Assessment of Efficacy of Trivalent Lanthanum Complex as Surface Modifier of Calcium Carbonate

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ABSTRACT: A complex of trivalent lanthanum stearate with stearin (REC) was used as a surface modifier to treat calcium carbonate, and its efficacy was assessed. The measurement of the viscosity of a $CaCO_3$/liquid paraffin suspension demonstrated that REC treatment could considerably improve the dispersion of filler in nonpolar media. The FTIR spectrum analysis revealed that the REC bonded to the $CaCO_3$ surface not only by physical absorption but also by a chemical reaction. The REC could change the surface properties of $CaCO_3$, resulting in greater hydrophobicity of the surface and enhanced compatibility with nonpolar matrices. The mechanical properties and melt flow rate (MFR) examination of polypropylene (PP)/$CaCO_3$ composites showed that REC treatment remarkably enhanced the toughness and MFR of composites at higher filler loading. The fractured surface observation with SEM showed improved filler dispersion and enhanced interfacial adhesion between the filler and matrix in PP composites filled with REC-treated $CaCO_3$. All these improvements demonstrated that REC is an effective surface modifier of $CaCO_3$. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1339–1345, 2001

Key words: lanthanum stearate with stearin complex; calcium carbonate; surface modifier

INTRODUCTION

The addition of inorganic solids is one of the most common methods used in modifying the properties of polymeric materials. Calcium carbonate is one of the most widely used fillers in the plastics industry. It is usually used as an extender to reduce cost or as an additive to improve properties such as the stiffness, hardness, dimensional stability, and heat performance.[1] After the concept of utilizing rigid particles to toughen polymers was introduced,[2] enormous attention was paid to $CaCO_3$ because of its spherical shape and low price.[3–7] However, $CaCO_3$ particles, like most inorganic fillers, have polar, hydrophilic, and high free energy surfaces and are incompatible with some nonpolar, hydrophobic, and low free energy polymer matrices such as polypropylene (PP) and cannot be wetted by the molten matrix. Incompatibility is the reason for agglomeration and poor dispersion, which results in the production of voids at the poorly adherent filler–matrix interface. As a consequence, many important properties of the composites such as the toughness, elongation at break, rheological properties, and so on, are dramatically reduced.[7–9] Improved compatibility of the filler with a nonpolar polymer can be achieved by surface functionalization via such

methods as oxidation, heat and chemical treatments, vapor deposition, or coating with modifiers.[10] Among these methods, coating with modifiers is the most effective and widely used. Improved dispersion, mechanical properties, and rheological characteristics and higher filler loading have all been achieved in this way.[3–7,10–14] The modifiers for $CaCO_3$ have been extensively reported in the literature and range from inexpensive fatty acids or their derivatives and surface active agents[6,15,16] to coupling agents, including titanates,[7,9,17] aluminates,[18] zirconates,[19] borates,[18] and phosphates,[13] as well as new treatments based on polymeric unsaturated acids.[20] Some of these modifiers are offered and used commercially, while others seem to be of little or no commercial use because of their difficulty of preparation and expensive implementation overheads. Hence, development of an effective, cheap, and accessible modifier remains an essential topic in the composite material research field.

We recently found that some trivalent lanthanum complexes, especially the complexes of lanthanum stearate with certain carboxylic ester derivants, may act as surface modifiers of $CaCO_3$. They can improve the dispersion of the filler in PP, increase the toughness and flowability, and perhaps be developed into a new series of effective, cheap, handy, and environmentally friendly modifiers of $CaCO_3$.

In the present study we used the complex of lanthanum stearate with stearin (REC) to treat $CaCO_3$ and assessed its modified efficacy in compounding of $CaCO_3$ with PP.

