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Polymer Composites with Plasma-Treated Fillers

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ABSTRACT

A Large-volume Microwave Plasma (LMP) generator has been used to irradiate mica and ground-wood fibers in inert and active gas environments. Irradiated fillers were subsequently incorporated in a polypropylene matrix at solids levels of 10 and 20%. Calorimetrically measured heats of immersion showed that substantial changes in surface properties of fillers were effected by irradiation in ethylene, ammonia, and similar active gases. These

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surface changes are reflected in ultimate tensile and elongation properties of composites which show marked improvement over controls based on unirradiated fillers. Although no appreciable response in melt viscosity has been observed, surface treatment of fillers does seem to increase significantly melt elasticity of filled composites. The implications of improved performance motivate a more detailed study of the use potential of LMP in the fomulation of polymer composites.

INTRODUCTION

The use of ionizing radiations in polymer technology is widespread, the rising level of interest being reflected in numerous review articles and texts [1-3]. Our present involvement in this field has two main points of origin. The first is the recent development [4] of a Large-volume Microwave Plasma (LMP) generator which presents an opportunity of exploring the use of LMP as a means of achieving novel and superior property balances in polymeric materials. The second is a long-standing concern for the nature of interactions among components of polymer compositions and the degree to which interfacial, mechanical, and other use properties of polymer compounds depend on such interactions [5, 6]. A desirable goal arising from the latter consideration is the optimization of properties in filler-reinforced polymers by suitably modifying the surface of the minor (filler) component and thus controlling, to advantage, the polymer-filler interaction variable. Surface modification here implies some chemical changes at the filler surface created by reactions occurring in an activated gas discharge, and this subject, again, has been frequently investigated [1, 7]. Microwave discharge, however, provides a particularly attractive means for such chemical reactions; among its principal advantages we note [4]:

Higher yield of active species than in other types of electrical excitation.

Wider pressure range over which LMP can be sustained.

A rather high electron/gas temperature ratio, the carrier gas remaining rather cool.

Absence of internal electrodes and thus elimination of a source of contamination of the plasma.

High safety factor in operation due to the absence of high voltage sources in the generator.

This paper presents the early results of our attempts to apply the LMP method for the surface modification of inexpensive particulate (mica) and fibrous (ground-wood) fillers for polymer matrixes. Some aspects of the melt flow behavior and of the mechanical properties of composites involving polypropylene and the irradiation conditioned fillers are also reported in order to suggest the degree and breadth of property modification attainable by this route to the control of polymer-filler interactions. No attempt has been made in this initial work to clarify the complex reaction mechanisms responsible for reported changes in the surface properties of the plasma-irradiated solids.

EXPERIMENTAL

Materials

The systems studied were chosen for their inherent technical as well as economic interest. The fillers—Suzorite mica and Aspen ground-wood fiber—are inexpensive and significant to the economy of regionally based industries. Polypropylene was selected as the matrix polymer. It is typical of commodity nonpolar polymers for which reinforcement effects are often sought, but which have poor wetting characteristics for polar and hydrophillic substrates such as the selected fillers.

The polypropylene was a commercial extrusion grade resin with a melt flow index of 1.5. Suzorite mica platelets were screened and the 60/100 mesh fraction retained for present purposes. The Aspen ground-wood fiber was a pressure-refined product, used as received from the supplier.

Surface Treatment and Tests Thereof

The LMP generator used to condition surface properties of mica and wood fibers has been described in detail elsewhere [4]. In the present application a quartz tube 90 cm long and 37 mm in diameter was used as a container for the solids to be treated, batch quantities of 3 to 5 g solid (either mica or ground wood) being used in any given irradiation sequence. The reactor tube was connected to the vacuum and gas metering system of the LMP assembly [4] through rotating joints, so that the material being irradiated could be tumbled continuously during the treatment. This ensured greater uniformity of surface treatment than could be attained in a stationary system.

