

New Polypropylene-boron Oxide Composite with a High Tensile Strength: A Possible Method for the Conversion of Microcomposite to Nanocomposite

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Abstract

Industrially viable blends having microstructures that can be converted into a nanostructured material by post chemical treatments, potentially should have a commercially viable solution to the development of nanostructured materials for practical applications. In this regard a polypropylene-boron oxide (PPBO) blend provides a model study here. In this paper we wish to report the synthesis of PPBO blends with different concentrations of boron oxide by melt grafting and through reactive extrusion. The tensile strengths of the ideal blend has been found to be 62% higher than polypropylene (PP). By chemically treating the blends for a period of 24 hours to 72 hours the tensile strength of the blends increased by 152%. The blends have been characterized by Fourier transform infra red spectroscopy (FTIR) and scanning electron microscopy (SEM). An interesting characteristic of the PPBO blend has been the development of surface potential that changes upon visible light excitation. The increased tensile strength has been attributed to the conversion of micro structured blends to nanostructured blends. The improvement in thermal stability can be attributed to a good PP matrix-oxide interaction and also due to the thermal conductivity of the boron oxide. The good dispersion of the nanotubes in the polymer matrix allows the spreading of heat uniformly along the fiber.

Key words: Polypropylene, polypropylene-boron oxide blend, boron oxide, tensile strength, SEM, surface potential

INTRODUCTION

Polymer blends made with nanocomposited materials have been predicted to have better engineering applications than the blends made with macroscopic materials. Two possible synthetic methods are considered for making nanocomposited polymer blends. In one method the blend could be made using bulk quantities of macroscopic materials and later converting it into nanocomposited structured material by chemical treatments. In the second method the polymer blends could be made directly by using nanoscopic materials. The second method although is an easy way of making the blends, the cost would be high and industrially not viable. In this paper we report the first time preparation of PPBO blend and an attempt at the conversion of a micropolymer blend to a nanopolymer blend.

In the literature, PPBN double layer composite has been manufactured for the neutron radiation shield (1-3). This polymer composite has been found to be useful to make articles without internal fissures having a tensile strength of 250 kg/cm^3 . Besides this composite, polyethylene-ZnO nano particles have been examined for the thermal stabilization (4). The thermal stabilization here has been attributed to the modification of surface properties by the ZnO particles. So far there has been no report of making the PPBO blend in the literature. We wish to report here hitherto unknown preparation of the PPBO blend by melt grafting and through reactive extrusion. The tensile strength, the thermal stability and post modification of the blend by chemical treatment are reported in this paper.

EXPERIMENTAL

a) **Chemicals:**

Boron oxide was purchased from Aldrich Chemical Company and was 99% pure. Polypropylene was obtained from EXXON MOBILE.

b) **Melt Grafting:**

Several blends were prepared by mixing polypropylene and boron oxide in ratios of 99:1, 95:5, 90:10, 85:15 and 50:50. The blends were stored in Petri dishes until further use.

c) **Extruded Sample:**

Wayne extruder has been used for making the polymer blends. It was operated at a temperature of 400°F . A weighed amount of PP and boron oxide was added such that the boron oxide composition is 12%. The chemical treatments were carried out with $\text{HCl:H}_2\text{O}$ (1:1), $\text{H}_2\text{SO}_4:\text{H}_2\text{O}$ (1:1) and NH_4OH .

d) **TGA** instrument was a TA instrument (Delaware). It is operated with air flowing into the system.

e) **Tensile strength** measurements were made on Instron instrument. It was calibrated before use.

f) **Surface potential** measurements were made using 46 range digital multimeter made by Radioshack

g) **FTIR** instrument was Bio-Rad make. The powdered samples were placed in the sample holder for recording the spectrum.

h) **Scanning Electron Microscope (SEM)** used is JEOL 6400. It was operated at 20kV.

RESULTS AND DISCUSSION

The PPBO samples were examined by TGA, tensile strength, FTIR and SEM. The samples were later chemically treated for examining the changes in the blend.

A physical examination of the melt grafted blends showed a homogeneous structure of fibular or rods like nature. From the results obtained in melt grafted blends a composition of PP: Boron oxide (88:12) was selected for the extruder experiments. All the data presented here refer to the extruded samples of the above composition. The TGA curve of the blend is shown in Figure 1. A temperature shift in the onset (T_o) to complete decomposition (T_d) is observed in Figure 1. PP alone shows an onset temperature of 310°C and the PPBO blend shows an onset temperature of 420 °C- a shift of nearly 110°C. While PP decomposes completely to carbon dioxide and water at about 475°C, the PPBO does not decompose completely but leaves behind liquid boron oxide at 500°C in the pan. Table 1 shows the analysis of the weight loss observed after the chemical treatment. The T_o and T_d values have marginally changed by the chemical treatment. However, there is a significant change in weight (%) with PPBO upon different chemical treatments. The chemically treated PPBO samples for 24 h shows an increase in the weight percent left in the pan at T_d Upon prolonged chemical treatment (72 h) this decreases. Figure 2 shows a plot of residual percentage amount remaining at T_d . vs duration of the chemical treatment. If the structure of the polymer blend has remained the same, then the percentage amount of boron oxide should be constant and follow the

