Ultrasonically Delaminated and Coarse Mica Particles as Reinforcements for Polypropylene

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Synopsis

The effect of the size of mica platelets used, at 30% by mass, to reinforce polypropylene was studied by comparing ultrasonically delaminated mica (diameter 5 μm, aspect ratio about 40) with a coarser mica (150–420 μm) with and without the coupling agent 3-(triethoxysilyl)-1-propanamine (Union Carbide A-1100). Reducing the particle size of the mica (treated with coupling agent) significantly increased the tensile modulus and strength but did not affect elongation at break; it gave a small improvement in Izod impact strength; the heat distortion temperature was lower and the melt flow index was increased. Dynamic mechanical evaluation (Rheovibron) was done with a series of coarse micas (<44 μm, 45–150 μm, 150–250 μm, and one with a broad distribution around 100 μm), and an ultrasonically delaminated mica made in a continuous process (<20 μm), all treated with *N*-(4-vinylphenyl)methyl-*N′*-(3-trimethoxysilylpropyl)ethylenediamine (Dow Corning Z-6032), at 20% by mass in polypropylene. Except for the disappearance of a peak at 0°C in the loss tangent due to the glass transition, the composite with delaminated mica did not differ from pure polypropylene, melting at 175°C. Use of the coarser micas raised the melting temperature to 200°C, increased the storage modulus, and lowered the loss tangent in the case of the three fractionated samples. The results were concordant with theories of reinforcement and microrheology. The hoped-for improvement in some properties on changing to the finer mica may not have been realized because of incomplete dispersion.

INTRODUCTION

Particle Size

In seeking to understand composite materials so as to design better ones, researchers normally attend first to the mechanical properties of the matrix and reinforcing particles and the bonding between them. A simple argument suggests that the size of the particles should not be of primary importance. If the composite can be regarded as a material in its own right, the length scale of specimens used to determine its properties does not matter. The geometric similarity between a large specimen of a composite containing coarse particles and a small specimen containing fine ones then implies that particle size does not influence the properties of the composite either. This idea is in fact embodied in simple concepts such as the rule of mixtures, as well as sophisticated theories of the modulus of a composite based on accurate solution of the equations of classical elasticity. Only when new features, such as interaction between particles or an energy proportional to their surface area, are considered, does a second scale of length emerge. This, together with the particle size, defines a new parameter

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on which the mechanical properties may now depend, thus explicitly bringing in particle size as an essential variable. Other geometric parameters are also relevant. The aspect ratio α is the longest dimension divided by the shortest of a particle. A standard deviation of particle sizes or their logarithms measures the width of the size distribution. But these parameters are still independent of the actual length scale of the particle.

The accumulated knowledge up to the early 1970s on mechanical properties of composites is presented by Nielsen.[1] He states that particle size can influence polymer properties through phenomena occurring at the interface, through changes in agglomeration, and through a skin effect associated with the finite size of the test specimen. The objective of the present study is to provide information on the effect of particle size in one system of importance, polypropylene reinforced with mica.

Reinforcement by Platelets

The principles by which a soft, weak matrix material can be made into a stiff, strong composite have been treated by Piggott,[2] for the cases of reinforcement by either fibers or platelets. The effect of particle shape on the mechanical properties is reviewed by Chow.[3] Short fibers, if aligned, reinforce in one dimension, while platelets provide planar or two-dimensional reinforcement. The different fillers that have the form of flakes or platelets are discussed by Woodhams and Xanthos.[4] Further information on these composites, application in design, and economics is provided by Rexer and Anderson.[5]

Early research[6] on the mica–polypropylene system established its advantages, as well as showing that irradiating the mica with ultrasound could delaminate the mica. This reduced the particle size without the degradation in aspect ratio that occurs when the mica is crushed and ground mechanically. The present study investigates in more detail the properties characteristic of polypropylene composites containing ultrasonically delaminated mica. Some previous work has examined the effect of coupling agents[7] or of glycerol treatment[8] on the rheological and mechanical properties of mica composites.