EXPERIMENTAL

Materials

The REC used in this study was prepared in our laboratory. Briefly, the $LaCl_3$ solution was prepared by dissolving La_2O_3 (99.95%) in hydrochloric acid. Then it was mixed with the $LaCl_3$ solution with appropriate amounts of a stock sodium stearate aqueous solution, as well as a stearin ethanol solution. The mixture was stirred for 2 h, the resulting precipitate was filtered and dried at approximately 50°C under a vacuum for 4 h, and REC was obtained. The sodium stearate and stearin were purchased from Beijing Chemical Factory (Beijing, China). The $CaCO_3$ (ground) used in this study was supplied by Huatai Corporation

(Guangzhou, China); its density was 2.71 g/mL, and its average particle size was 3.6 μm. The PP employed in this work was F401, a product of Guangzhou Petrochemical Factory (Guangzhou, China); it had a melt flow rate (MFR) of 2.5 g/10 min and a density of 0.91 g/mL. Liquid paraffin with a viscosity of 25 cps at 23°C was purchased from Shanghai 3rd Reagent Factory.

$CaCO_3$ Treatment and Characterization

Treatment of $CaCO_3$ with REC was carried out in a super-speed mixer at 60–80°C by means of adding REC to the filler and mixing them for 12 min. To eliminate any effects of the mixing process on the surface properties of the filler, a sample of as-received $CaCO_3$ powder was subjected to an identical mixing schedule in the absence of REC and used as a control.

To investigate the interaction of $CaCO_3$ with REC, 5 g of $CaCO_3$ treated with 2.5% (w/w) of REC was first extracted with 250 mL of xylene at 140°C for 10 h, then extracted with 250 mL of boiled alcohol for 10 h. The insoluble fraction was filtrated and dried in a vacuum oven at 140°C to a constant weight. The FTIR spectra of pure $CaCO_3$ and treated $CaCO_3$ before and after extraction were recorded with a FTIR spectrometer (model RFX-65A) from 400 to 4000 cm^{-1}.

The hydrophobicity of $CaCO_3$ was simply estimated by a sedimentation experiment carried out as follows: equal small amounts of untreated and treated $CaCO_3$ were sprinkled onto water at room temperature, and the surface floating or depositing of the powder was observed. Furthermore, untreated and treated $CaCO_3$ with 0.5–10% of REC were added to liquid paraffin and stirred into suspensions. The viscosity of the $CaCO_3$/liquid paraffin suspension was measured with an NDJ-1 rotational viscometer.

Preparation and Characterization of PP/$CaCO_3$ Composites

The PP/$CaCO_3$ composites were prepared with a two-step procedure. The $CaCO_3$ was first mixed with PP on a two-roll mill at 170°C for 12 min, and then it was molded at 190°C and 150 kgf/cm^2 pressure into 1.0 and 4.0 mm thick sheets. The 1.0 mm thick sheets were punched to a dumbbell shape, and the tensile strength was tested on a DXLL-2500 Tensile Tester according to the standards of GB1040-86. The 4 mm thick sheets were machined into bars according to the standards of
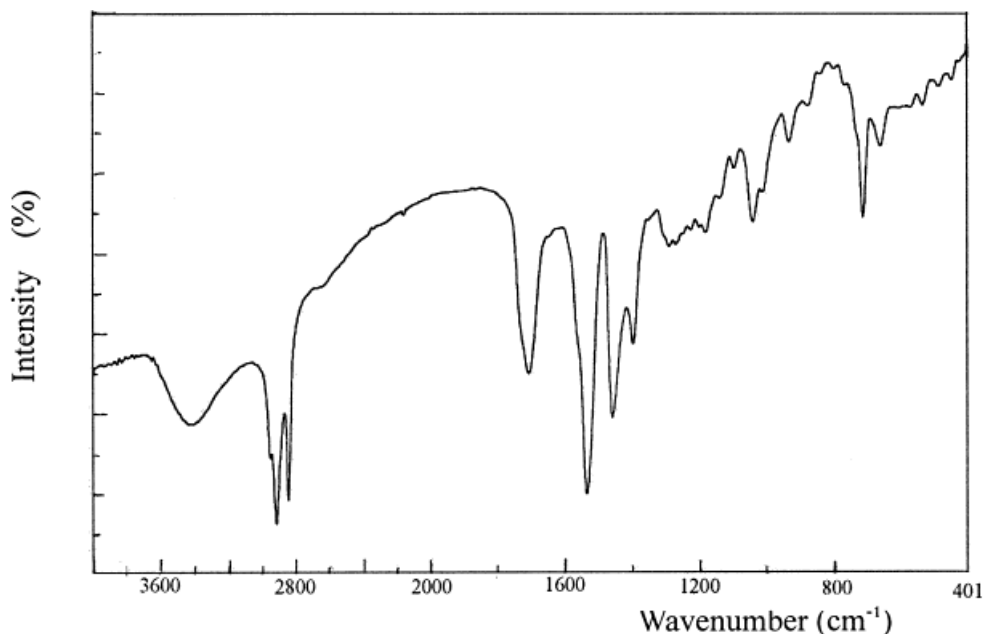
Figure 1   The IR spectrum of a complex of trivalent lanthanum stearate with stearin (REC).

