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Sample Preparation for Textile Nanofiber Composites

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Introduction

The increased emphasis on nano-structured materials is placing an ever increasing demand on sample preparation techniques to unveil such fine structure. Nano-structured fibers are even more difficult because of the ease with which these materials can smear even when prepared under liquid nitrogen (LN_2) as shown (Figure 1). This is especially true for the island-in-the-sea structures where it is rather hard to reveal the island structures due to smearing. In the search for a possible solution, a sample preparation technique that has shown great results in other composite structures of different polymer blends was applied to these structures [1]. This technique involves microtoming the specimen to produce a smooth surface followed by an oxygen plasma treatment. The oxygen plasma oxidizes the thin sections and, due to differential oxidation rates of the matrix and island phases, the phases are etched to reveal the structure. In this article we will compare the past and the present techniques to demonstrate the advantages associated with the use of oxygen plasma etching. Although the results are presented for a PP/PE composite, this technique can be applied to other polymer composite combinations.

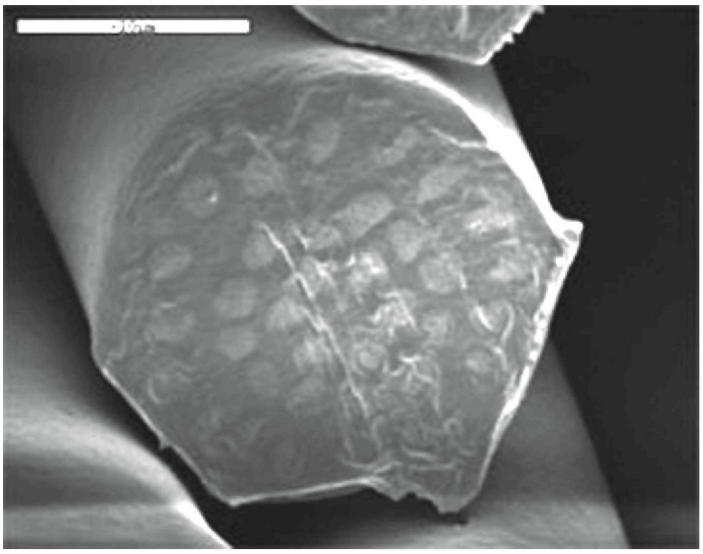

Figure 1. SEM image of PP/PE nanocomposite fiber after cryofracture.

Plasmas at low pressure and atmospheric conditions are used to modify the surface properties of materials without changing their bulk properties. In particular, oxygen plasmas are commonly used to improve adhesion, wettability, and dyeability in polymeric and fibrous materials [2-4]. The modification is a result of a dual process of ion bombardment and surface oxidation from reactive species in the plasma [5]. Ion bombardment enhances the surface oxidation process by breaking bonds in the polymer chain and creating active sites where new bonds can be formed. The chain scission stimulates the formation of a number of oxygen containing functional groups on the surface of the polymer such as carbonyl (C=O), ester (C-O-C=O), and carboxylic acid (C-O-O-H) [5]. Additionally CO, CO_2, H_2O, and H_2 are created as gas phase products from ablation of the polymer material [6].

Samples

Samples used in this study are drawn bicomponent fibers made through a spunbonding process using the island-in-the-sea technique. Fibers were produced at the Nonwovens Cooperative Research Center's Partners Laboratory located at North Carolina State University by using Hill's bicomponent fiber spinpacks. The polymer used for islands (small filaments inside of matrix (sea) of another polymer) is CP-360-H polypropylene (Sunoco Inc.) with a melt flow rate of about 34 g/10 min, a density of 0.905 g/cm^3 and melting point of 163 ˚C. The sea polymer is ASPUN 6811A polyethylene (DOW Chemical Company) with a melt flow rate of about 27 g/10 min, a density of 0.9410 g/cm^3 and melting point of 125 ˚C. The fibers produced and investigated in this study consist of 36, 108, 216 and 324 islands with ratios 50/50, 25/75 and 75/25 island polymer to the sea polymer.

Procedure

Samples of the PP/PE nanofibers were prepared and analyzed under four conditions; 1) cryo-fracture of bare fibers under liquid nitrogen (LN_2), 2) cryo-fracture of fibers embedded in epoxy under LN_2, 3) cryo-fracture of fibers embedded in epoxy under LN_2 followed by an oxygen plasma etch, 4) room temperature microtomy followed by an oxygen plasma etch. All oxygen plasma treatment was conducted in a Plasmod plasma etcher (Tegal Corp.) with flowing oxygen.

