

Chlorinated Hydrocarbon Coupling Agents for Mica-Polypropylene Composites

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Synopsis

The incorporation of small amounts of a chlorinated hydrocarbon wax into polypropylene (PP) when making mica-PP composites is shown to produce a layer of degraded chlorinated hydrocarbon at the interface between the polymer and the reinforcement. Mica is shown to accelerate the thermal degradation of the chlorinated hydrocarbon, and the chlorinated hydrocarbon, or its degradation products, are shown to react with hydrocarbon analogues of the polymer. As well as modifying the chemical nature of the interface, the layer of degraded chlorinated hydrocarbon is shown to modify the morphology of the interface by inhibiting the ability of the mica to nucleate the crystallization of PP from the melt.

INTRODUCTION

Mica is an abundant naturally occurring mineral with high strength, good thermal stability, and good corrosion resistance. If appropriate grinding and grading techniques are used, high aspect-ratio mica platelets (platelet diameter:thickness >50) may be obtained, and these platelets are finding increasing application as a high-modulus reinforcement for plastics.¹⁻³ Mica-reinforced polypropylene (PP) has received particular attention because of its high stiffness, low cost, good dimensional stability, and adequate temperature performance.^{1,4-7}

It has recently been reported that the addition of certain chlorinated hydrocarbon (chlorohydrocarbon) waxes, either by blending at ~1% with the resin or by coating on the mica at a similar equivalent loading, appreciably improves the strength, stiffness, and heat distortion temperature of mica-PP and mica-polyethylene (PE) composites.⁵⁻⁷ This behavior justifies their description as "coupling agents," even though their chemistry and mode of action may be very different from the better-known silane coupling agents. The chlorohydrocarbon is either used alone, when there is a considerable cost advantage over silane coupling agents,^{5,6} or is used, in conjunction with a peroxide initiator, to improve the performance of a conventional silane coupling agent.⁷ The disadvantage of using the chlorohydrocarbon alone is a requirement for a relatively long residence time in the extruder barrel to produce effective coupling.^{5,6} The present study describes the application of a range of spectroscopic and analytical techniques to examine the mode of action of chlorohydrocarbon coupling agents.

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EXPERIMENTAL

The PP (Monomer Polymer Laboratories) used for all but the wetting experiments and experiments in solution was in powder form, of 400,000 molecular weight,⁸ predominantly isotactic, and contained no added processing antioxidant. For wetting experiments, pellets of a commercial moulding grade resin (Shell 550) were used. When a soluble PP was required, a commercially available amorphous polymer (Hercules A-FAX) was used after reprecipitation twice from a toluene/decahydronaphthalene solvent mixture using methanol as nonsolvent. The chlorohydrocarbon was a commercial grade (Chlorez 700, Dover Chemical Company) in the C₂₀-C₂₆ range and contained about 70% chlorine. When required, the chlorohydrocarbon was incorporated into the polymer as a dichloromethane solution. After thorough mixing, the solvent was removed by vacuum evaporation. Mica samples were of the Suzorite variety (Marietta Resources International Ltd.). Various grades were used including H200 (platelet diameters mostly in the range 75-150 μm), and 325 HK (platelet diameters mostly $\leq 45 \mu\text{m}$). All samples were dried at 120°C for 1 h immediately before use. For model studies, freshly cleaved sheets of Muscovite mica were used. 2,6,10,14-Tetramethylpentadecane (TMPD, Eastman) was passed through a silica-alumina column to remove polar impurities. All other solvents were reagent grade or better and were redistilled before use.

Infrared (IR) spectra were obtained using a Nicolet 7199 Fourier Transform (FTIR) spectrometer.⁹ For examining sample surfaces, the internal reflection spectroscopy (IRS) technique was used with a germanium or KRS-5 reflection element.⁹⁻¹¹ X-ray fluorescence (XRF) analysis for chlorine was performed on a Philips XRF spectrometer. Rates of HCl evolution were measured by thermogravimetric analysis (TGA) using a DuPont 990 instrument. A Mettler thermostatted hot stage was used for the microscopical study of the molten polymer. Water droplet contact angles on mica and polypropylene surfaces were measured as described previously.¹² UV/visible spectra were obtained with a Hewlett-Packard 8450A spectrometer.