As the temperature is varied over a wide range, qualitative changes in properties occur, principally through the glass transition region and at the crystalline melting point. Both crystallites and reinforcing particles behave approximately like crosslinks in that their presence raises transition temperatures, as well as moduli.[9] Fine particles should do this more effectively. In our system, based on semicrystalline polypropylene, the main transition is crystalline melting, but there is also a glass transition at a much lower temperature. An amorphous matrix, poly(methyl methacrylate), was used by Iisaka and Shibayama[10] in a study of the influence of reinforcing particle size on dynamic mechanical properties. The primary dispersion temperature T_α (which may be the glass transition), and also the storage modulus E', increased as the size of dispersed glass beads was reduced, as expected. However, T_α and E' decreased with decreasing size of mica platelets; orientation appeared to be a complicating factor.

In our present test program, first six mechanical properties were measured on polypropylene unfilled and reinforced with mica, both coarse and ultrasonically delaminated, with and without a coupling agent. The properties studied were tensile modulus, tensile strength, elongation at break, Izod impact strength, heat distortion temperature, and melt flow index. In a second set of experiments, dynamic viscoelastic behavior was observed in the Rheovibron over a wide temperature region for polypropylene and its composites with four fractions of coarser mica as well as ultrasonically delaminated mica, all with a coupling agent.

EXPERIMENTAL

Materials

Polypropylene powder, grade SY 5101, an unstabilized material, was provided by Shell Canada Ltd.

Mica of the Suzorite variety was supplied by Marietta Resources International. The grades used were 60H (with a high aspect ratio, about 32), 60S, 200S, 325S, and 200HK (with a broader size distribution).

The coupling agents were 3-(triethoxysilyl)-1-propanamine (Union Carbide A-1100), and *N*-(4-vinylphenyl)methyl-*N′*-(3-trimethoxysilylpropyl)ethylenediamine (Dow Corning Z-6032).

Sample Preparation

The six mechanical tests employed grade 60H mica. In the samples designated 60H it was used as supplied, with flake diameters 150–420 μm. The other samples contained ultrasonically delaminated mica made by irradiation in batches at 20 kHz until the flake diameter was 5 μm, with an aspect ratio of about 40. Both forms of mica were then either dried at 140°C for at least 24 h or else treated with A-1100 by a slurry process. In this procedure, 0.5 parts by mass of A-1100 (as a 40% solution in ethanol by volume) was added to 100 parts of mica slurried in distilled water. The slurry was basic enough for hydrolysis of the silane, adjustment of the pH being unnecessary. After slow mixing for 24 h and standing for 12 h more, the slurry was evaporated, and the product finally dried for 12 h at 50°C.

The composite was produced by tumble mixing 30 parts of mica and 70 parts of polypropylene by mass for 40 min, followed by extrusion from a Brabender twin screw compounder at 210°C. After the extrudate was chopped into pellets, specimens for mechanical testing were made by injection molding with the barrel at 215°C for pure polypropylene or 259°C for the composites. After 1.5 min heating in the barrel, a shot was injected at a maximum pressure of 1.2 MPa through heated runners into a mold at 50°C, where it was retained for 30–40 s. Some holdup of mica during these operations was noticed, causing the actual mass fraction in the test specimens to be about 0.25, as estimated from experience in other studies in which samples were analyzed by ashing. The resulting molded bars were then tested.

A wider variety of micas was used in the experiments on dynamic viscoelastic behavior. Fractions having different sizes were obtained by drying and sieving 60S, 200S, and 325S; these yielded samples with flake diameters 150–250 μm, 44–150 μ, and <44 μm, respectively. An ultrasonically delaminated mica was made from 200S in a continuous process in which the mica suspension had a residence time of 50 s in a cell irradiated with ultrasound at 20 kHz; the resulting flakes were less than 20 μm in diameter and had an aspect ratio α of about 40. In addition, 200 HK mica, with a broad size distribution around 100 μm, was used as supplied. All these micas were treated with coupling agent at 0.5% by mass. A solution 60% by volume of Z-6032 in methanol was used in the slurry process, with a few drops of acetic acid being added to aid hydrolysis. After mixing for 3–6 h and drying, the product was sieved to remove any agglomerates of mica.

Specimens for dynamic testing were made by mixing 20 parts of mica and 80 parts of polypropylene by mass and compression molding the mixture for 1.5 min at 240°C and 2.2 MPa into a film about 0.5 mm thick. From this, specimens 30 × 5 mm were cut, ready for testing.

