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Colloidal scale blend of rigid and flexible polyamides

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Summary

A two step procedure was employed to prepare a colloidal scale, uniform dispersion poly(p-aminobenzoic acid) (PAB) in Nylon 6(3)T. In the first step, a colloidal suspension of PAB was prepared via direct polycondensation, starting from a concentrated solution of AB in dimethyl acetamide (DMAc) containing suitable activators. In the second step, a solution of Nylon 6(3)T in DMAc was mixed with the colloidal suspension. The composite powder was generated by precipitation in water and the composite film obtained by redispersing the powder in DMAc and casting. The films contain PAB particles, below 100 nm in size, uniformly distributed in the Nylon 6(3)T matrix. The mechanical properties and the thermal transitions of these composites were investigated.

Introduction

Polymer composites containing a rigid and a flexible component are of particular interest, since the rigid component can reinforce the flexible one. Theoretically, when the two components are mixed at a molecular level, a maximum reinforcing effect can be achieved; such a composite was called "molecular composite"[1-3]. However, due to the low entropy of mixing and to the high orientation of the rigid component, it was difficult to prepare stable molecular composites. In addition, in most cases, the molecular composites underwent phase separation during processing or end use.

In the past two decades, molecular composites were extensively studied[1-8]. The conventional way of preparation was the co-dissolution of a rigid polyamide, such as poly(p-phenylene terephthalamide) (PPTA), and a flexible polyamide, such as Nylon, in concentrated sulfuric acid. The molecular composite could then be obtained by rapid precipitation into a non-solvent, such as water, provided that the rate of precipitation is faster than that of phase separation.

An alternative approach to prepare a binary blend containing a rigid component was to polymerize one monomer in the presence of the other polymer[9-10]. For instance, Stein et al.[9] synthesized such composites by dissolving a rigid polyamide in a vinyl monomer, followed by polymerization of the latter in situ via photoinitiation. Ogata et al.

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[10] prepared rigid polyamide/flexible polyarylate composites by in-situ polycondensation of p-aminobenzoic acid (the monomer of the rigid polyamide) in a polyarylate solution in chloroform. The former method is limited by the difficulty in dissolving a rigid polyamide in the monomer of a flexible polymer, while the composites prepared by the latter method possess unsatisfactory mechanical properties.

Recently[11], a two-step method was suggested to prepare composites containing rigid poly(p-aminobenzoic acid) (PAB) dispersed at colloidal scale (< 100 nm) in flexible poly(vinyl chloride-co-vinyl acetate-co-2-hydroxypropyl acrylate) (PVVH). The method was almost quantitative and the PAB particles, with a size range between 50 - 70 nm, were uniformly dispersed in the PVVH matrix. The mechanical properties were enhanced 2-3 fold at a PAB content of 25 wt%. The favorable interactions between PAB and PVVH were considered responsible for the formation of the stable colloidal dispersion of the former in the latter polymer. This observation suggests to couple the rigid PAB polyamide with a flexible one, such as Nylon 6(3)T, because of the favorable cross-hydrogen bonding interactions expected to occur between the two polyamides.

Experimental

Materials

P-aminobenzoic acid (99%) (AB), triphenyl phosphine (99%) (TPP), hexachloroethane (99%) (HCE), pyridine (anhydrous), N,N'-dimethyl acetamide (anhydrous) (DMAc), Nylon 6(3)T (poly(trimethyl hexamethylene terephthamide)) (Scientific Polym. Products) were used as received. Except for Nylon 6(3)T, all chemicals were purchased from Aldrich.

Preparation of PAB/Nylon 6(3)T Polymer Composites

In the first step, PAB was synthesized by direct polycondensation of AB at 40 °C in the presence of pyridine/TPP/HCE as activators, using DMAc as solvent. A transparent and highly viscous solution was obtained which became turbid as the reaction continued, because colloidal PAB particles were obtained. In the second step, the PAB dispersion was mixed with the corresponding amounts of a Nylon 6(3)T solution in DMAc to obtain final composites with a PAB content of 8, 15 and 25 wt%. Another part of the PAB dispersion was poured into methanol to generate a PAB powder. When the turbid PAB solution was mixed with the Nylon 6(3)T solution with stirring, a clear and homogeneous system was obtained. The powder of the polymer composite was collected by pouring the viscous solution into pure water, filtering, washing the precipitate repeatedly with pure water and acetone, and finally drying in a vacuum oven at 60 °C.