RESULTS

TMPD Model System

Because of the difficulties involved with characterizing chemical changes in a solid polymer, the behavior of mica was first examined in a liquid analogue of PP (TMPD) containing the chlorohydrocarbon. A mica sheet (2 \times 2 cm) was immersed in TMPD containing 3% of the chlorohydrocarbon and heated to 200°C for 6 min, and then allowed to cool, thus mimicking the thermal history of an extruded composite. The mica was then removed, washed with isooctane, and examined to determine whether any physical or chemical changes had occurred on the mica surface as a result of this treatment. As a reference, another mica sample was heated for the same time in the TMPD/chlorohydrocarbon solution to only 100°C, and then cooled and washed in an identical fashion.

The 200°C-heated sample was found by XRF analysis (Fig. 1) to have a chlorine-containing layer adhering to its surface even after washing with isooctane. A comparison with mica samples coated with known amounts of the chlorohydrocarbon indicated that the chlorine content of the surface layer was

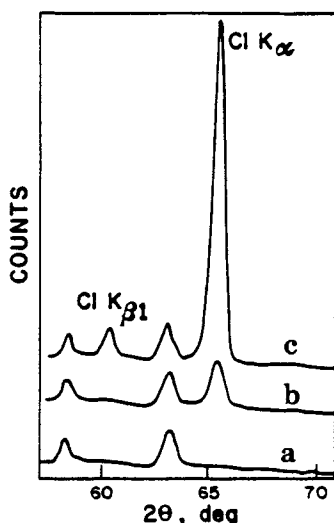


Fig. 1. X-ray fluorescence spectra of mica samples: (a) untreated mica; (b) 100°C chlorohydrocarbon-treated mica (see text); (c) 200°C chlorohydrocarbon-treated mica (see text).

equivalent to a layer of the chlorohydrocarbon about 100 nm thick. The reference sample heated to 100°C had much less chlorine-containing material adhering to its surface (Fig. 1).

The chlorine-containing surface coating on the mica was at least partially soluble in dichloromethane. XRF analysis of the 200°C treated mica before and after washing showed that dichloromethane at room temperature dissolved about 75% of the chlorinated material from the surface. Figure 2 shows the IR spectrum of the dichloromethane-soluble component obtained by placing the solution on a salt disk and evaporating the solvent. The spectrum is similar to that of the chlorohydrocarbon with the exception of the 1600–1800 cm^{-1} region, which shows the presence of large amounts of α -halogenated carbonyl compounds (1740 cm^{-1}) and olefinic unsaturation (1630 cm^{-1}), and an intensification of the CH strength adsorption at 2900 cm^{-1} . This implies that the layer adhering to the

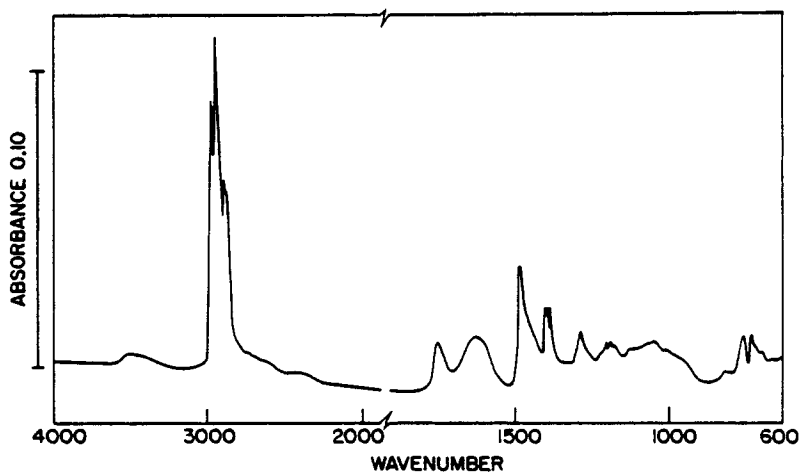


Fig. 2. IR spectrum of dichloromethane soluble component of mica surface coating.

surface of the mica, after thermal treatment similar to that experienced during extrusion, consists largely of highly degraded chlorohydrocarbon. This conclusion is supported by the UV/visible spectrum of the dichloromethane-soluble component, which shows a broad absorption tailing into the visible region (Fig. 3), characteristic of conjugated olefinic unsaturation.

