Structure Development and Property Changes in High-Density Polyethylene/Calcium Carbonate Blends During Pan-Milling

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Received 30 September 1998; accepted 22 April 1999

ABSTRACT: A new self-designed mechanochemical reactor, inlaid pan-mill, was used in studying high density polyethylene (HDPE) and calcium carbonate ($CaCO_3$) blends. The effects of $CaCO_3$ on the crushing and structure of HDPE matrix and the properties of HDPE/$CaCO_3$ blends were investigated. Scanning electron microscopy, Fourier transformed IR spectroscopy, dynamical mechanical testing analysis, capillary rheometer, and Instron material testing system were used to characterize the structure of HDPE and evaluate the properties of HDPE/$CaCO_3$ blends. The introduction of calcium carbonate during milling improved milling efficiency, and time needed for each cycle was greatly reduced. Oxygen-containing groups on HDPE chains, which were produced during milling, increased interfacial interactions and improved the dispersion and distribution of calcium carbonate particles in HDPE/$CaCO_3$ blends. Rheological, thermal, and mechanical properties were also improved. The elongation at break of milled blends with high concentrations of calcium carbonate was significantly higher than that of unmilled blends. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1459–1464, 1999

Key words: high-density polyethylene; pan-milling; blends; calcium carbonate; properties

INTRODUCTION

Adhesion between polymers and fillers plays an important role in the performance of plastic composites. Fillers with hydrophilicity or polarity and polymers with polar groups could facilitate interfacial bonding. Therefore, whether or not polymer molecules bear polarity is an important factor in determining the reinforcement effect in plastic composites. In order to achieve good interfacial adhesion between polyolefins and fillers, it is necessary for this kind of plastics to bear polar groups before a good affinity with fillers can be brought about.[1]

High-density polyethylene (HDPE) is a nonpolar, hydrophobic polymer, while calcium carbonate ($CaCO_3$) is a polar and hydrophilic filler. To avoid reduction in mechanical properties of HDPE/$CaCO_3$, adhesion between HDPE matrix and fillers has to be enhanced. Traditionally, this can be achieved by coupling agent treatment of fillers[2,3]; however, toughness improvement is often accompanied by the deterioration of tensile strength because of the plasticizing effect of coupling agents. Another possible way is to use chemically modified HDPE.[4]

Stress-induced reaction, a field commonly called mechanochemistry, must be considered when handling high molecular weight polymers.

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Contract grant sponsor: National Science Foundation of China and State Education Commission of China.

Journal of Applied Polymer Science, Vol. 74, 1459–1464 (1999)

CCC 0021-8995/99/061459-06

With increased molecular weight, the conversion of mechanical energy applied to a polymer is shifted increasingly from viscous to elastic, i.e., from thermal dissipation toward molecular energy storage. This energy storage leads first to changes in supermolecular structures, then to molecular bond rotations, chain orientation and elongation, bond bending and extension, and ultimately to the rupture of chemical bonds. Macroradicals are generated and can be terminated by oxygen in air, leading to the introduction of polar groups onto polymer chains.[5] Introduction of polar groups can assist in the enhancement of the adhesion between a nonpolar polymer and a polar filler.

A new type of mechanochemical reactor, inlaid pan-mill,[6] has recently been designed on the basis of Chinese stone pan-mill. It has been reported that the inlaid pan-mill is effective in pulverizing not only brittle materials such as polystyrene (PS) but also ductile materials such as HDPE.[7–9] In another report,[10] Wang et al. ground PS and TiO_2 together in a pan-mill, and found that the ground blends had better impact, rheological, and thermal properties than simple blends. They concluded that TiO_2 contributed to the crushing of PS when they are ground together.

In this paper, an inlaid pan-mill was used in studying HDPE/$CaCO_3$ blends. The effects of $CaCO_3$ fillers on the crushing and structure of HDPE matrix and the properties of HDPE/$CaCO_3$ blends were investigated.

EXPERIMENTAL

Materials

The HDPE used was HDPE6098 with a melt flow index of 0.1 dg/min and a density of 0.948 g/cm^3, supplied by Qilu Petrochemical Company. Commercial precipitated $CaCO_3$, a product of Sichuan Mianzhu Chemical Engineering Factory with a particle size of 300 mesh, was used as received.

Pan-Milling

An inlaid pan-mill type mechanochemical reactor,[6] with water-cooling and a rotating speed of 25 rpm, was used. HDPE was milled alone or together with $CaCO_3$ at different concentrations for 10 times (cycles). The process from the beginning of feeding to the end of material discharge was considered as one cycle.

Property Testing

Milled HDPE or HDPE/$CaCO_3$ blends were plasticated in a Brabender W50H mixer at 180°C and 40 rpm for 10 min, followed by compression molding at 190°C. Tensile tests were performed on a Instron 4302 Materials Testing System at a rate of 50 mm/min according to GB1040-79. DMTA was performed on a Rheometric Scientific MK III type analyzer. Rheological measurements were taken on a Goffert 2002 capillary rheometer, Bagley correction was not done.