Thin Film Preparation

The composite powder (1.2 g) was redispersed in DMAc solution at 50 °C with stirring and a slightly turbid dispersion was obtained. A semitransparent thin film was obtained by casting the dispersion onto a glass plate at 50 °C and evaporating the DMAc.

Tensile Testing

The thin films were cut into dumbbell-shaped specimens, as required by ASTM D. 638-58T, after which they were thoroughly dried in a vacuum oven at 50 °C over night to remove the DMAc. Tensile testing was performed with an Instron Universal Testing Instrument (model 1000) at room temperature, with an elongation rate of 10 mm/min.

Thermal Transition Determinations

The glass transition temperature (Tg) was determined with a Perkin-Elmer Series 7 differential scanning calorimeter (DSC). The samples, dried under vacuum at 60 °C, were scanned under nitrogen, from 50 to 300 °C, with a heating rate of 20 °C /min.

Scanning Electron Microscopy (SEM)

The morphology of the PAB/Nylon 6(3)T composite films was examined with a Hitachi S-800 scanning electron microscope. The films were fractured under liquid nitrogen and the fractured surfaces were coated with a thin layer of carbon before scanning.

Results and discussion

Blend of PAB and Nylon 6(3)T in DMAc

PAB is a rigid polyamide insoluble in common organic solvents. During the direct polycondensation of p-aminobenzoic acid, the solution became turbid as the reaction continued. However, when the turbid PAB solution was mixed with the Nylon 6(3)T/DMAc solution, a clear and homogeneous solution was obtained, even for a PAB content in the composite as high as 25 wt%. The obtained composite powders could be re-dissolved in DMAc, but the solutions were slightly turbid. The slightly colored and semitransparent films obtained by solution casting indicated a rather small scale dispersion of the PAB in Nylon 6(3)T. When, however, the turbid PAB solution was poured into methanol, a yellowish powder formed which could not be redissolved in DMAc. The most likely explanation for the formation of a clear solution when the turbid PAB and Nylon 6(3)T solutions were mixed, is that the turbid solution contains small aggregates which disaggregate because of the adsorption of Nylon 6(3)T upon the surface of colloidal PAB particles. This adsorption increases the compatibility between the particles and the solvent. In the two step method employed, the yield of polymer composites was almost quantitative, even for a PAB content as low as 8 wt%. In contrast, for PAB/polyarylate composites, prepared by Ogata et al.[10], via in situ direct polycondensation in chloroform, the dispersions and the thin composite films were opaque, indicating much larger PAB particle sizes, and the yield was as low as 50 wt% for low PAB contents.

Stress-Strain Curves

Figure 1, which shows stress-strain curves of Nylon 6(3)T and PAB/Nylon 6(3)T composites, reveals that the materials change from thermoplastic to brittle as the PAB content increases. Nylon 6(3)T (curve a) shows a typical thermoplastic behavior with a yield point at about 7.5% strain. Curve b, for a PAB content of 8 wt%, has a stress-strain behavior similar to curve a, whereas curve c shows that, when the PAB content increases to 15 wt%, the specimen breaks during stress softening. For the 25 wt% PAB (curve d), the material breaks before the yield point is reached.