Not surprisingly, the water droplet contact angle of the mica was greatly increased by treatment with the chlorohydrocarbon solution. Typically, contact angles of 60–80° were found for the 200°C-treated mica, but reproducibility of this measurement was poor and the contact angle also appeared to be time dependent, probably because water was able to partially disrupt the surface coating and so gain access to the high-energy mica surface.

Acceleration of the Degradation of the Chlorohydrocarbon by Mica

The degradation of poly(vinyl chloride) is well known to be accelerated by many inorganic compounds.¹³ It is therefore conceivable that mica might influence the thermal degradation of the chlorohydrocarbon additive. The accelerative effect of mica flakes (Suzorite 325 HK) on the degradation of the chlorohydrocarbon was demonstrated by thermogravimetric analysis (TGA) in air at 200°C (Fig. 4). The rate of weight loss by the chlorohydrocarbon, assumed to be through HCl evolution, was markedly accelerated by the presence of an equal weight of mica. The weight loss data were normalized to a constant weight of chlorohydrocarbon, and the weight after 4 min was taken as 100% to allow time for the samples to reach the desired temperature and to allow for the evolution of volatile materials (e.g., water or low molecular weight organics) as the sample heats up. In a separate experiment it was demonstrated that the mica loses no weight at 200°C in air after a rapid initial evolution of what is probably loosely bound water.

Reaction of the Chlorohydrocarbon with the Polymer

Because of the difficulty in extracting and analysing reaction products in a solid polymer, two model systems were studied. A solution of 2 g of the chlorohydrocarbon in 20 cm³ decahydronaphthalene (DHN) was refluxed (195°C) in air for 10 min. DHN was used in preference to TMPD because TMPD was

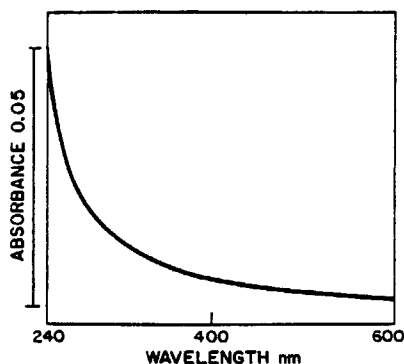


Fig. 3. UV/visible spectrum of dichloromethane soluble component of mica surface coating.

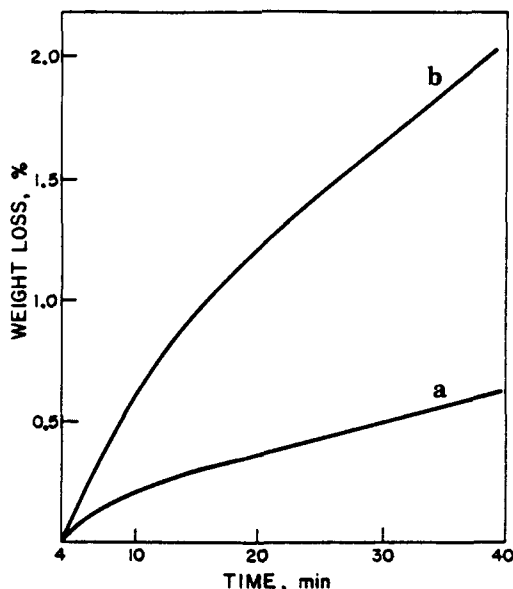


Fig. 4. Weight loss by the chlorohydrocarbon at 200°C in air by TGA: (a) chlorohydrocarbon alone; (b) chlorohydrocarbon with an equal weight of mica.

difficult to subsequently distill away. The solvent was removed by vacuum distillation and the involatile material collected (3.4 g). This difference in weight between the residue and the original chlorohydrocarbon must then correspond to an involatile reaction product between the chlorinated hydrocarbon and the hydrocarbon solvent, because heating DHN alone under these conditions produces no involatile residue. Elemental analysis showed the residue to contain 48.6% carbon, 6.7% hydrogen, 41.0% chlorine, and 4% oxygen, as compared to 27.8% carbon, 2.8% hydrogen, and 69.4% chlorine for the original chlorohydrocarbon. Extensive reaction therefore must have occurred between the chlorohydrocarbon and a hydrocarbon which is a reasonable model for PP.