GB1043-86, and the Izod notched impact strength was tested with a WPM impact tester. All tests were carried out at 23 ± 0.5°C and repeated at least 5 times. The MFR was determined according to the standards of GB3682-83.

The fresh impact-fractured surfaces were aurum sputter coated and observed under a Hitachi S-430 scanning electron microscope.

RESULTS AND DISCUSSION

FTIR Spectrum

Figure 1 is the FTIR spectrum of REC. The spectra of CaCO₃, REC-treated CaCO₃, and the REC-treated CaCO₃ that underwent the two-step extraction process in xylene and alcohol are recorded in Figure 2 as spectra 1, 2, and 3, respectively. There was a strong peak at 2919 cm⁻¹ (which is the dissymmetry flex oscillation of C—H) and a weak peak at 2850 cm⁻¹ (which is the symmetry flex oscillation of C—H) in the spectrum of REC. This revealed the existence of —CH₂— in REC. As expected, these two peaks were also present in the spectra of the treated CaCO₃. Most notably, the —CH₂— still existed in the sample in which the free REC had been removed using the two-step extraction process. As can be seen in spectrum 3, although the intensity

of the —CH₂— absorption peaks was weaker than that in spectrum 2, these two characteristic peaks could still be clearly observed and the intensity of the 2919 cm⁻¹ one was stronger than that of the 2850 cm⁻¹ one. This suggested that REC adhered and formed a nonextractable layer on the filler surface via a chemical reaction, as well as a simple physical absorption. The detailed chemical mechanisms of REC coupling with CaCO₃ are under study and will be reported in another article.

CaCO₃/Liquid Paraffin Suspensions

Unlike untreated CaCO₃, the CaCO₃ treated with REC floated on the water surface in the sedimentation experiment. This hydrophobic behavior clearly demonstrated that an attached hydrophobic substance was coated on the CaCO₃ surface and changed the highly hydrophilic CaCO₃ to hydrophobic.