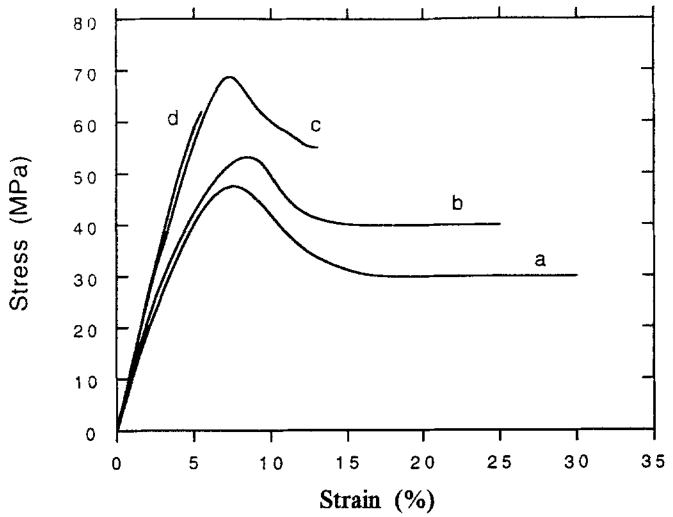

Figure 1, Stress-Strain behavior of Nylon 6(3)T and PAB/Nylon 6(3)T composites
a: pure Nylon 6(3)T; b: 8 wt% PAB; c: 15 wt% PAB; d: 25 wt% PAB

Mechanical Properties

The mechanical properties of PAB/Nylon 6(3)T composites are listed in Table 1. According to the data the yield and tensile strengths and Young's modulus increase, while the elongation decreases with increasing PAB content. Compared to pure Nylon 6(3)T, the yield strength increases by 40% for the 15 wt% PAB content, but no yield point is present for the composite containing 25 wt% PAB. The tensile strength at break increases 100 % and Young's modulus increases 40 % for the 25 wt% PAB composite, indicating that the PAB reinforces the flexible Nylon 6(3)T matrix. Yang et al.[12] reported the mechanical properties of PPTA/amorphous Nylon (AN) composites, prepared by co-dissolution/co-precipitation in concentrated sulfuric acid/water systems and processed by compression molding. The modulus for the 30 wt% PPTA increased 3 fold, but no increase in the tensile strength was achieved. For PAB/polyarylate composites[10], prepared by in situ direct polycondensation in chloroform, the tensile strength decreased by about 27% and Young's modulus increased by only 17% at 23 °C, as the PAB content increased from 0 to 29 wt%.

Table 1, Mechanical Properties of Nylon 6(3)T and PAB/Nylon 6(3)T Composites

PAB Content wt%	Yield Strength MPa	Tensile Strength MPa	Young's Modulus GPa	Elongation %
0	50	30	1.0	30
8	55	40	1.1	25
15	70	54	1.2	13
25	-	62	1.3	5.5

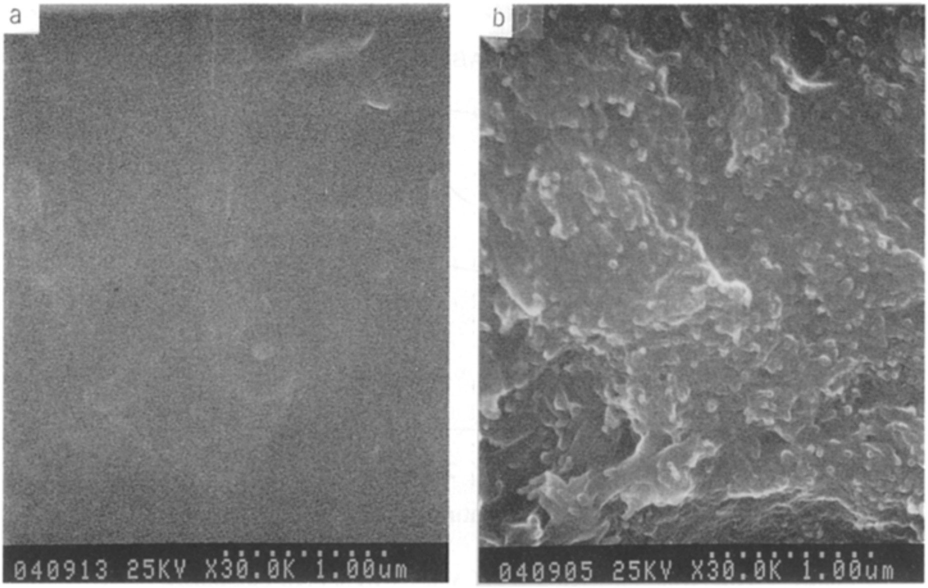

Figure 2, SEM micrographs of the fractured surfaces
a: pure Nylon 6(3)T; b: 15 wt% PAB