To determine whether grafting of the chlorohydrocarbon to the polymer chain occurs under these conditions, a mixture of 4% of the chlorohydrocarbon in amorphous PP (with an equal weight of TMPD to reduce the viscosity of the system and so facilitate mixing) was heated to 195°C for 10 min. The polymer was then reprecipitated twice from a toluene/DHN solvent mixture (using ethanol as nonsolvent) before being washed with toluene at 25°C. The reprecipitated polymer was then found by X-ray fluorescence to contain $\leq 0.03\%$ chlorine, indicating that very little grafting of the chlorohydrocarbon to the polymer had occurred. Reaction between the chlorohydrocarbon and the polymer is therefore likely restricted to such processes as hydrogen abstraction, backbone scission, or reaction with low molecular weight fragments.

Characterization of Mica-PP Composites

In order to assess the relevance of data obtained from model liquid systems, it is necessary to demonstrate that qualitatively similar processes occur in mica-PP composites. The composite system most amenable to direct chemical analysis was a sandwich structure produced by moulding a layer of PP about 100

μm thick between two freshly cleaved sheets of mica. The composite was maintained at 200°C for 4 min and then rapidly cooled in the press. The sandwich structure was then separated into its components by immersion in cold water. The exposed PP surface was vacuum dried at room temperature and examined by the IRS technique. This involves pressing the sample against a germanium IRS element for spectroscopic examination using 45° incidence. The depth to which the surface is sampled depends upon the wavelength of the IR radiation but will typically be about $0.5\ \mu\text{m}$ for the mid-IR range.¹¹

Figure 5 shows the IRS spectrum of the polymer surface produced when 2% of the chlorohydrocarbon was incorporated into the polymer prior to moulding. The spectrum shows a strong absorption at $1650\ \text{cm}^{-1}$ with a shoulder at $1740\ \text{cm}^{-1}$ presumably associated with olefinic unsaturation and halogenated carbonyl groups, respectively (cf. Fig. 2). When an IRS element of lower refractive index was used (KRS-5), a greater depth of the surface was sampled ($\sim 5\ \mu\text{m}$), and the degradation product absorptions were appreciably less intense, relative to the PP absorptions (data not shown). When the polymer film was examined by transmission IR (thus sampling the total thickness), the degradation product absorptions were barely significant relative to the polymer absorptions (Fig. 5, inset). These observations indicate that the degraded chlorinated hydrocarbon was located preferentially in the $0.5\ \mu\text{m}$ of the polymer adjacent to the mica surface. A precise calculation of the local degradation product concentration would require a more exact knowledge of the nature of the olefinic unsaturation, but a comparison with spectra of reasonable models indicates that the level of unsaturation in the $0.5\ \mu\text{m}$ thick layer was $\geq 1\ \text{mol/kg}$ and was at least 10 times the level in the bulk of the polymer. For an equivalent sample containing no chlorohydrocarbon, the IRS spectrum of the polymer surface was similar to that expected from PP, except for a weak absorption at $1720\ \text{cm}^{-1}$, which is probably associated with thermal oxidation of the polymer.

The chemical modification of the interface could be observed indirectly by measuring the water droplet contact angle on the polypropylene surface. Figure 6 shows that the water contact angle on the polypropylene surface adjacent to the mica was appreciably reduced by the presence of the chlorinated hydrocarbon in the melt. For comparison, glass-PP composites were prepared in a similar

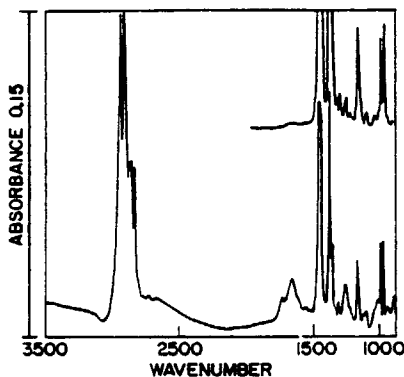


Fig. 5. IRS spectrum of PP surface exposed by cleaving mica/PP interface. Inset is the transmission spectrum of the same sample, scaled such that the PP absorptions are similar to those in the IRS spectrum.