Fillers placed into the reactor tube were evacuated to a residual pressure of about 10^{-3} Torr, whereupon the gas to be used as irradiation environment was metered continuously into the tube so as to maintain a pressure in the range 0.5 to 2.0 Torr. In irradiation experiments the LMP unit was operated at constant (1.5 kW) power for 30 to 120 sec. The irradiated solids were then exposed to dry nitrogen, stopcocks at either end of the reactor tube were closed, and the entire assembly was stored for 15 to 24 hr prior to further use of the solids. This precaution was taken to minimize the effects of post-irradiation reaction of solids with atmospheric oxygen—an occurrence reported previously [7]. In the present exploratory series of experiments Ar, N_2, C_2H_4,

TABLE 1. Effect of LMP Irradiation on Heats of Immersion of Fillers in Water

	ΔH_{imm} (cal/g) at 25°C	
Treatment	Mica	Ground wood
Control, no treatment	0.092	8.5
Vacuum only	0.090	12.3
N_2 plasma[a]	0.090	-
Ar plasma[a]	0.086	11.9
SO_2 plasma[b]	0.081	10.8
SO_2 plasma[a]	0.078	10.4
C_2H_4 plasma[b]	0.134	-
C_2H_4 plasma[a]	0.139	9.4
C_2H_4 plasma[c]	0.142	-
NH_3 plasma[a]	0.107	6.4
C_2H_4/NH_3 plasma[a] cond. a.	0.300	-

[a]Irradiation at 2 Torr and 90 sec.
[b]Irradiation at 2 Torr and 60 sec.
[c]Irradiation at 2 Torr and 120 sec.

SO_2, NH_3, and a 1/1 mixture of C_2H_4 and NH_3 were used as irradiation gases.

Following the post-irradiation conditioning, the reactor tube was opened in a dry box swept by dry nitrogen, and the effect of plasma irradiation was assessed by measuring the heat of immersion of mica and ground wood in double-distilled water. For this purpose samples of irradiated solids were transferred to brittle glass ampules designed for use with the LKB, Model 8700 Microcalorimeter. Heat of immersion data, using this apparatus, were obtained at 25°C.

Composites and Property Tests

Surface-treated solids as well as control quantities of fillers without previous LMP exposure were incorporated into polypropylene by mixing in a Brabender Plasticorder operating at 190°C and 60 rpm. Composites at 10 and 20% by weight of solids were prepared in this manner; 0.1% by weight of a commercial thermal stabilizer for polypropylene was added during the compounding cycle.

The flow behavior of the materials was examined by capillary viscometry, using the well-known CIL Viscometer [8] fitted with a die having L/R = 11.6. All extrusion data were collected at 190°C. Compression-molded plaques (190°C) of the composites were used to cut specimens suitable for stress-strain measurements. In this report comparisons are restricted to ultimate tensile and elongation properties. The familiar Instron Universal Tester was used to generate these results.

RESULTS AND DISCUSSION

Calorimetry

The calorimetric data, expressed in calories per gram of solid immersed in water, are recorded in Table 1. It is clear that LMP irradiation has very significant effects on the surface condition of the fillers. In the case of mica, it is reasonable to assume that no chemical changes occur during irradiation in inert media (N_2, Ar). This analog to CASING [9] could not be expected to produce significant effects on the surface of the mineral. Although the nature of surface modifications brought about by irradiation in the active gases and the gas mixture cannot be specified, the importance of such conditioning in terms of wetting by water

is quite evident. This exploratory work did not include a systematic evaluation of the influence of irradiation variables on heats of immersion, though in the case of C_2H_4, time is confirmed as one such (significant) variable. Our objective being to produce surface-localized changes in the fillers, quite short irradiation periods were used. This followed the evidence of Hall and co-workers [10] who note that the properties of polymer complexes at first change rapidly with irradiation time, but more slowly when the dwell time of the components in activated gas environments is increased into the range of several minutes.

The response of ground wood to surface conditioning is more complex, the application of vacuum alone causing an important increase in the hydrophilic nature of the solid. This may be attributed to the removal of labile water fractions during evacuation. In active-gas environments, and particularly in NH_3 and C_2H_4, significant permanent changes in the nature of ground-wood surfaces have been effected. The possible influence of these modifications on properties of polymer composites appears worthy of investigations.

Tensile Properties of Composites

The effect of surface treatment on the mechanical properties of polypropylene composites filled with mica and ground wood was indicated by comparing ultimate tensile and elongation-at-break data. These are given in Table 2; for convenience of comparison the data have been normalized to the corresponding behavior of unfilled polypropylene, so that the overall change in the mechanical properties is immediately perceived. [$(U.T.)_r$ and $(E)_r$ refer to the ratio of ultimate tensile and elongation-at-break, respectively.]

