cross-section analysis in order to investigate the dispersion of the metallic particles inside the matrix.

2. Experimental

The polymer used as the matrix was low density polyethylene (LDPE). The metal filler consisted of aluminum spherical particles with an average diameter of 1 μm. The composition of the hybrids was varied from 0.5 to 10 wt.% of Al powder. The

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doi:10.1016/j.matlet.2006.07.026

blends were prepared in a Brabender Type 6 mixer at 150 °C with the blade-speed of 80 rpm and 5 min mixing time. The resulting blends were pelletized and then injection molded (AB-100 injection molder from AB machinery) to obtain the final specimens. In order to have suitable samples for SEM and FIB, the hybrids were gold-coated before the analysis.

Secondary electrons and backscattered electrons imaging were performed in a JEOL JSM-5800 scanning electron microscope at 20 keV. The FIB analysis was carried out in a FEI analytical dual beam FIB. The ion beam was tilted 52° with respect to the electron beam and was only used for milling, not for imaging. The hybrids were milled with a Ga^+ ion beam current of 7 nA with the acceleration voltage of 30 keV. The cross-sectioned face was then polished with a low beam current (3 nA) prior to the imaging with SEM. In order to investigate the cross-sections, the samples were cooled down to liquid nitrogen temperature where they behave in a brittle manner and then broken.

3. SEM results

Fig. 1A shows a secondary electron SEM image of the microhybrid containing 7.5% aluminum. We can observe clearly the surface morphology in the micron scale, but more important is the determination of spatial distribution of the particles in the material. To distinguish between the polymer matrix and the metal particles, backscattered electron imaging provides a suitable option; the contrast results mostly from the difference in atomic masses of the constituents. Fig. 1B shows a backscattered image of the same area as Fig. 1A. Now we can see very clearly where the particles are located; the bright spheres are the Al particles.

As noted before, for improved tribological and mechanical properties the distribution of the filler inside the material is very important (i.e. the surface interactions for tribological applications versus bulk behavior for mechanical properties). Fig. 2A shows a backscattered image of the composite surface with 3% Al while Fig. 2B presents a fracture cross-section image of the bulk material with the same concentration. As we can see, the amount of Al in the surface as well as in the bulk material is for all practical purposes the same. Thus, the particles are well dispersed throughout the hybrid.

4. FIB milling

During the process Ga^+ ions are deposited in the cross-sectioned wall, impeding its visualization. This is the reason for cleaning the wall with a low beam current (3 nA).

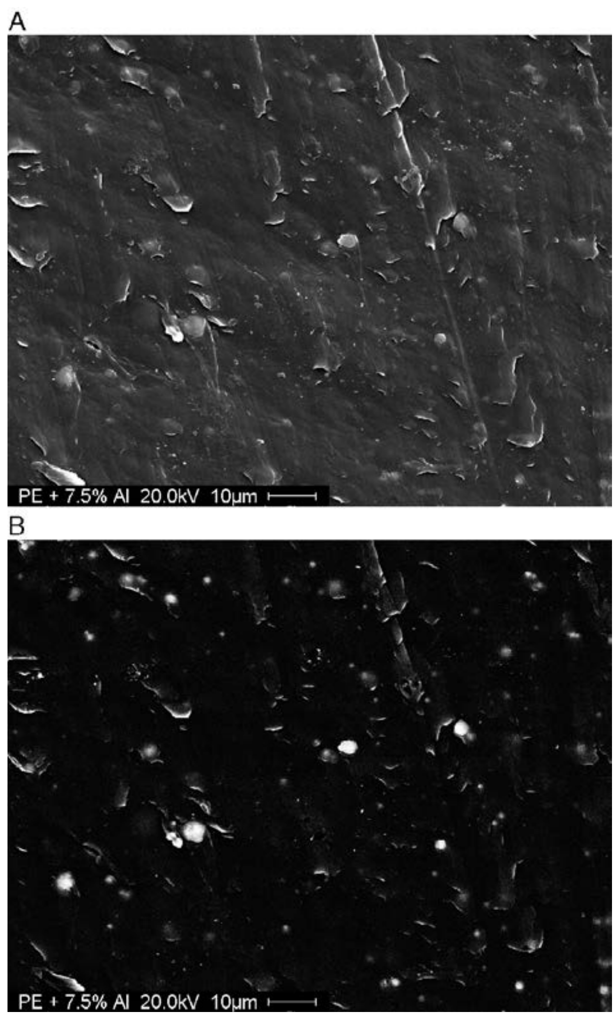

Fig. 1. A) Secondary electron image of PE+7.5 wt.% Al powder. B) Backscattered electron image of PE+7.5 wt.% Al powder.