Monte[21] used mineral oil to simulate poly(vinyl chloride) (PVC) melt and studied the modification of organotitanate coupling agents in PVC/CaCO₃ systems. He found that the viscosity of CaCO₃/mineral oil suspensions could be used to qualitatively assess the surface properties of the modified powder and the dispensability in low molecular weight media. In general, lower viscosity
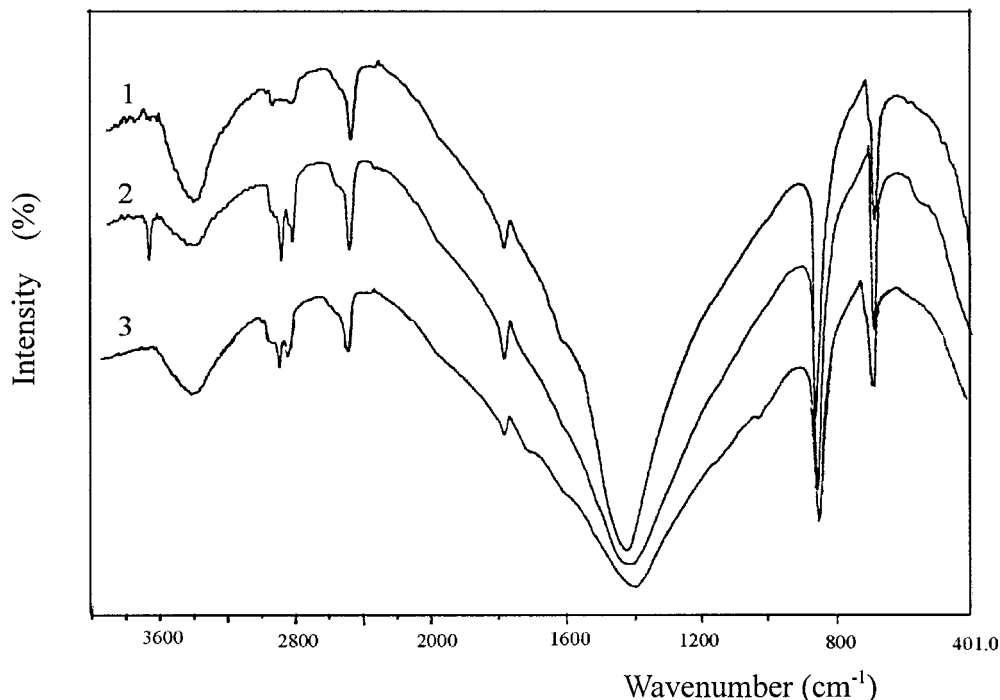
Figure 2 The IR spectra of three kinds of $CaCO_3$ samples: $CaCO_3$ (spectrum 1), REC-treated $CaCO_3$ (spectrum 2), and sample 2 after the extraction process (spectrum 3).

means better compatibility and more dispersion in the matrix.[10,21]

Similarly, the $CaCO_3$/liquid paraffin suspension can be viewed as a model for $CaCO_3$-filled PP in molten form. The effect of the REC level on the viscosity of liquid paraffin suspensions containing 75 phr (w/w) $CaCO_3$ is shown in Figure 3. The viscosity decreased as the REC level increased.
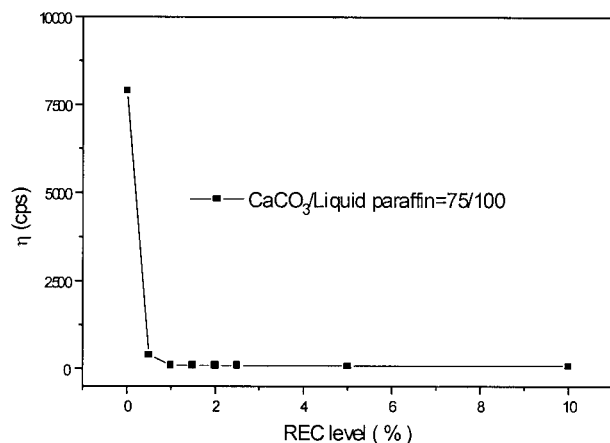

Figure 3 The effects of the complex of trivalent lanthanum stearate with stearin (REC) level on the viscosity of $CaCO_3$/liquid paraffin systems.

When the REC content ranged from 0 to 0.8%, based on the total weight of the filler, the viscosity decreased sharply from 7900 to 950 cps. However, a REC content in excess of 0.8% appeared to have no clear influence on the viscosity. A turning point was reached at a REC level of approximately 0.8%, which might be the minimum amount of REC to form monomolecular layers on the surface of $CaCO_3$. In general, the formation of a monomolecular layer is sufficient to modify a filler surface while too much modifier produces no further improvement on surface properties.[17,21,22]

