

PLASMA SURFACE FUNCTIONALIZED NANOPARTICLES FOR USE IN SYNTHESIS OF INORGANIC/ORGANIC NANOCOMPOSITES

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Introduction

Synthesis of inorganic-organic nanocomposite materials represents an active research topic at the present time. Although significant advances have been achieved to date, a persistent challenge encountered is the problem of achieving uniform dispersion of the inorganic nanoparticles in the organic matrices. In part, this difficulty is created by the typically large differences in the surface energies of the generally hydrophilic character of the inorganic material contrasted with the more hydrophobic nature of the organic matrices. This problem is further exacerbated by the fact that nanoparticles exhibit increased aggregation as the particle sizes are decreased. An uneven distribution of particles results in poor particle-polymer interfacial interactions thus compromising physical properties of the resultant nanocomposites.

The present investigation centers on an attempt to achieve improved nanoparticle dispersions by minimizing the large surface energy difference existent between the inorganic-organic components. For this purpose, a gas phase plasma process is employed to functionalize the nanoparticles prior to synthesis of inorganic-organic nanocomposite. The purpose of the surface functionalization is two-fold: (1) to reduce the hydrophilicity of the inorganic oxide; (2) to introduce reactive surface groups to promote formation of covalent bonds between the particles and organic monomers during the polymerization process. Herein we describe results for nanocomposites synthesized using plasma modified TiO₂ and BaTiO₃ nanoparticles, as employed in formation of urethane and epoxy composites.

Experimental

Materials

TiO₂ nanoparticles (Degussa P-25 standard, 99.5% purity, with average particle size 25 nm), were obtained from Degussa Inc. Barium titanate (BTO) nanoparticles (99.6% purity, with average particle size 85-128 nm) were purchased from Nanostructured & Amorphous Materials Inc. Diglycidyl ether of bisphenol F (Epoxy; Epon Resin 862) and triethylene tetramine (Epikure

3234) were supplied by Hexion Specialty Chemicals. Dibutyl tin laurate (DBTL) was obtained from Gelest Inc. Both rigid and elastomeric urethanes were synthesized employing diisocyanates. For soft elastomeric composites, isophorone diisocyanate terminated prepolymer (CAAP COAT FP002 resin with a molecular weight < 10,000; 80% solid content in methyl propyl ketone) and diamine (Type II catalyst, 65 wt% in methyl propyl ketone and p-chlorobenzotrifluoride) were supplied by CAAP CO. Inc., Connecticut. Both diisocyanate terminated prepolymer and diamine are aliphatic based system and have low viscosity.

The other, more common, organic chemicals employed were obtained from Aldrich and were of the highest purity available.

Plasma Surface Modifications

A custom built 360° rotating plasma reactor, operable under vacuum conditions, was employed to modify the surfaces of the nanoparticles[1]. An initial high power O₂ plasma discharge was employed to remove adsorbed carbonaceous materials and simultaneously activate the surfaces of these crystals. A high power plasma discharge, using ethylene diamine (EDA) vapor, was employed to graft a strongly adherent, amorphous carbon-like layer, to the particles to overcome the inherent chemical incompatibility between the inorganic and organic components. Subsequently, a variable duty cycle pulsed plasma was used to deposit gradient layered films in which the amine content of the plasma polymer film increased as the pulsed plasma duty cycle is decreased.

Synthesis and Characterization

The TiO₂ nanoparticles were employed in synthesis of polyurethane composites, and the BaTiO₃ particles were employed in fabrication of epoxy based materials, using standard synthetic procedures. The extent of particle loading was varied between 1 and 5% mass percent for both types of composites.

XPS, FT-IR, XRD and microscopic analyses were carried out to characterize the materials at various stages.

Physical property measurements included thermal (TGA and DSC) and mechanical stress-strain measurements.

Results and Discussion

The successful plasma surface modification of the nanoparticles was documented using XPS, FT-IR and microscopy. The presence of surface N atoms on the particles after the plasma treatment was shown by XPS and amine groups were observed by FT-IR. Additionally, it was observed that both the TiO_2 and BaTiO_3 nanoparticles dispersed preferentially in hexane, rather than water, following the plasma treatment, thus confirming the surface energy change produced by the plasma deposited films (Figure.1).

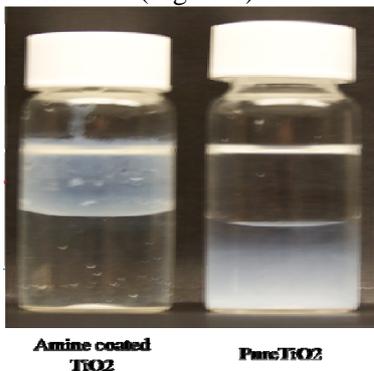


Fig.1. Dispersion of plasma treated TiO_2 in hexane (top)/water (bottom): treated particles (left); untreated particles (right).

These amine groups were subsequently reacted with the diisocyanate or diglycidyl ether to produce the poly urethane and epoxy polymeric composites, respectively. With each system, three different types of samples were prepared, namely: pure polymers; composites with untreated nanoparticles; and, composites with plasma treated particles. The synthetic procedure employed for all 3 types of materials was identical for each polymer with the only difference being the presence of the nanoparticles for the composites.

Physical evaluation of the materials synthesized involved comparison of the pure polymers with each type of composite, i.e. treated or non-treated nanoparticles. A typical example of the results is shown in Figure 2 for stress-strain data for the BTO/epoxy materials. In this figure, the curves presented are for the pure polymer (4), composite with untreated particles (5) and composite with plasma treated particles (6). The number after the decimal point represents the 3 weight % loading of the particles.

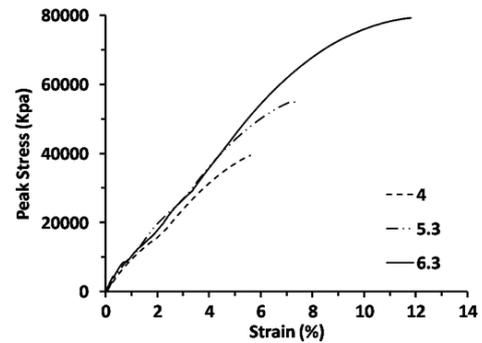


Fig.2. Stress-strain elongation data up to break point for pure polymer (4); composite with untreated BTO (5); and plasma treated BTO (6), 3% loading.

In general, for all systems examined, significantly improved thermal and mechanical properties were observed in contrasting data from the nanocomposites containing the plasma modified particles with the corresponding results from the pure polymers or composites containing untreated nanoparticles, as documented in this presentation.

Conclusion

Plasma treatment technology provides a viable route to modification of surface energies of inorganic nanoparticles while simultaneously introducing reactive functional groups to enhance particle dispersions, as well as the direct particle-organic interfacial bonding interactions. In principle, this approach is applicable to essentially any inorganic nanoparticle and a wide range of surface functional groups can be introduced, as desired, via appropriate choice of monomer during the plasma deposition step.

References

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