

Interface-Property Relationships in Hybrid Nanocomposites from Near Net-Shape Manufacturing

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ABSTRACT

Mechanical attrition and Hot Isostatic Pressing can be used in tandem to create novel hybrid nanocomposite with high interfacial surface areas, which can be manipulated to control bulk properties. A description of these interfacial characteristics in a series of hybrid nanocomposites is given.

Keywords: nanocomposites, mechanical attrition, hybrid materials

1 INTRODUCTION

Near Net-Shape Manufacturing is a two-step materials processing technique, in which nanoparticles are formed via mechanical attrition, from which nanocomposites are formed by consolidation and densification using Hot Isostatic Pressing (HIP). The technique is general to all materials classes: metals, ceramics, polymer and even biological materials. A great deal of work has been performed on the effects of mechanical attrition on the structure of various homogeneous materials [1-3]. Mechanical attrition can manifest itself in different ways in different materials; *e.g.*, molecular weight reduction in polymers, or amorphization of metals. However, little has been reported on the use of mechanical attrition to control interface formation in dissimilar materials. It is the production of highly interfacial regions in these hybrid materials that lead to bulk property control, and ultimately, to property enhancement in nanocomposites. New classes of hybrid materials, including metal-ceramic, polymer-polymer, and polymer-ceramic nanocomposites, are but three examples in which, corrosion resistance, improved miscibility, and improved membrane performance, respectively, have been linked to the interfacial characteristics of the component nanoparticles.

2 EXPERIMENTAL

All nanocomposites were formed using near net-shape manufacturing technology, which involves

high energy ball milling to form nanoparticles, followed by consolidation using Hot Isostatic Pressing (HIP). Aluminium/mullite nanocomposites were formed as previously described [4,5]. In brief, commercially available aluminum and mullite were milled in either stainless steel or nylon vials with the same grade milling media in a SPEX model 8000D (Metuchen, NJ) high-energy ball mill. The temperature was maintained at 0°C by placing the unit in a temperature-controlled laboratory refrigerator. A description of the particle size distribution and grain size in the milled particles has been previously reported [4]. The powder samples were compacted in a stainless steel mold, then vacuum sealed. The preform was then placed into a Hot Isostatic Press (HIP) (AIP Inc, Columbus, OH). The HIPing was performed by applying isostatic pressure at 45,000 psi (nitrogen atmosphere) on the sample at 450°C for 30 min. Corrosion studies were performed according to ASTM G 31-72.

Nafion-ceramic nanocomposites were formed in a similar manner, but with slight process modifications as previously described [6]. Nafion 1100EW, a perfluorosulfonated ionomer, was purchased in the form of pellets from Ion Power Inc. ($M_n = 13,000$) and subjected to a sequence cryogenic milling at -196°C in composite polycarbonate/stainless steel vials. PRONAS®, a proton-conducting crystalline oxide from Ceramtec, Inc. that belongs to the $\text{Na}_3\text{Zr}_2\text{Si}_4\text{PO}_{12}$ (NaSICON) family of materials, was ball milled in stainless steel vials. The nanoparticles were mixed, and pressed in a mechanical pressing at pressures of 7,000 - 8,000 psi and 165°C to shape the membranes, then hot isostatically pressed for 1 hour at 45,000psi and 35 -110°C. Proton conductivity tests were performed on a Nafion 117 membrane hydrated and protonated in boiling 0.5M H_2SO_4 , and an experimental 20% PRONAS/ 80% Nafion nanocomposite membrane without the pre-hydration step. Both membranes were tested under identical conditions in wet hydrogen.

Polymer blends of poly ethylene oxide (PEO) and poly p-phenylene (PPP) were formed by co-milling in a SPEX 6750 cryogenic mill with steel impactors and polycarbonate vials. The blended powders were then analyzed using Transmission Electron Microscopy.

3 RESULTS AND DISCUSSION

3.1 Metal-Ceramic Nanocomposites

Recent results from Mitchell, et al. [7] have shown that the interfacial composition in aluminum-mullite nanocomposites formed by Near Net-Shape Manufacturing can be quantified and its effect on bulk properties, such as corrosion resistance, explained in terms of interfacial chemistry [8]. As shown in Figs. 1 and 2, the interface between the aluminum and mullite nanoparticles is sharp; i.e., no migration of the component elements takes place. However, other TEM studies on these same samples have shown that carbon is present at the interface [8]. Carbon occurs as a result of thermal decomposition of polymeric (nylon) impurities that are introduced during the mechanical attrition step [5]. Improved corrosion resistance to hydrochloric acid (Fig. 3) is attributed to the presence of carbon which reduces intergranular attack.