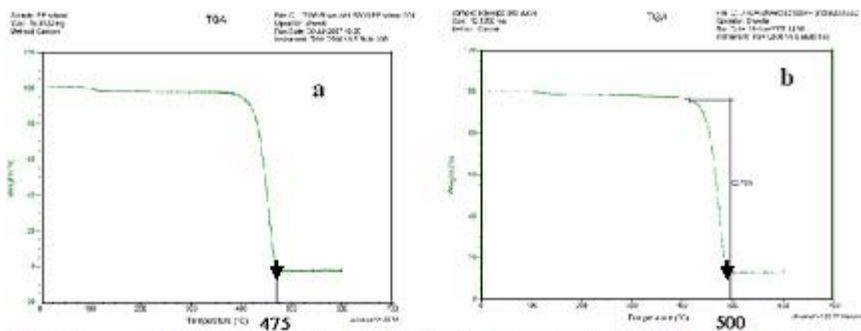


Figure 1. The thermogravimetric analysis curves of a) Polypropylene and b) Polypropylene-boron oxide extruded sample

Table 1 Thermogravimetric Data

Sample	T_{on} , °C	Decomposition Temperature, T_d , °C	Weight (%) at T_d^a	Starting weight (g)	End weight (g)
PP	310	475	0	7.49	0
PP+B ₂ O ₃	420	490	12.00	12.13	2.18
HCl, 24 hrs	410	490	18.29	10.78	2.05
HCl, 48 hrs	425	485	16.00	12.88	1.47
HCl, 72 hrs	400	480	8.50	11.70	1.17
H ₂ SO ₄ , 24 hrs	400	490	21.4	11.17	2.34
H ₂ SO ₄ , 48 hrs	400	475	15.00	13.21	1.84
H ₂ SO ₄ , 72 hrs	360	475	15.00	12.53	1.83
NH ₄ OH, 24 h	325	480	5.00	9.99	0.50
NaBH ₄ , reflux	350	470	10.00	10.37	1.04

T_{on} : Onset temperature, T_d : Decomposition temperature a: Mass at leveling temperature

line 3 in Figure 2. Curve 2 in Figure 2 shows that by hydrochloric acid treatment the residual percentage value goes up initially and for prolonged treatment the value goes below the initial starting value. These results are interpreted as due to the protonation of PPBO (addition of hydrogen to boron oxide segment) resulting in a higher residual value. A prolonged acid treatment appears to result in the conversion of a fraction of boron oxide into a gaseous molecule that escapes out. With sulfuric acid treatment, a similar trend of initial increase followed by a decrease is noticed.

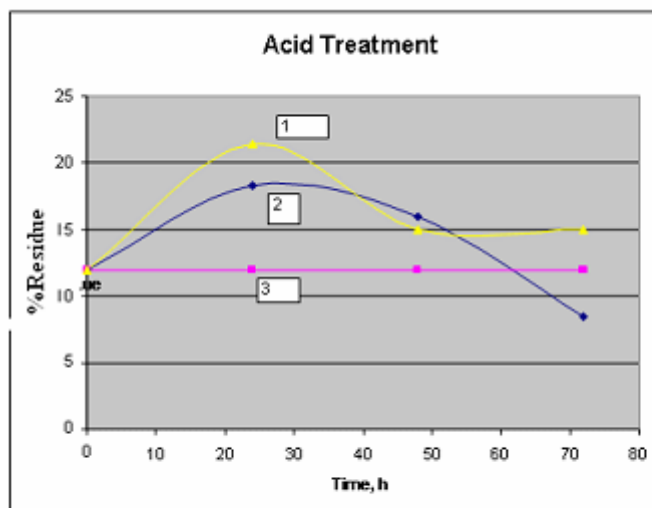


Figure 2 The percentage boron oxide left in TGA after the chemical treatment. 1. H₂SO₄ 2. HCl and 3 No treatment

However, in this case there is a leveling off that occurs after 48 h of acid treatment. Visual observations of the blend show a smoothening of the polymer surface with the

acid treatments. This suggests that the polymer has undergone structural modification (see SEM section).