The data divide readily into two groups. The analog to CASING has no measurable result on the behavior of filled materials using either of the solids. The removal of water during evacuation (and irradiation) of the wood fiber, clearly affecting the calorimetric results, has no corresponding effect on tensile-elongation behavior: presumably reabsorption of water occurs well within the time span needed to form and test the filled polymer samples. Filler irradiation in active environments has produced interesting improvements in mechanical properties at failure. The results for C_2H_4-treated mica and NH_3-irradiated ground wood are particularly noteworthy since, in both cases, the tensile properties of the polypropylene control itself are exceeded, even at 20% filler level. Reviewing the immersion data, it is suggested that enhanced interfacial adhesion results from the surface modification induced by the plasmas. The beneficial effects of this on mechanical properties

TABLE 2. Comparison of Mechanical Properties of Composites Using LMP-Treated Fillers[a]

Filler:	Mica				Ground wood			
Level:	10%		20%		10%		20%	
Property: Treatment	$(U.T.)_r$	$(E)_r$	$(U.T.)_r$	$(E)_r$	$(U.T.)_r$	$(E)_r$	$(U.T.)_r$	$(E)_r$
Nil	0.86	0.60	0.76	0.55	0.85	0.53	0.79	-
N_2	0.87	-	-	-	-	-	-	-
Ar	0.84	0.66	0.79	0.55	0.84	0.55	0.80	-
SO_2	0.92	0.75	0.85	0.60	1.03	0.62	0.94	-
C_2H_4	1.13	0.90	1.06	0.70	0.92	0.60	0.90	-
NH_3	1.09	0.90	1.01	0.70	1.11	0.67	1.07	-
C_2H_4/NH_3 (1/1)	1.05	0.82	1.00	0.65	1.04	0.59	-	-

[a]All data are relative to properties of unfilled polypropylene controls.

TABLE 3A. Viscous Response (Flow Rate, g/min) in Capillary Extrusion of Composites Using Irradiated Fillers

Filler:	Mica				Ground wood			
Pressure (psi):	200		700		200		700	
Solids (%):	10	20	10	20	10	20	10	20
Treatment								
Control	0.228	0.174	4.38	3.44	0.152	0.110	2.25	1.73
Ar	0.242	0.180	-	-	0.160	-	2.08	-
NH_3	0.261	0.168	4.39	3.52	0.157	-	2.13	-
C_2H_4	0.235	0.170	4.75	3.30	0.143	0.120	2.06	1.88
C_2H_4/NH_3	0.274	0.169	4.78	3.64	0.139	0.111	1.98	1.76

TABLE 3B. Elastic Response (Swelling Ratio) in Capillary Extrusion of Composites Using Irradiated Fillers; Mica Filler Only

Pressure (psi):	200		700	
Solids (%):	10	20	10	20
Treatment				
Control	1.26	1.07	1.52	1.30
Ar	1.26	-	1.60	-
NH_3	1.29	-	2.18	-
C_2H_4	1.38	1.16	2.02	1.38
C_2H_4/NH_3	1.41	1.20	2.38	1.52

of the composites suggests the desirability of more detailed research intended to clarify and optimize the effects involved.

Melt Properties

Two sets of rheological parameters are reported in this initial work. The flow rates of filled compounds at 200 and 700 psi indicate the effect of filler on the melt viscosity (processability) of the materials over an appreciable range of shear stress. Swelling ratio measurements (filament diameter/die diameter) have been used to suggest the response of melt elasticity to irradiation treatment. Because of considerable distortion in the extrudates of wood-filled samples, however, the swelling ratios are restricted to mica composites. The pertinent results are given in Tables 3A and 3B.

The flow rates (melt viscosities) of filled compounds (Table 3A) do not appear to be significantly affected by the irradiation treatment of the filler surfaces. There is an indication of some loss of processability at higher extrusion pressures in mica composites, when C_2H_4 was used for surface conditioning, but since the data reproducibility is of the order of ±5%, the effect is barely above the limits of accuracy in the present sequence.

The effect of filler surface treatment (mica) on melt elasticity (Table 3B), on the other hand, is very apparent. Associating post-extrusion swelling with the existence of long-range interactions among chain molecules which lead to the stabilization of elastically deformable networks [11], it is suggested that mica when irradiated in active gas environments, and especially in the C_2H_4/NH_3 mixtures, promotes the creation of such networks. Speculatively, active sites for adsorption of polymer are created by the LMP conditioning of filler, particularly in the mixed gas environment. The consequences of this would be reduced slippage of polymer chains in the velocity gradient of a shear field and an increase in the amount of reversibly stored elastic energy [11, 12]. The implications of this conclusion, once again, warrant more detailed study.

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