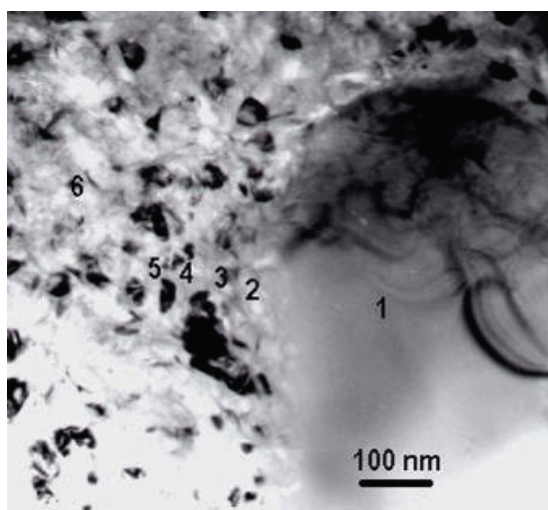


Figure 1 TEM image of aluminum/mullite nanocomposite showing aluminum phase (left) surrounding a mullite nanoparticle (right) and the interfacial analysis points in Figure 2.

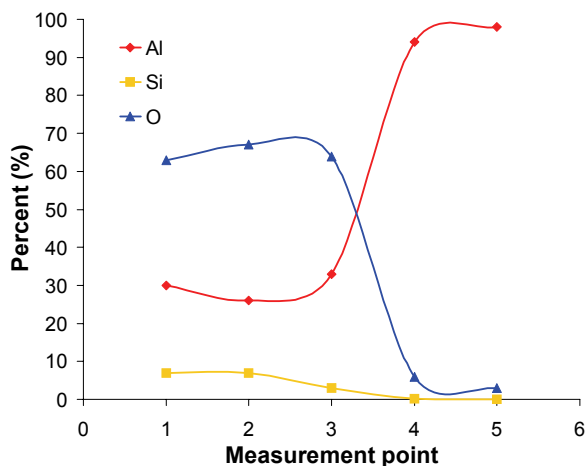


Figure 2 EDS compositional analysis of points in Fig. 1.

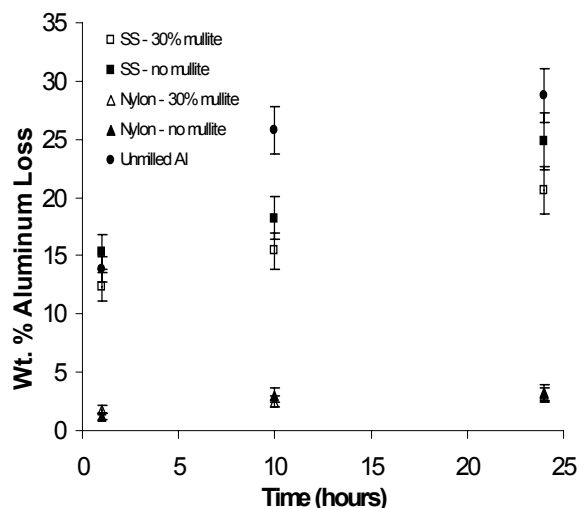


Figure 3 Corrosion resistance in aluminum/mullite nanocomposites milled in stainless steel (SS) and nylon.

3.2 Polymer-Ceramic Nanocomposites

In Nafion®/ceramic nanocomposite proton-exchange membranes, concurrent increases in operating temperature, reduction in water uptake, and increased proton conductivity have been linked to the interfacial formation between polymer and ceramic components at the nanoscale. Thermogravimetric analysis (TGA) indicates that the NNS nanocomposite membranes take up less water than commercial Nafion®, as illustrated in Fig. 4. This effect is attributed to an interfacial reaction between the polymer and ceramic components.

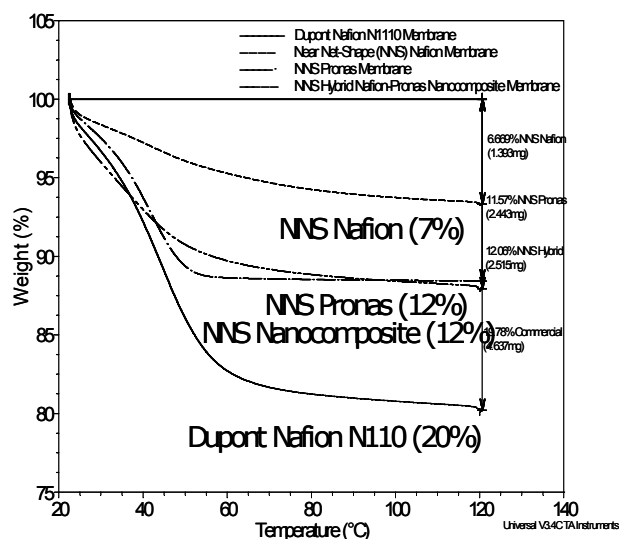


Figure 4 TGA analysis of Near Net-Shape (NNS) processed Nafion, ceramic (PRONAS) and nanocomposite membranes compared to commercial Nafion.