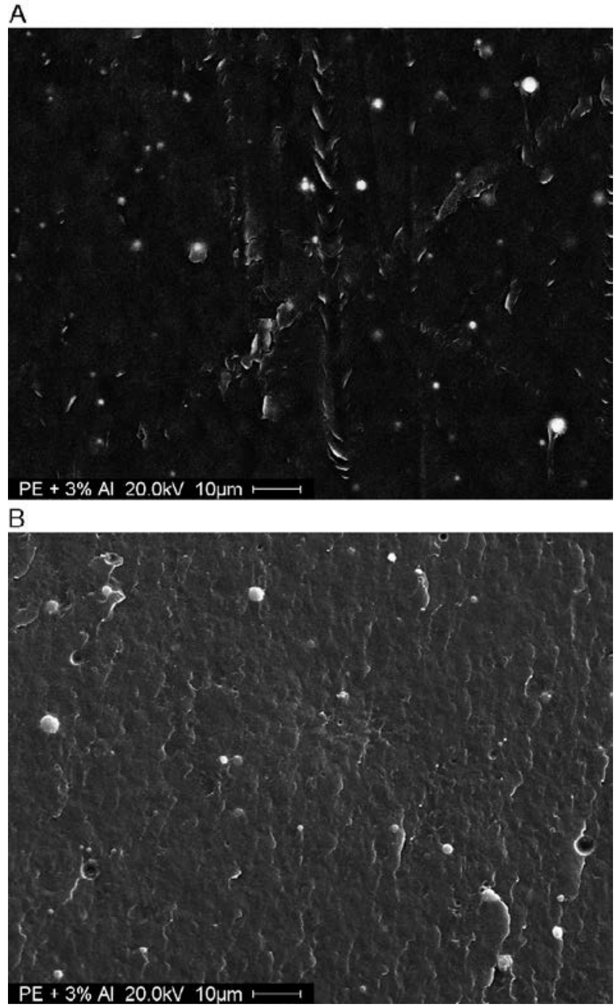

Fig. 2. A) SEM image of the composite surface of PE+3 wt.% Al powder. B) SEM image of the composite cross-section of PE+3 wt.% Al powder.

In order to perform FIB analysis, 10% of Al content was chosen, a sufficient concentration of particles per volume to be studied by this technique. Fig. 3 shows a FIB cross-section of the hybrid. It is possible to observe the Al particles well distributed inside the material. Another interesting phenomenon is the cracking of the edges of the milled box. This cracking is due

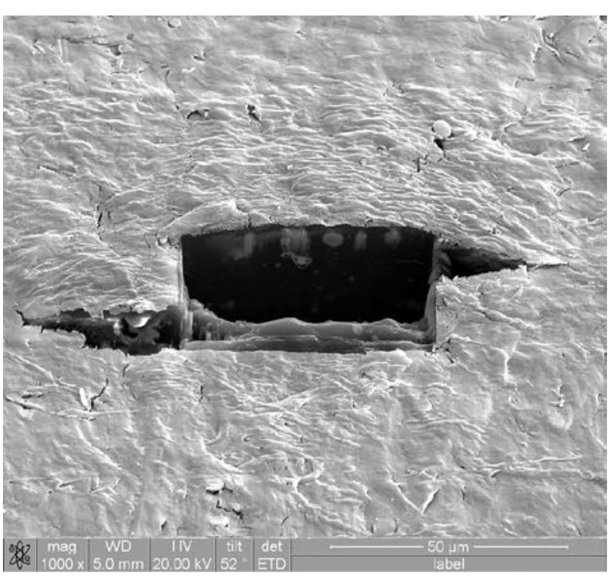

Fig. 3. FIB cross-sectioned box of PE+10% Al microhybrid.

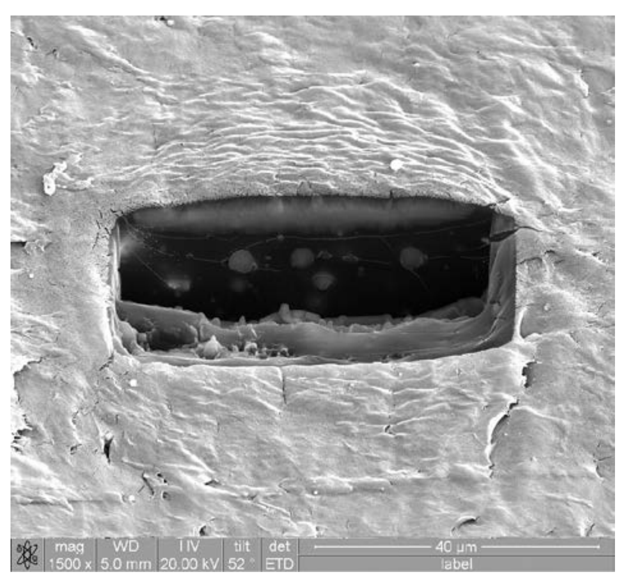

Fig. 4. FIB cross-section after low current beam cleaning.

to the rapid changes of temperature provoked by the Ga^+ beam. This problem was overcome by changing the overlapping in the passes that the beam does from 50% to 0%. Fig. 4 shows the surface of the cross-section after the cleaning process. It is observed that the cracking of the box edges stopped when we changed the beam overlapping to 0%.