Characterization

HDPE samples were compression molded into thin films with a thickness of about 100 μm for Fourier transform IR (FTIR) characterization. For milled HDPE/$CaCO_3$ blends, $CaCO_3$ was removed before sample preparation by dissolving in dilute hydrochloric acid. Nicolet 170X Fourier transformed IR spectrometer were used.

Milled and unmilled HDPE/$CaCO_3$ blends were plasticated in a Brabender W50H mixer at 180°C and 40 rpm for 10 min, followed by compression molding at 190°C. The blend samples were then fractured under liquid nitrogen, coated with gold, and observed on a Hitachi 8520 scanning electron microscope. Scanning electron microscopy was also performed for tensile fractured samples.

RESULTS AND DISCUSSION

Effect of Pan-milling with $CaCO_3$ on Crushing of HDPE Matrix

Figure 1 shows the influence of $CaCO_3$ concentration on the average particle size of HDPE when HDPE was milled together with $CaCO_3$ for 10 times. HDPE particles reduced to much smaller sizes after milling compared to an average particle size of 3.9 mm for unmilled HDPE. For HDPE milled with $CaCO_3$, average particle size decreased with increasing $CaCO_3$ concentration and reached about 0.5 mm at a $CaCO_3$ concentration of 30 wt %. These results are similar to those obtained in the milling of brittle PS with TiO_2.[10]

Since HDPE is a ductile material, it cannot be easily crushed as brittle PS. During the milling process, HDPE pellets were firstly pressed into thick pieces, then into thin pieces, and lastly into very small pieces. Between the 5th and 8th milling cycle, the volume of the materials increased

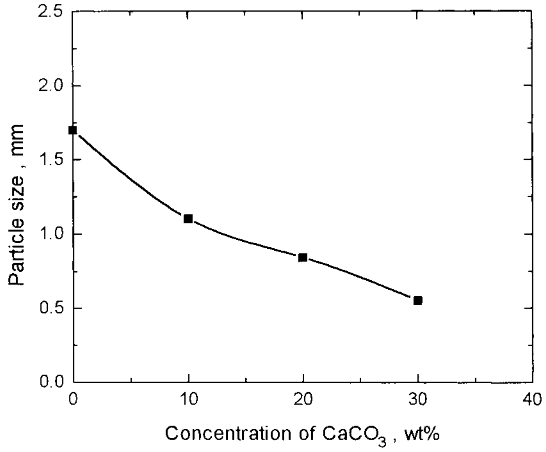


Figure 1 Average particle size of milled HDPE versus concentration of CaCO$_3$ in blends. (Average particle size of unmilled HDPE was about 3.9 mm.)

greatly, resulting in difficulty for inletting and outletting of materials. With the introduction of CaCO$_3$, the time needed for each milling cycle was reduced greatly, as shown in Table I. The time needed for the fifth cycle of milling was reduced from 185 min for milling HDPE alone to 20 min for milling HDPE with 30 wt % of CaCO$_3$. Therefore, milling of HDPE together with fillers can greatly improve the milling efficiency.

Effect of Pan-Milling with CaCO$_3$ on HDPE Structures

FTIR spectra of unmilled and milled HDPE are shown in Figure 2. The intensity of carbonyl absorbance of milled HDPE is stronger than that of unmilled HDPE, indicating that reactions occurred between oxygen in air and free radicals generated as a result of mechanochemical degradation of HDPE under pan-mill stress. When milled together with CaCO$_3$, the intensity of carbonyl absorbance is even stronger, indicating that milling with CaCO$_3$ had a further effect on the structural change of HDPE under stress. Introduction of the polar groups containing oxygen would facilitate interfacial interactions between HDPE and CaCO$_3$, and thus enhance the interfacial adhesion.

Table I Time Period of Milling of HDPE/CaCO$_3$ for Each Cycle (min)

Times of Milling	5th	6th	7th	8th
HDPE	185	90	50	35
HDPE/CaCO$_3$ (10%)	50	50	40	27
HDPE/CaCO$_3$ (20%)	35	30	25	25
HDPE/CaCO$_3$ (30%)	20	20	20	20