Morphology

The SEM micrographs of the fractured surfaces of Nylon 6(3)T and of 15 wt% PAB composite films are presented in Fig. 2. The pure Nylon 6(3)T film is transparent and has a homogeneous structure. For the 15 wt% PAB composite, a heterogeneity in the phase structure can be identified, since PAB particles, with a narrow size distribution between 50 - 70 nm, are dispersed in the Nylon 6(3)T continuous phase. This observation indicates that a colloidal level of mixing is achieved between the two polymers. In contrast, the PAB particle size in PAB/poly(arylate) composite[10], prepared in a single step by in situ direct polycondensation of AB in chloroform, was much larger, 1000 nm.

DSC Measurements

Figure 3 depicts the DSC traces of the pure Nylon 6(3)T and the 25 wt% PAB composite during the first and the second thermal scanning. Pure Nylon 6(3)T exhibits a Tg at about 151 °C, which is reproducible during the second scanning. The composites exhibit a single Tg within the scanning range, which increases with increasing PAB content. For the 15 wt% PAB composite, the Tg is around 190 °C, and for the 25 wt% sample, around 200 °C. During the second scanning, a single Tg was found at about 151 °C, the same as the Tg of pure Nylon 6(3)T. This happens because there are strong interactions between PAB and Nylon 6(3)T via cross-hydrogen bonding. These

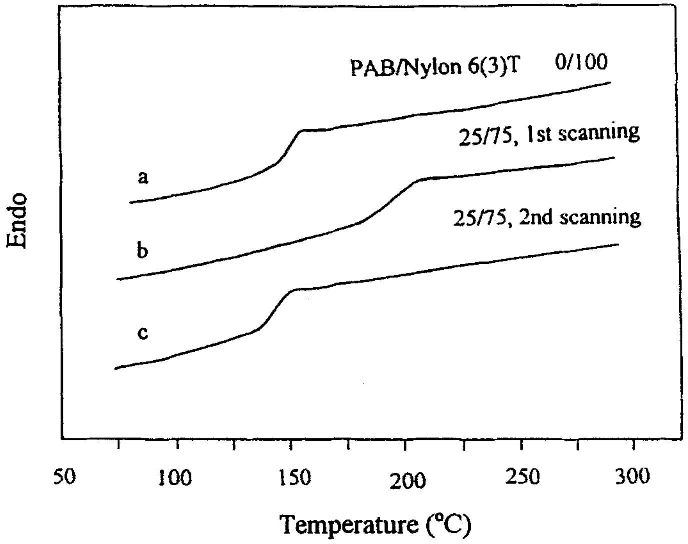

Figure 3, DSC traces of Nylon 6(3)T and 25 wt% PAB composite

a: pure Nylon 6(3)T; b: 25 wt% of PAB, 1st scanning; c: 2nd scanning

interactions, prevent the aggregation of PAB particles and inhibit the movements of the Nylon 6(3)T segments, resulting in an increase in Tg with PAB content. However, the hydrogen-bonding becomes negligible at high temperatures and, as a result, the composites undergo phase separation and only the Tg of Nylon 6(3)T could be identified during the second scanning. The sample film became opaque after the scannings, because of the aggregation of the PAB particles. The Tg of the 25 wt% PAB composite during the second scanning was at 140 °C, which is somewhat lower than that of pure Nylon 6(3)T. This might have been caused by some low molecular weight compounds introduced during preparation which were not completely eliminated during purification.

Conclusion

Polymer composites consisting of rigid poly(p-aminobenzoic acid) (PAB) dispersed at colloidal scale in flexible Nylon 6(3)T (poly(trimethyl hexamethylene terephthamide)) were prepared. The stress-strain behavior of the composites shows that the materials change from thermoplastic to brittle as the PAB content increases, and that the PAB reinforces the flexible Nylon 6(3)T matrix. The Tg of the composites increases with increasing PAB content, because the movements of Nylon 6(3)T segments are inhibited by the PAB particles, as a result of the strong interactions between the two. The second scanning indicated a single Tg, namely that of Nylon 6(3)T. This happens because aggregation of the PAB particles (phase separation) occurs during the first scanning.

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