Test Procedures

Six mechanical properties were studied, in four tests. First, a flow model Instron tester was used with three to five specimens of each material to get tensile modulus, strength, and elongation to break, according to ASTM D638. Greater accuracy for the modulus was obtained by use of an extensometer clamped to the specimen during the early part of its elongation in order to measure the small strain there. Before testing, the cross section of each specimen was measured in three places; some shrinkage after injection molding was seen.

In a second test, the impact strength was measured using four to six specimens, the notched Izod test ASTM D256 being followed. The third test was for heat distortion temperature, by ASTM D648. Tensile test bars were cut down to the prescribed dimensions and loaded with 624 g in order to obtain a maximum fiber stress of 1820 kPa. The temperature of the immersion bath was raised from 25°C at 2°C/min; the test result was recorded as the temperature at which the deflection was 0.25 mm. Finally, the fourth test, ASTM D1238, gave the melt flow index. After 4–5 g of sample was heated in the cylinder for 4 min, it was extruded under condition L: 230 ± 1°C, 298.2 kPa.

In the other series of experiments, the dynamic viscoelastic behavior was studied using a model DDV-II Rheovibron viscoelastometer, at the fixed frequency of 110 Hz. Dynamic force and loss tangent tan δ were directly read from the balance settings of the instrument as the temperature gradually rose from about −70°C to the specimen's softening point (around 200°C). The observations were processed off-line on the IBM 3033 system, the results being displayed by a Gould plotter. The calculations included a correction for clamp extension.

RESULTS AND DISCUSSION

Mechanical Properties

The results of the six mechanical tests are listed in Table I, with standard deviations. It is also noted whether use of a coupling agent or changing from 60H (coarse) to ultrasonically delaminated mica leads to a difference that is statistically significant at the 95% confidence level in a two-sided comparison.[11]

All the micas stiffen the composites, raising the tensile modulus by a roughly similar extent. The formula of Padawer and Beecher[12] is customarily used to

TABLE I
Mechanical Properties of Polypropylene and Its Mica Composites

		Mica reinforcement				
Property	Unit	None	60H (coarse)		Ultrasonically delaminated	
Coupling agent (%)		—	0	0.5	0	0.5
Tensile modulus	GPa	1.74	3.80	4.06[a]	2.76[b]	4.20[a]
		0.25[c]	*0.13*	*0.12*	*0.08*	*0.37*
Tensile strength	MPa	30.6	27.2	27.8	29.7[b]	34.8[ab]
		1.2	*0.3*	*0.6*	*0.2*	*3.1*
Elongation at break	%	[d]	9.2	8.1	7.6	8.2
			2.2	*0.6*	*1.4*	*1.3*
Izod impact strength	J/m	54.0	44.5	49.2[a]	52.0[b]	52.1
		3.3	*2.7*	*2.6*	*1.5*	*4.5*
Heat distortion temperature	°C	56	94	97	[e]	73
Melt flow index	deg/min	29.7	5.6	7.3	10.8	14.6[ab]
		5.5	*0.9*	*1.1*	*0.8*	*3.0*
Einstein coefficient		—	47	34	19	11

[a] Significantly different from the value with no coupling agent.
[b] Significantly different from the value with 60H (coarse) mica.
[c] Italicized numbers are standard deviations.
[d] Polypropylene without mica did not break in this range of strains.
[e] No specimen was tested.

estimate the modulus of composites with discontinuous reinforcement by flakes; it is a rule of mixtures modified by a modulus reduction factor. For a volume fraction of 0.09 (corresponding to our effective mass fraction of 0.25) of mica having a tensile modulus of 172 GPa[4] and aspect ratio 40, that formula predicts a modulus of 4.02 GPa. The formula of Riley,[13] embodying a different modulus reduction factor, yields 5.59 GPa. The experimental modulus values (Table I) agree with Padawer and Beecher when a coupling agent is used, but Riley's formula overestimates them.