The amount of REC needed to form a molecular thickness of coverage may be estimated from the surface area of $CaCO_3$ to be treated. Here the value was estimated according to the following formula[23]:

$$w_a/w_f = [6(d + D)^2\mu]/(rN_Ad^2D^3) \times 100\%$$

where w_a/w_f is the amount of REC needed to form a monomolecular layer of coverage, r is the density of $CaCO_3$, d is 2 times the bond length of an REC molecule, D is the average particle size of $CaCO_3$, μ is the molecular weight of REC, and N_A is Avogadro's number
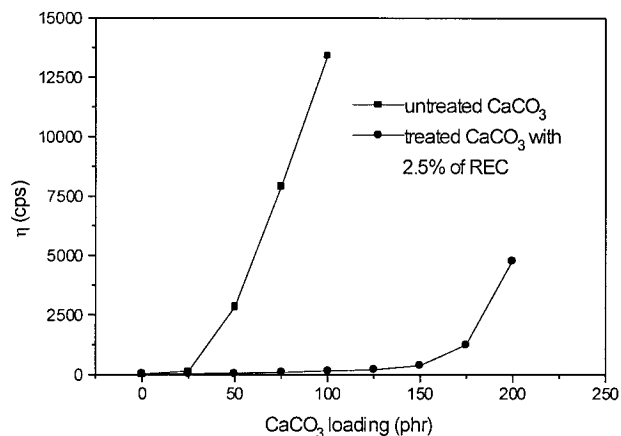
Figure 4 The effects of $CaCO_3$ loading on the viscosity of liquid paraffin systems.

The calculated amount was 1.02%, which was larger than the value of 0.8% obtained from the viscosity experiment. In fact, the REC was not a pure complex; there were some free compounds such as lanthanum stearate or stearin present in it, which had smaller μ values than that of REC. Thus, it was reasonable that the amount calculated from the formula was larger than what was in fact needed and the experimental result was in agreement with the estimated value.

The effect of filler loading on the viscosity is illustrated in Figure 4. The curve for the untreated systems shows that the viscosity increased with the amount of filler and began to rise sharply at about 30 phr of $CaCO_3$. In contrast, on the curve for suspensions containing treated $CaCO_3$ with 2.5% REC, the viscosity was very low in the filler content range from 0 to 165 phr with a dramatic increase in viscosity occurring at about 165 phr. The suspension containing 175 phr of treated filler had a viscosity similar to the suspension containing only 35 phr of untreated filler. These results suggested that REC caused a significant improvement in the surface properties of the filler.

PP/CaCO₃ Composites

The MFRs of various composites are listed in Table I. The MFR values of the composites decreased as the untreated filler loading increased. The addition of untreated $CaCO_3$ led to an increase in the melt viscosity of the systems. Conversely, REC treatment considerably reduced the melt viscosity of the composites. The composite containing 70% of $CaCO_3$ treated with 2.5% of

REC had a MFR of 2.40 g/10 min, which was equal to that of virgin PP, while the composite containing 70% of untreated $CaCO_3$ had a MFR of only 0.86 g/10 min. After REC treatment the sustainable filler loading amount in PP was much higher than that of the untreated one. The enhanced flowability and higher filler level achieved by the use of REC revealed that this modifier may have improved the dispersion and wettability of the filler in the PP matrix. These results were in agreement with the data obtained in the viscosity tests of $CaCO_3$/liquid paraffin systems.

As shown in Figure 5, the outstanding effectiveness of REC-treated $CaCO_3$ in increasing the impact strength of PP composites was demonstrated. As the filler loading was increased in the composites filled with treated $CaCO_3$ the impact strength was remarkably increased at a large range of filler content and then decreased. The maximum impact strength of the treated composites was achieved at a loading of approximately 50% (w/w). At lower REC levels the impact strength increased as the REC increased. However, a REC level that was too high caused no further increases of the impact strength, instead even decreasing it. For example, the 50/50 composite containing 0.5, 1.0, 2.5, and 5.0% of REC (based on the overall filler weight) had Izod notched impact strengths of 8.10, 8.92, 9.32, and 9.01 kg/cm cm², respectively, which were 50, 70, 80, and 70% more than virgin PP, respectively. The level of 2.5% seemed to give the maximum impact strength under the REC level adopted in present study. By contrast, in the composites filled with untreated $CaCO_3$ the impact strength slightly increased at lower filler loading of approximately no more than 30% and then de-