For room temperature ultramicrotomy, fiber samples were embedded in a modified Spurr's resin using flat molds. Small fiber bundles were tied in a knot, trimmed and placed into the mold with the fibers oriented perpendicular to the plane of sectioning. After curing overnight at 70˚C, excess resin was removed using a jeweler's saw and then the block face was trimmed with a razor blade perpendicular to the fibers. Sections were obtained

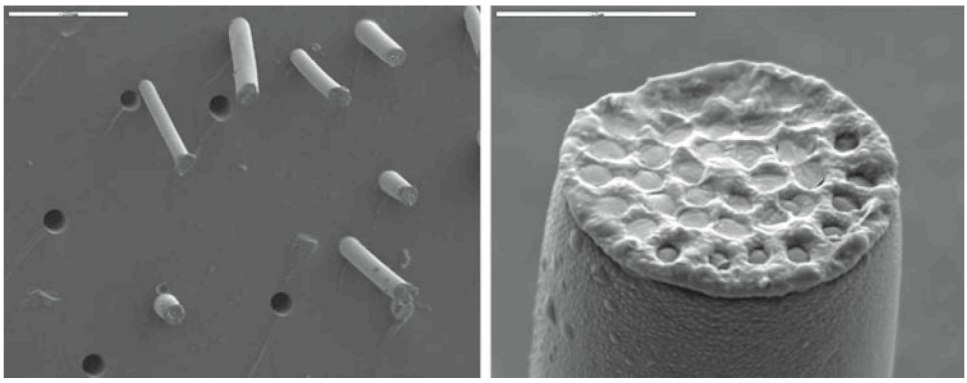

Figure 2. SEM image of PP/PE nanocomposite fiber embedded in epoxy after cryofracture.

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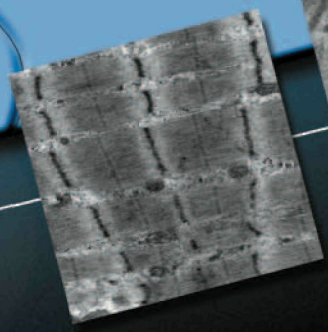

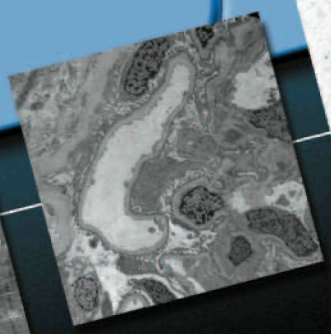

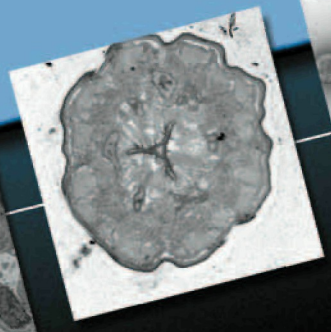

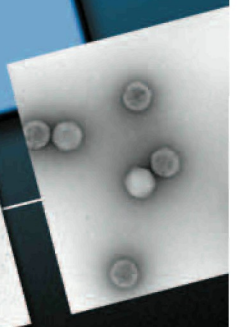

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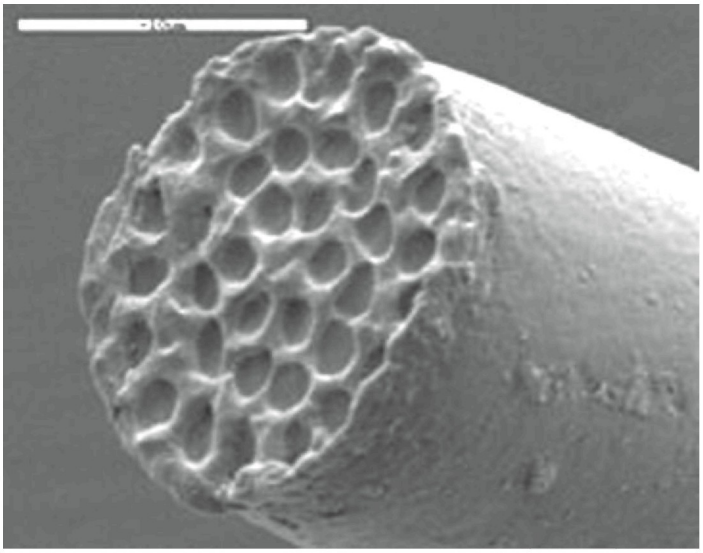

Figure 3. SEM image of PPPE nanocomposite fiber after embedding, cryo-fracturing and oxygen plasma etching.