The tensile strength, modulus of elasticity and yield elongation data of the PPBO are given in Table 2. The tensile strength of PPBO is nearly 62% more than PP. After the acid treatment it increased further to 150%. This increase is similar to that has been observed with PP-multiwalled carbon nanotube fibers (4). (The tensile strength after acid treatment increases but upon prolonged treatment it decreases). This trend is in conformity with the thermogravimetric data shown in Figure 2. The structure of the blend is restructured due to the chemical reaction of PPBO with the acid. The FTIR data reveals

Table 2 Tensile strength of PPBO

Sample	Tensile strength MPa	Modulus of elasticity, MPa	Yield elongation (%)
PP	7.08	220.82	2.83
PPBO	11.55	772.60	2.00
PPBO, H ₂ SO ₄ 24 h	17.90	532.33	2.76
PPBO_HCl 24 h	16.23	574.8	2.48

the appearance of the new bands upon acid treatment. Table 3 shows the infra red transitions of the PPBO. In comparison the PP and boron oxide exhibit absorptions at 1375 cm⁻¹, 2837-2868 cm⁻¹ (due to PP), 1454 cm⁻¹ (due to B-O) and 2949 (due to B-OH). Several characteristic PP bands at 956 cm⁻¹, 1174 cm⁻¹ and 1681 cm⁻¹ are absent in the blend. From this data and the acid treatment results, it appears that boron oxide is well

Table 3 Fourier Transform Spectroscopy of Polypropylene Blends Before and After the Chemical Treatment

PP	PPBO	PPBO, NH ₄ OH, 24 h	PPBO HCl, 24h	PPBO, H ₂ SO ₄ , 24h	PPBO, HCl, 48 h	PPBO, H ₂ SO ₄ , 48h
956.69	1375.25	972.12	972.12	972.12	972.12	972.12
970.19	1454.33	997.2	997.2	997.2	997.2	1165
1016.49	2837.29	1043.49	1045.42	1103.28	1103.28	1255.66
1041.56	2868.37	1078.21	1101.35	1166.93	1166.93	1357.89
1093.64	2949.16	1101.35	1165	1193.94	1193.94	1375.25
1114.86		1166.93	1195.87	1255.66	1217.08	1452.4
1174.65		1255.66	1219.01	1296.16	1255.66	2837.29
1240.23		1303.88	1255.66	1328.95	1303.88	2916.37
1371.39		1328.95	1294.24	1357.89	1330.88	2949.16
1408.04		1357.89	1328.95	1375.25	1357.89	
1452.4		1375.25	1357.89	1435.04	1375.25	
1681.93		1433.11	1375.25	1454.33	1454.33	
1712.79		1454.33	1415.75	2837.29	2723.49	
2854.65		1743.65	1454.33	2866.22	2837.29	
		2723.49	2721.56	2916.37	2866.22	
		2837.29	2837.29	2949.16	2916.37	
		2866.22	2868.15		2949.16	
		2916.37	2916.37			
		2949.16	2949.16			
			3095.75			
			3136.25			
			3174.83			
			3192.19			

blended. It appears to have produced cross linking of the polymer through boron oxide. When the acid treatment is done, the conversion of microstructure to the nanostructure appears to occur resulting in the appearance of new bands in the spectrum (see Table 3 and Figure 3). The treatment of the blend with ammonium hydroxide results in the appearance of PP bands.

SEM

A large number of samples were recorded by SEM and they all showed structural changes upon acid treatment of PPBO. Figure 3A shows the PPBO sample before the acid treatment. A rod like structure is exhibited by this blend. Upon chemical treatment, the morphological change is observed in the SEM. The sizes of the particles are in nanometer dimensions interspersed with a few unreacted sites. Previously in the literature a nanometer surface morphology was noticed by exposing boron oxide film to humid air (6) resulting in better mechanical strength.

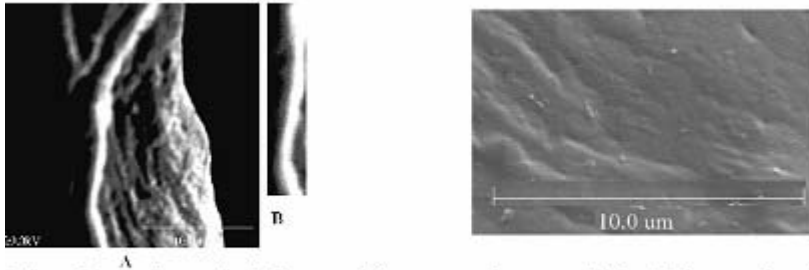


Figure 3 Scanning Electron Microscope Images of the Polypropylene-boron oxide blends A) Multistrand structure in the blend. B) Focused on a single strand . Lower Picture: The Blend after 24 h acid treatment

SURFACE POTENTIAL

The PPBO rods show a surface potential that changes upon exposure to light. PP rods do not produce this light effect. The development of this potential suggests its possible usage in device controls.

Table 4 Photo Surface Potential Data

DISTANCE ^a Inches	DARK mv	LIGHT mv	ΔmV
1	-47.1	-64.1	-17
2	-78.2	-84.1	-5.9
3	-87.2	-98.5	-11.3
4	-106.2	-111.6	-5.4
5	-143	-140.1	2.9

a. Distance between the two measurement terminals

CONCLUSIONS

The results obtained in this study show that it has been possible to form PPBO blend with a higher tensile strength than PP and convert it from microscopic to nanoscopic structured material by a chemical treatment. The development of surface potential that is sensitive to light is unique for this blend.

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