Table I   MFR Value of Different Composites

REC Level (%)	CaCO₃ Content (%)	MFR (g/10 min)
0	0	2.52
0	10	2.27
0	30	2.19
0	50	1.90
0	70	0.86
2.5	10	3.86
2.5	30	3.22
2.5	50	2.98
2.5	70	2.40

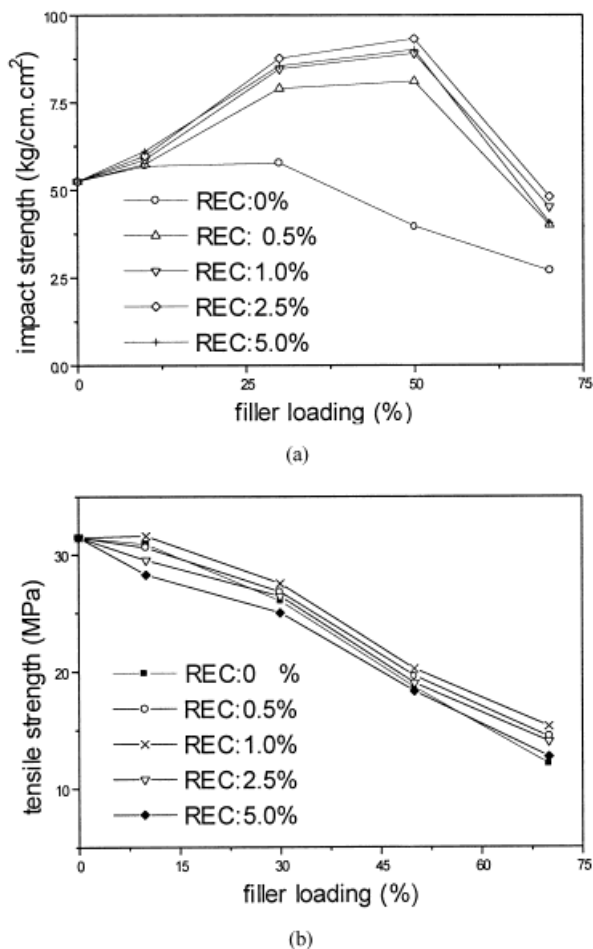The REC level is based on the overall filler weight.

(a)

(b)

Figure 5 The influence of filler on the mechanical properties of PP/CaCO$_3$: (a) the impact strength versus the filler content and (b) the tensile strength versus the filler content.

creased monotonically with a further increase of filler loading. The untreated 50/50 composite was brittle and had an impact strength of 3.92 kg/cm cm^2, only 75% that of virgin PP.

As expected, the tensile strength of composites containing treated or untreated CaCO$_3$ was lessened with the increasing of filler loading. Notably, when the REC level was no more than 2.5% of the overall filler weight, the composites filled with no less than 30% of REC-treated filler had slightly higher tensile strength than composites containing the same amount of untreated CaCO$_3$. The REC-treated CaCO$_3$ achieved a minor tensile strength reduction compared with the untreated CaCO$_3$. The tensile strengths of 50/50 composites containing 0, 0.5, 1.0, 2.5, and 5.0% of REC (based on the overall filler weight) were 18.6, 19.8, 20.2, 18.9, and 17.4 MPa, respectively. A level of 1.0%

seemed to give the optimum strength, but a REC level that was too high resulted in a negative effect on the tensile strength that was perhaps due to the lubrication effect.