5. Concluding remarks

Our microhybrids have a uniform dispersion of the metal particles in the surface as well as in the bulk, which is important for tribological and mechanical applications. Since the microhybrids consist of materials with a considerable difference in atomic mass, backscattered electron imaging proved to be a suitable technique to determine the position of the particles inside the material. We see how the FIB+SEM technique is useful to elucidate the morphology of hybrids with polymer matrices. Although there can be certain problems during milling, such as heating which provokes cracking, it is possible to optimize the experimental parameters so as to overcome the problems. Our combined technique can be applied also to other systems containing particles with diameters in the micron range dispersed in a matrix. Since the size of our Al particles is only ≈ 1 μm, particles with the size of several microns will be even easier to locate.

As noted above, we are trying to make connections of structures at the mm level to tribological and mechanical properties. Information on such connections for polymer tribology is still limited, although the existing information has been reviewed [17]. Thus, the present work is a part of a larger project involving the determination of scratch and wear resistance [5] and the effects of magnetic field orientation on friction and wear resistance [18]. Our molecular dynamics computer simulation of scratch testing, the first for a non-crystal [19] provides guidance in the interpretation of experimental results. Tribological and mechanical properties of our LDPE+Al micropowder hybrids will be reported in later publications; since we have now excluded non-uniformity of space distribution of the metal particles, meaningful results are expected.

Acknowledgements

A partial support for this work was provided by the Robert A. Welch Foundation, Houston (Grant B-1203). One of us (O. O.-M.) is the recipient of a fellowship from Consejo Nacional de Ciencia y Tecnologia (CONACyT), Mexico.

References

[1] G.H. Michler, Kunststoff — Mikromechanik, Hanser, Muenchen-Wien, 1992.
[2] P.H. Fangand, L. Hou, Reotaxial diamond growth by chemical vapor deposition, Mater. Res. Innov. 3 (2000) 360.
[3] U.W. Gedde, Polymer Physics, Kluver, Dodrecht–Boston, 2001.
[4] D.A. Ersoy, M.J. McNallan, Y. Gogotsi, Carbon coatings produced by high temperature clorination of silicone carbide ceramics, Mater. Res. Innov. 5 (2001) 55.
[5] M.D. Bermudez, W. Brostow, F.J. Carrion-Vilches, J.J Cervantes, G. Damarla, J.M Perez, Scratch velocity and wear resistance, E-polymers (2005) No. 003.
[6] J. Goldstein, et al., Scanning Electron Microscopy and X-ray Microanalysis, Springer science + business media, New York, 2003.
[7] N.P. Picard, et al., Focused ion beam-shaped microtools for ultra-precision machining of cylindrical components, Precis. Eng. 27 (2003) 59.
[8] H.W. Sun, et al., Optimization and experimentation of nanoimprint lithography based on FIB fabricated stamp, Microelectron. Eng. 82 (2005) 175.
[9] C. Aubry, et al., Polymer gratings achieved by focused ion beam, Synth. Met. 127 (2002) 307.
[10] D. Chiron, et al., Optical waveguides etched in 6FDA–ODA by focused ion beam, Synth. Met. 124 (2001) 33.
[11] J. Li, et al., Recent advances in FIB–TEM specimen preparation techniques, Mater. Charact. 57 (2006) 64.
[12] S. Zanini, et al., Surface properties of HMDSO plasma treated polyethylene terephthalate, Surf. Coat. Technol. 200 (2005) 953–957.
[13] A.C.K. Chang, et al., The impact of non-uniform channel layer growth on device characteristics in state of the art Si/SiGe/Si p-metal oxide semiconductor field effect transistors, Thin Solid Films 496 (2006) 306–310.
[14] S. Brunner, et al., Investigation or multilayered aluminum-coated polymer laminates by focused ion beam (FIB) etching, Surf. Coat. Technol. 200 (2006) 5908.
[15] W. Osterle, et al., Friction layers and friction films in PMC break pads, Wear 257 (2004) 215–226.
[16] K. Ghosh, et al., Mechanical properties of silver-powder-filled polypropylene composites, J. Appl. Polym. Sci. 60 (1996) 323–331.
[17] W. Brostow, J.-L. Deborde, M. Jaklewicz, P. Oszynski, Tribology with emphasis on polymers: friction, scratch resistance and wear, J. Mater. Educ. 24 (2003) 119.
[18] W. Brostow, M. Jaklewicz, Friction and scratch resistance of polymer liquid crystals, J. Mater. Res. 19 (2004) 1038.
[19] W. Brostow, J.A. Hinze, R. Simoes, Tribological behavior of polymers simulated by molecular dynamics, J. Mater. Res. 19 (2004) 851.