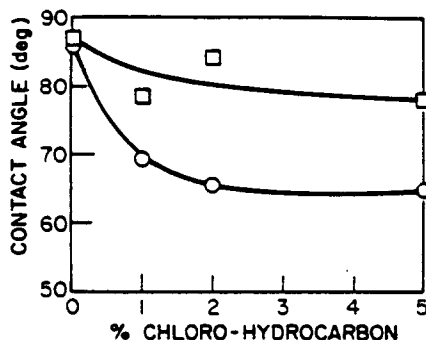


Fig. 6. Water droplet contact angles on polypropylene: (□) interfacial polymer originally in contact with glass; (○) interfacial polymer originally in contact with mica.

fashion, using cleaned pyrex microscope slides instead of mica. The water contact angle on the PP surface was then reduced only slightly by the presence of the chlorohydrocarbon in the polymer (Fig. 6).

Composites made using mica flakes are clearly less amenable to direct chemical analysis than the sandwich composites described above, because the interfacial region cannot be examined in isolation. Chemical or physical changes at the interface must therefore be inferred indirectly by, for example, observing how a particular treatment modifies the crystallization kinetics of the PP. We have reported previously^{9,10} how mica flakes provide a high energy surface of suitable geometry capable of nucleating the crystallization of PP. Here we exploit this observation and use the presence or absence of mica-surface nucleation as an indication of whether modification has occurred to the mica-PP interface. In such a way it was confirmed that the undegraded chlorohydrocarbon is retained only weakly by the mica surface (cf. first subsection). A sample of H200 mica was coated with 2% chlorohydrocarbon from dichloromethane solution. A small amount of the coated mica was then mixed with an excess of PP and heated to 180°C in the hot stage of the microscope. When the sample was subsequently cooled to 125°C to induce crystallization, nucleation of the PP crystallization occurred predominantly on the mica surface [Figs. 7(a,b)], just as occurred with uncoated mica.^{9,10} Presumably, the chlorohydrocarbon was dissolved away by the excess PP and diluted to an insignificant level before the degraded surface layer could be produced. If a degraded surface layer was formed on the mica surface before mixing with the PP (by tumbling the coated mica in air at 200°C for 15 min), the mica no longer nucleated the crystallization of PP [Figs. 7(c,d)], implying that the degraded chlorohydrocarbon was retained at the interface in the presence of an excess of PP, at least under these relatively mild conditions of 180°C and zero shear.

Wetting of the Mica Surface by PP

For satisfactory adhesion to occur between mica and PP, the molten PP obviously must first wet the mica surface. The effect of the chlorohydrocarbon on the wetting process was examined using a method suggested by Professor R. T. Woodhams of the University of Toronto. A pellet of PP was placed on the