The tensile strength of particulate-filled polymers is influenced by the surface interaction between the filler and matrix.[24] The gain in both the impact and tensile strengths of PP/CaCO$_3$ composites demonstrated that REC not only promoted the wettability and dispersity of CaCO$_3$ in the PP matrix, but it also provided some degree of adhesion between the treated filler and matrix. However, the unremarkable difference in tensile strength between composites with and without REC revealed that the interaction in such systems was weak. The likely reason for this was that the 18–21 carbon atoms' long nonpolar chain tails in the ligands of REC were not long enough to entangle with PP molecules. In other conditions the adhesion strength might be greatly enhanced by introducing some reactive group into the organic ligand of REC. According to Monte and Sugarman,[25] the formation of a nonextractable monolayer of modifier on the filler surface might provide the probability of achieving improved process rheology and an overall balance of good properties for filled polymers without or with less of the negative side effects that are often experienced when using extractable physical wetting agents. Our investigations in the present work support this theory to some extent.

The modification of REC in PP/CaCO$_3$ composites was also corroborated by SEM observation. Figure 6 contains photographs at different magnifications of the impact-fractured surfaces of filled PP with 50% of untreated and 50% of treated CaCO$_3$. There are obvious differences between the two groups of photographs. In the composite without REC [Fig. 6(a,b)], the particles are poorly dispersed and some large-sized aggregates exist separately in the polymer matrix. The particle surface is clean and no resin is cohered to it. The debond interface between the particle and matrix is wide open and has no plastic deformation. In contrast, in the composite containing 2.5% of REC [Fig. 6(c,d)], the particles are uniformly dispersed and combined closely with the matrix. The particle surface is resin bonded and has a large plastic deformation (which is the reason for the high toughness[26]), which shows enhanced adhesion between the filler and resin.
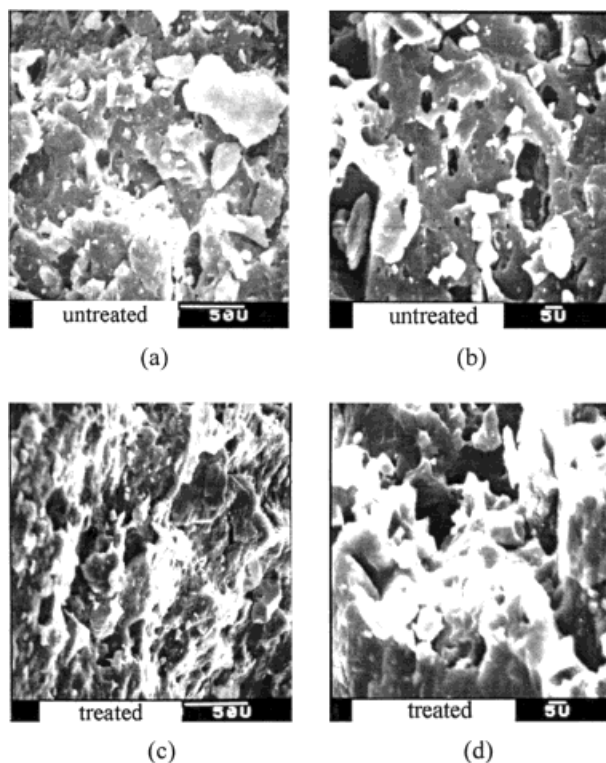
Figure 6 The fractured surface of 50/50 PP/CaCO₃ composites: (a) PP/untreated CaCO₃, (b) PP/untreated CaCO₃ at a higher magnification, (c) PP/treated CaCO₃, and (d) PP/treated CaCO₃ at a higher magnification.

CONCLUSIONS

A complex of trivalent lanthanum with stearin, REC, was used as a surface modifier to treat CaCO₃ and its efficacy was assessed. The sedimentation experiment and viscosity examination of CaCO₃/liquid paraffin suspensions showed that REC treatment changed the highly hydrophilic CaCO₃ to hydrophobic and made it more compatible and completely dispersible in a nonpolar matrix. The FTIR and SEM examinations revealed that REC was not only physically absorbed on the surface of the particles but was also chemically reacted with the CaCO₃ and formed a nonextractable organofunctional layer. Meanwhile, REC provided some degree of adhesion between the treated filler and PP matrix. As a consequence, notable improvements in the MFR and impact resistance, as well as higher filler loading and minor tensile strength reduction, were achieved in PP composites filled with REC-treated CaCO₃.

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