A degradation in tensile strength, which often occurs when mica is added to polypropylene,[7,8] was also seen here when the mica was either coarse (60H) or without a coupling agent. However, the ultrasonically delaminated mica treated with coupling agent showed improved tensile strength; even without treatment the result was better than that of the coarse counterpart. Nevertheless, the applicable theory[2] predicts the still higher value of 40.4 MPa, when the mica's strength is 275 MPa[4] and the polypropylene's shear strength is 11 MPa. All the reinforced samples broke after some 8% elongation, in contrast to the pure polypropylene, which failed in a ductile manner. In the course of elongation, whitening of the specimens was observed in many cases, showing voids to be forming. This was most pronounced for the 60H mica without coupling agent (less so with coupling agent), but was eliminated when ultrasonically delaminated mica was used with the coupling agent.

According to Woodhams and Xanthos,[4] Izod impact strengths of these composites rarely exceed about 50 J/m, a generalization confirmed here (Table I). The treated ultrasonically delaminated mica again appears to give a superior composite, but the scatter in the data lower the significance of these results.

The two remaining properties in Table I relate more to thermal effects and viscous flow. For these, the heat distortion temperature and the melt flow index, the finer mica gives values between those for the coarse mica and unfilled polypropylene. This is unexpected, because with its larger specific surface area and increased opportunity for interaction between particles, the finer mica should increase the viscosity more.[14] The heat distortion temperature actually represents just one point on a curve determined by both thermal and viscoelastic effects; this curve for each composite sample showed no creep, but the curve for pure polypropylene did. The melt flow index i is roughly inversely proportional to the viscosity, so that an Einstein coefficient ν can be estimated from $i_1/i = 1 + \nu\phi_2$ (Table I). Here the volume fraction ϕ_2 is 0.09.

Microrheological theory[15] can only give minimum and maximum values between which ν must lie, the uncertainty being due to ignorance of how the particles' orientations are distributed. For all oblate spheroids (modelling platelets) of aspect ratio $\alpha > 8$, the minimum ν is close to 2.1. However, the maximum ν is given by a formula[15] which can be simplified to

$$\nu = 4(\alpha^2 - 1)/\{3\alpha^2(\alpha^2 - 1)^{-1}[\alpha^2(\alpha^2 - 1)^{-1/2}\sec^{-1}\alpha - 1] - 2\}$$
$$\sim 1/(3\pi/8\alpha - 2/\alpha^2 + 15\pi/16\alpha^3 - 4/\alpha^4 + \ldots) \quad \text{for } \alpha > 8.$$

As α becomes very large, ν approaches $(8/3\pi)\alpha$ asymptotically, so that the maximum Einstein coefficient rises without limit as the aspect ratio increases. For $\alpha = 40$, the maximum ν is 35.5; the experimental values for ultrasonically delaminated mica are under this maximum, but those for the coarse 60H mica are not. It may be that the larger mica particles are more hindered from entering the small orifice of the extrusion plastometer, thus lowering the melt flow. Microrheological theory[15] takes no account of interactions or surface effects: The former are small at this low volume fraction, while the latter are evidently significant because the melt flow increases when a coupling agent is used.[7]

The theories for reinforcement in the solid state[2–5] differ significantly from that for melt viscosity.[15] In the solid, the aspect ratio α influences the reduction factor for modulus or strength through a slowly varying function that approaches unity as $\alpha \rightarrow \infty$. On the other hand, the maxima of both ν and the viscosity increase without limit as α becomes large. As one seeks to improve mechanical properties by using platelets of higher aspect ratio, processing difficulties are likely to be aggravated. Indeed, in our experiments a greater variation between pure polymer and composite is found in the melt flow index than in any of the properties of the solid.

Dynamic Viscoelastic Behavior

The tensile storage modulus E' and loss tangent, $\tan\delta$, obtained from measurements in the dynamic viscoelastometer on six materials are shown in Figure 1. The semicrystalline pure polypropylene (a) has a loss peak at 0°C (commonly identified as T_g); it melts at 175°C. When ultrasonically delaminated mica is added (d), no loss peak is detected, but otherwise the behavior is not changed; melting still occurs at 175°C. The samples containing coarser micas (b, c, e, f) may have a weak transition around 50°C, but the onset of melting is delayed until the temperature attains 200°C. These micas effectively impart their elasticity to the composite, raising E' and lowering $\tan\delta$. The increase in E' is more