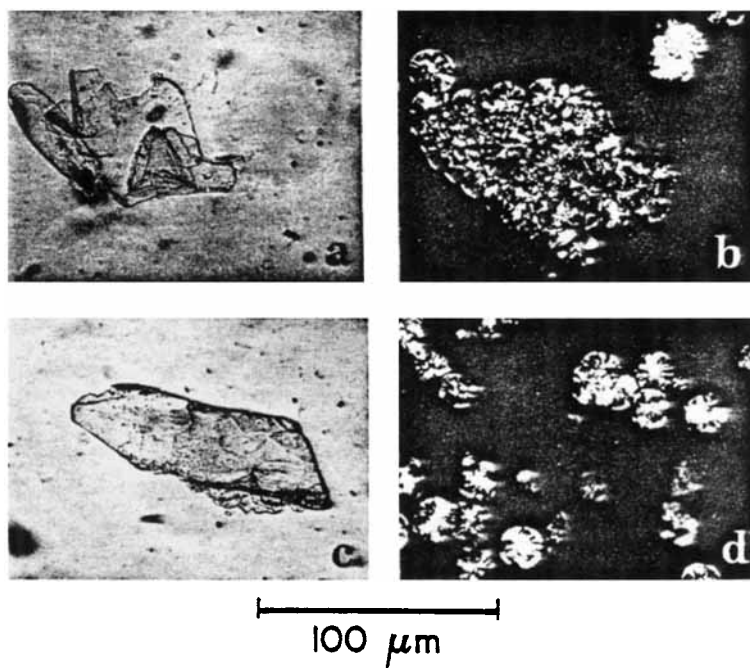


Fig. 7. Crystallization of PP in the presence of mica platelets: (a, b) mica coated with 2% chlorohydrocarbon; (c, d) mica coated with 2% chlorohydrocarbon and heat treated (see text). Micrographs (a) and (c) were taken at 180°C to show location of mica platelets. Micrographs (b) and (d) correspond to the same areas as (a) and (c) but were viewed with crossed polarisers and show crystallization occurring at 125°C.

surface of a mica sheet in an air oven at 200°C, and the contact angle measured after various heating times. The observed contact angle is probably a complex product of the thermodynamics of wetting, the kinetics of wetting, and the kinetics of viscous flow, but it provides a useful empirical measure of the wetting process. The mica surface for these experiments was artificially “aged” by immersion in water and then dried at 120°C to better resemble the mica surface likely to be encountered in the fabrication of composites. After 20 min at 200°C, the contact angle of the PP droplet with the mica surface was typically 80° while PP pellets containing 2% chlorohydrocarbon typically had contact angles of 70°. After 40 min, the PP contact angle had decreased to about 70° while the PP containing chlorohydrocarbon had a contact angle of 55°. Clearly the chlorohydrocarbon assists the wetting process, but it is not clear how this observation relates to the wetting process in an extruder under high shear conditions.

A separate qualitative wetting experiment confirmed the earlier observations (first and fourth subsections) that the undegraded chlorohydrocarbon is not strongly retained by the mica surface. A thin film of the chlorohydrocarbon was cast on to an “aged” mica surface from dichloromethane solution. This continuous flow was observed to spontaneously “de-wet” on heating to 150°C, i.e. to break up into small globules with contact angles of about 30°. Such behavior is inconsistent with the chlorohydrocarbon being strongly adsorbed by the mica surface.

DISCUSSION

The experimental observations may be summarized.

(a) The chlorohydrocarbon, in its undegraded state, is retained only weakly by the mica surface (first, fourth, and fifth subsections of Results).

(b) After a thermal history which mimics extrusion, a layer of degraded chlorohydrocarbon is formed adjacent to the mica surface. This occurs both in semicrystalline PP samples (fourth subsection of Results) and in liquid analogues (first subsection of Results).

(c) Mica accelerates the degradation of the chlorohydrocarbon (second subsection of Results).

(d) The chlorohydrocarbon reacts with PP (or models) at elevated temperatures but does not graft to the polymer chain, at least under these chosen conditions (third subsection of Results).

(e) The presence of the chlorohydrocarbon modifies the mica-PP interface in such a way as to reduce the ability of the mica to nucleate the crystallization of PP (fourth subsection of Results).

(f) The addition of the chlorohydrocarbon to PP facilitates the wetting of the mica surface by the polymer (last subsection of Results).

The localization of the degraded chlorohydrocarbon at the mica surface [observation (b)] will have a profound effect on the adhesion between the mica and PP. It is important to consider in more detail the mechanism of this localization and its consequences.

Concentration of the degraded chlorohydrocarbon at the interface could be caused by reaction of the chlorohydrocarbon with the mica, by simple adsorption of the chlorohydrocarbon (or its degradation products) on to the mica, or by precipitation or phase-separation of the chlorohydrocarbon (or its degradation products) at the interface. Chemical reaction between the chlorohydrocarbon and the mica seems unlikely both from a general knowledge of their chemistries and from the ease with which the mica-PP interface is disrupted by water. Chemical bonding would be expected to impart a degree of water resistance as has been postulated for silane coupling agents.¹⁴ Simple adsorption of the undegraded chlorohydrocarbon also seems unlikely since no evidence was found here that the chlorohydrocarbon had a strong affinity for the mica surface.