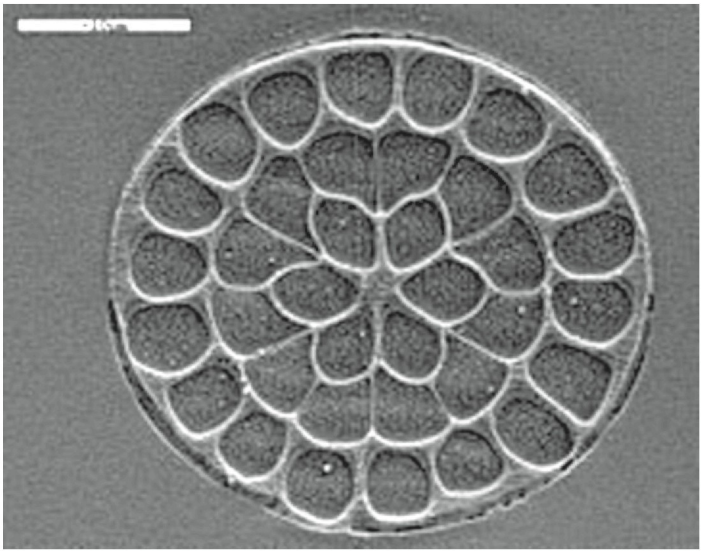

Figure 4. SEM image of PP/PE nanocomposite fiber after embedding, microtoming and oxygen plasma etching.

using a DDK Histoknife and an LKB NOVA ultramicrotome at a thickness of 2.5-3 microns. Sections were mounted onto SEM stubs with carbon tape prior to oxygen plasma etching. After microtomy the samples were subjected to the oxygen plasma for a period of 10 min.

All samples were coated with a layer of AuPd prior to SEM analysis. SEM analysis was performed at a 5kV accelerating voltage in a Hitachi S-3200 SEM. All images were acquired digitally and have had their histogram levels adjusted for improved image presentation.

Results

Figure 1 shows an image of the bare fibers cryo-fractured under LN2. A razor blade was used to facilitate the fracture of the fibers. Knife marks can be seen in the image and while the two phases can be seen, they are not well defined. Figure 2 shows the results of embedding the fibers in an epoxy previous to a cryo-fracture in LN_2. A razor blade was used again to facilitate the fracturing. Figure 2a is a low magnification image showing that fiber pull-out has occurred and that the fibers ends are not sharply fractured. Figure 2b is an image of one of the better fibers. The fiber shows that some phase detail is available and not obscured by knife marks. However, this type of fiber detail was rare and the technique did not produce a large amount of suitable cross sections.

Figure 3 shows fibers prepared in the same manner as the fibers in figure 2 followed by an oxygen plasma etch for 10 min. The nanofibers can be clearly distinguished in the image and their size and morphology can be studied. Fibers with similar detail could be found in the sample but the majority of the fibers were still unsuitable for analysis. Figure 4 is an image of a sample that has been microtomed and plasma etched for 10 min. The size and morphology of the fibers is clearly visible. Figure 5 shows other examples of fibers with extremely small sub-fibers showing the great amount of detail that is available with the oxygen plasma etching.

Discussion

The use of oxygen plasma etching has been shown to greatly enhance the features in the preparation of the PP/PE nanofiber composites. Simple cryo-fracture and plasma etching show a marked improvement over cryo-fracture only methods. Microtomy followed by plasma etching produced the best results. This method is more time consuming and requires costly equipment, but the phases could be clearly seen and measured even when the fibers were much less than 1 micron in diameter.