3.3 Polymer-Polymer Nanocomposites

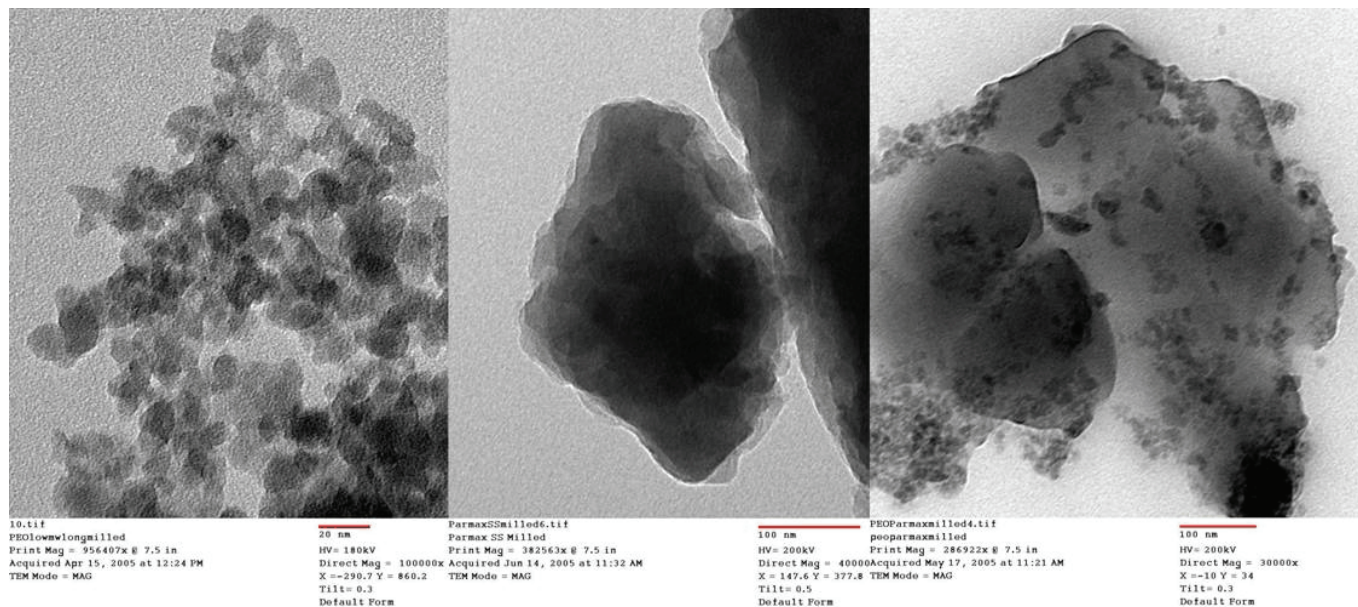


Figure 5 TEM photomicrographs of milled PEO (left), PPP (center), and co-milled PEO/PPP blends (right).

Transmission electron microscopy (TEM) was performed on the PEO/PPP polymer blends to corroborate domain/crystallite sizes estimated by XRD and to contrast crystalline and amorphous regions of blends. The images reveal the contrast between PPP, PEO. The darkest regions are those of PPP. The PEO image shows distinct PEO crystalline domains on the order of 10s of nm in size, which agrees with XRD findings. No crystalline domains are visible in the PPP since it is highly amorphous. The superposition of the two contrasting structures is evident in the blend photograph on the far right. Characterization of glass transition temperatures and mechanical properties of these novel blends from immiscible polymers are currently being conducted.

4 CONCLUSIONS

The enhancement of properties in metal/ceramic polymer/ceramic and polymer/polymer nanocomposites formed by near net-shape processing is described. Corrosion properties in aluminum/mullite nanocomposites are improved due to carbonaceous species in the nanoparticle interfacial regions imparted during milling and HIPing. Similarly, hydrogen conductivity in Nafion/PRONAS nanocomposites is improved due to favorable polymer-ceramic nanoparticle interactions. Finally, polymer-polymer nanocomposite blends can be formed from immiscible polymer pairs.

5 ACKNOWLEDGMENTS

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REFERENCES

- [1] H. Gleiter, *Prog. Mater. Sci.* **33**, 223 (1989).
- [2] C. C. Koch, *Nanostruct. Mater.* **2**, 109 (1993).
- [3] C. De Castro and B.S. Mitchell, *Advances in Nanophase Materials and Nanotechnology*, M.I. Baraton, editor, American Scientific Publishers, 2002, p.1.
- [4] C.L. De Castro and B.S. Mitchell, *Mat. Sci. Eng. A*, **396**(2005)124
- [5] C.L. De Castro and B.S. Mitchell, *J. Mat. Res.*, **17** (2002) 2997
- [6] S.D. Haynes and B.S. Mitchell, *J. App. Pol. Sci.*, **93** (2004) 2275
- [7] H.Y. Zhang, N. Maljkovic, and B.S. Mitchell, *Mat. Sci. Eng. A*, **326**[2], 315-321 (2002).
- [8] C. De Castro and B.S. Mitchell, *Mat. Sci. Eng. A*, submitted (2005).