It is significant that a moderately severe thermal history is required to produce effective coupling between the mica and the PP.^{5,6} The effective temperature range coincides with the temperatures at which the chlorohydrocarbon will degrade. The demonstrated accelerative effect of mica (second subsection of Results) will result in an initial localization of the degradation at the interface. For this degraded material to be retained at the interface, however, either the degraded chlorohydrocarbon must have an affinity for the mica surface (adsorption) or its reduced solubility in the polymer must cause it to precipitate at the interface. In a complex system such as this, it is difficult to separate the two processes (adsorption and precipitation). Halogenated carbonyl compounds can reasonably be expected to have an affinity for the ionic mica surface. In addition, anhydrous HCl, as is produced by the degradation process, is highly hygroscopic and will assist in displacing water from the mica surface, so facilitating adsorption. The poor solubility of the degraded chlorohydrocarbon in aliphatic hydrocarbon solvents is also demonstrated here (first subsection of "Results").

The production of the degraded chlorohydrocarbon layer will have several consequences. No evidence was found here of primary chemical bonds between the mica and the chlorohydrocarbon. The polar nature of the degraded surface layer (as evidenced by the water droplet contact angle of the interfacial polymer, fourth subsection of Results) will, however, increase the secondary bonding (polar interactions) with the mica surface. The ability of the chlorohydrocarbon to react with the polymer (third subsection of Results) will result in a continuous gradation in chemical constitution from the mica surface out into the polymer. Whether this corresponds to an "interpenetrating polymer network" as discussed by Plueddemann and Stark⁷ cannot be confirmed on the basis of the data reported here.

The modification of the chemical state of the polymer at the interface also explains the modification of the morphology at the interface. PP containing a high concentration of degraded chlorohydrocarbon and which is also extensively modified by reaction with the chlorohydrocarbon will not have sufficient structural regularity to be able to crystallize. The mica surface is therefore prevented from nucleating the crystallization of PP by an intervening layer of noncrystallizable polymer. Although surface nucleation (transcrystallization) has been claimed by some authors^{15,16} to improve adhesion between the polymer and the reinforcement by increasing the modulus of the interfacial polymer, in this case the beneficial effects of the *elimination* of transcrystallization (the retention of polar, noncrystallizable, polymer at the interface, the effects on shrinkage stresses) outweigh the effects on the modulus of the interfacial polymer. This point has been discussed in more detail elsewhere.^{9,10}

The effect of the degraded chlorohydrocarbon layer on the rheological behavior of mica-polypropylene composites was considered beyond the scope of this study, other than to perform a simple qualitative wetting experiment (last subsection of Results). Since, however, chlorohydrocarbon waxes are used commercially as processing aids to reduce polyolefin viscosity,¹⁷ it is reasonable to speculate that localization of the degraded chlorohydrocarbon at the interface will result in a decrease in local viscosity at the interface. This will assist wetting of the mica by the polymer and may improve alignment of mica platelets. Any improvement in alignment of the mica platelets will improve the mechanical properties of the composite in the alignment direction.^{4,18}

Finally, two technological observations should be considered. First, it is reported that precoating the mica with the chlorohydrocarbon appreciably reduces the melt-residence time necessary to produce adequate "coupling."^{6,19} This may result from the chlorohydrocarbon coating improving the kinetics of wetting of the mica by the polymer or from the elimination of the requirement that the chlorohydrocarbon migrate to the interface. Even though the undegraded chlorohydrocarbon is shown here to have little affinity for the mica surface, kinetic limitations on the rate of its removal from the surface may facilitate the production of the degraded surface layer. Second, the blending of 1% chlorohydrocarbon with PP has been shown to improve the effectiveness of conventional silane coupling agents if a peroxide initiator is incorporated into the silane formulation.⁷ The melt-residence time requirement is also reduced by this procedure, which is again consistent with a mechanism involving degradation of the chlorohydrocarbon since a peroxide initiator will markedly accelerate the rate of that degradation.

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