References

1. Jeong-Min Kim, M.L., Seohwa Kim and Sung-yi Kang, A Novel Characterization Method for Investigating the Morphology of Polymer Blends Including Polyolefin/Polyolefin Blends. ANTEC, 2003: p. 1931-1935.
2. G. Borcia, C.A. Anderson, N.M.B. Brown, "Dielectric Barrier Discharge for Surface Treatment: Application to Selected Polymers in Film and Fibre Form," Plasma Sources Science and Technology, 12 (2003), 335-344.
3. K.K. Wong, X.M. Tao, C.W.M. Yuen, K.W. Yeung, "Low Temperature Plasma Treatment of Linen," Textile Research Journal, 69 (11) (1999), 846-855.
4. N.Y. Cui, N.M.D. Brown, "Modification of the Surface Properties of Polypropylene (PP) Film Using an Air Dielectric Barrier Discharge Plasma," Applied Surface Science, 189 (2002), 31-38.
5. R. Dorai, M.J. Kushner, "A Model for Plasma Modification of Polypropylene Using Atmospheric Pressure Discharges," Journal of Physics D: Applied Physics, 36 (2003), 666-685.

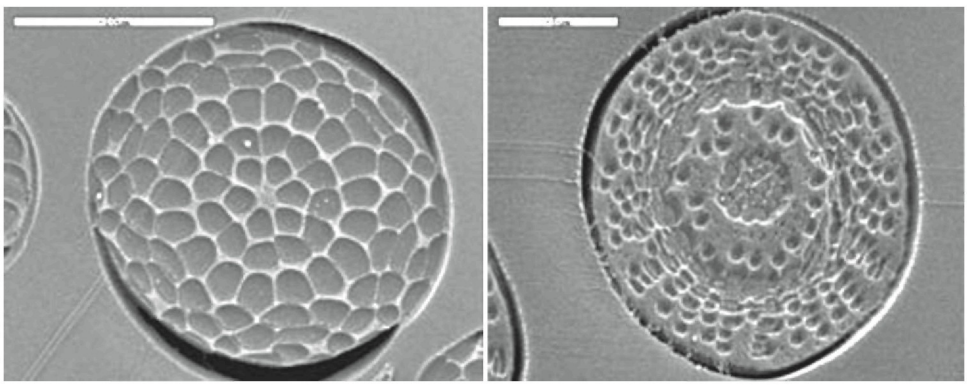

Figure 5. SEM image of different types of PP/PE nanocomposite fiber after embedding, microtoming and oxygen plasma etching.

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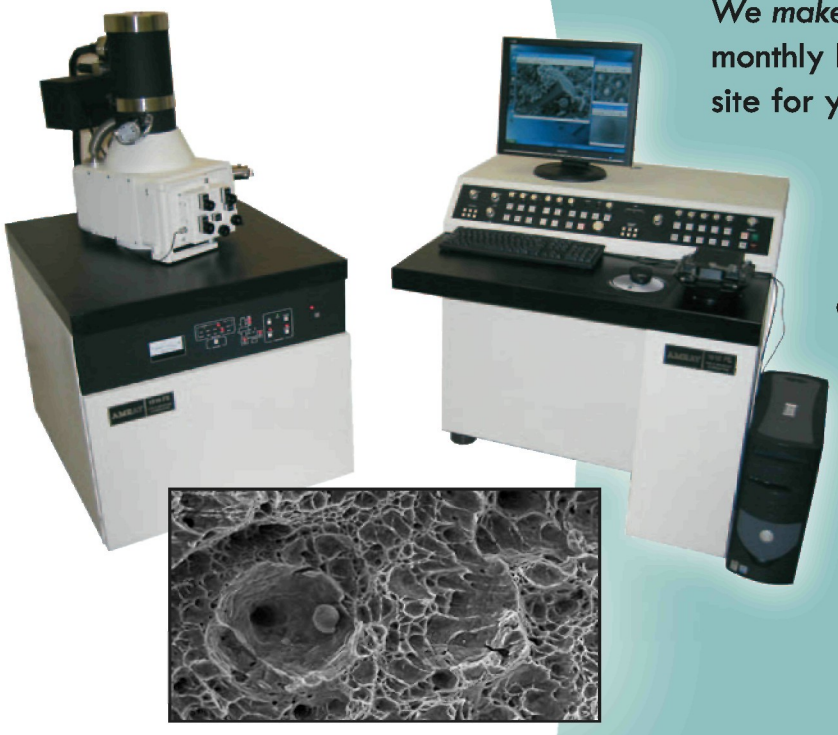

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