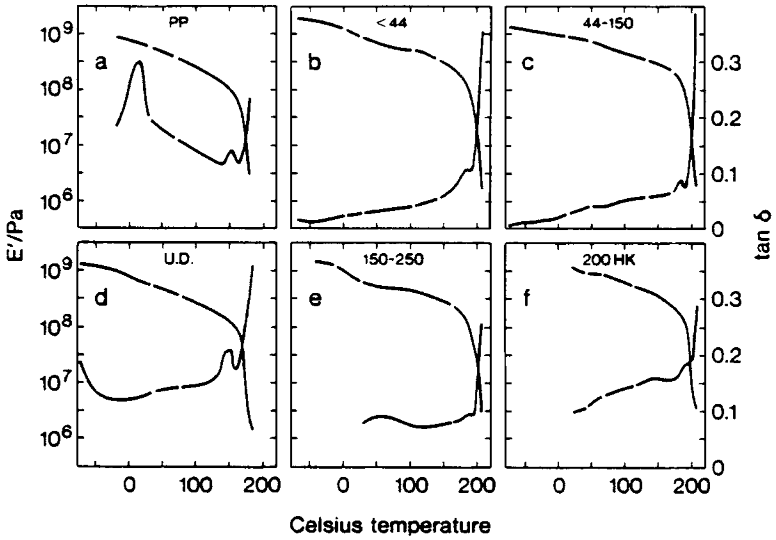

Fig. 1. Dynamic viscoelastometer (Rheovibron) plots, against temperature. Upper curves, tensile storage modulus, referred to left-hand scale (logarithmic). Lower curves, loss tangent, referred to right-hand scale (linear). Mica reinforcements for the polypropylene: (a) none; (b) < 44 μm; (c) 44–150 μm; (d) ultrasonically delaminated (< 20 μm); (e) 150–250 μm; (f) 200 HK. Breaks in the curves indicate places where the instrument readings showed scatter or shifts in baseline, perhaps due in some cases to the composite nature of the samples.

pronounced at higher temperatures, and the mica fractions (b, c, e) lower tan δ more effectively than 200HK (f) with its broader distribution of sizes. Around 100°C the modulus E' may increase with increasing particle size (on Fig. 1, in order d, b, c, e) but the order is unclear in the glassy region, say around −20°C. In mica-reinforced poly(methyl methacrylate), E' and a transition temperature both increased with the platelet diameter.[10] The effect of fillers on raising the glass transition temperature is well known.[1,9]

Quantitatively, the theories[2–5] for static tensile modulus of platelet-reinforced composites overestimate E' when applied without modification to the viscoelastic modulus. A different class of theories, for purely elastic materials with inclusions having different elastic constants, remain valid for dynamic viscoelastic behavior, if the elastic constants are replaced by their complex counterparts.[16] Features such as the increases in E' and transition temperature with increasing volume fraction of filler are predicted, but particle size does not enter these theories.

The dynamic viscoelastic behavior of our samples is consistent with the mechanical properties described above, which were obtained using another grade of mica and a different coupling agent. Unfortunately, delaminated mica was inferior to coarser micas both in raising the static heat distortion temperature and in delaying melting in the dynamic test. Increases in moduli in both series of experiments were broadly concordant. The lessened effectiveness of ultrasonically delaminated mica in the dynamic test may be due to the difference in how the specimen was made. There, the treated mica and polypropylene were directly compression molded, whereas the samples used for the mechanical properties had been compounded in an extruder before injection molding. This procedure breaks up agglomerates of filler particles, the presence of which is known to degrade reinforcement.[17]

CONCLUSIONS

Replacement of coarser mica particles by very fine ones produced by ultrasonic delamination in a polypropylene composite improves tensile strength and impact strength, treatment with coupling agent being necessary to achieve this. There is some lowering of the heat distortion temperature but an improvement of processibility, as measured by the melt flow index. These observations are consistent with available theory and with dynamic experiments in the Rheovibron viscoelastometer. In these, the composite with ultrasonically delaminated mica differed little from pure polypropylene, apart from the disappearance of a loss peak at 0°C. Materials containing coarser micas had higher storage moduli, lower loss tangents, and softened about 25°C higher than pure polypropylene. To get maximum benefit from ultrasonic delamination of mica platelets, it will be essential to disperse the reinforcement effectively. Agglomeration may have prevented realization of optimum properties in this study.

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