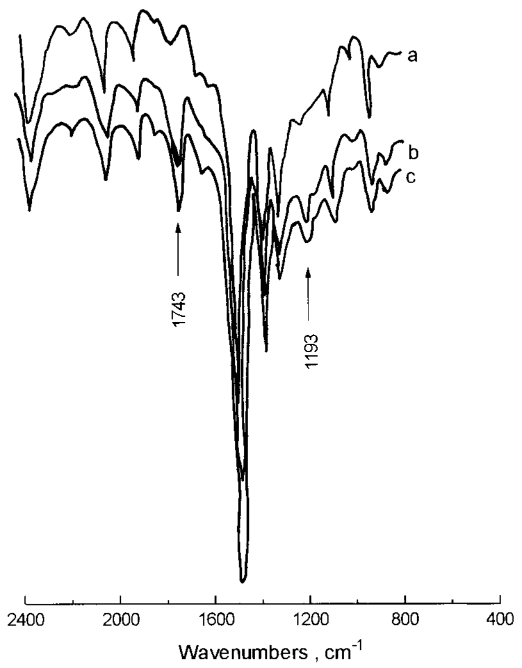


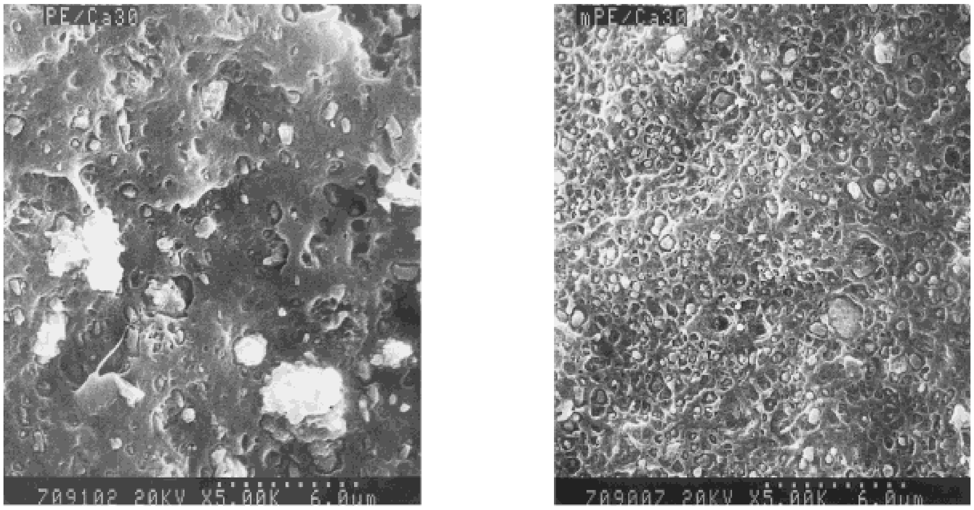
Figure 2 FTIR spectra of (a) unmilled HDPE, (b) milled HDPE, and (c) HDPE milled with 30 wt % of CaCO$_3$.

Effect of Pan-Milling on Blend Morphology

The effect of milling with CaCO$_3$ on blend morphology is shown in Figure 3. It can be seen from sample surfaces fractured in liquid nitrogen that the agglomeration of CaCO$_3$ particles was reduced significantly and distribution of CaCO$_3$ particles was more uniform in the pan-milled blends than that in unmilled blends. Scanning electron micrographs of tensile fractured samples are shown in Figure 4. The fractured surface of unmilled HDPE/CaCO$_3$ samples [Fig. 4(a)] was smooth with coarse agglomeration of CaCO$_3$ particles, indicating brittle failure. The fractured surface of milled HDPE/CaCO$_3$ samples [Fig. 4(b)] showed regular fine fibrous structures, indicating strong interfacial interaction between HDPE and CaCO$_3$ fillers.

Effect of Pan-Milling on Dynamic Mechanical Properties of Blends

The dynamic mechanical spectra of HDPE/CaCO$_3$ blends are shown in Figure 5. It can be seen that



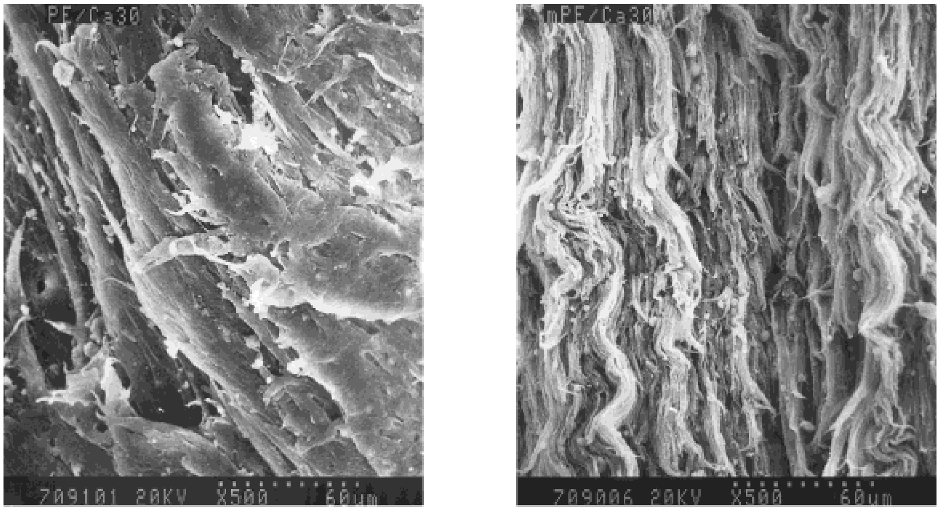
(a) Unmilled blends (b) Milled blends

Figure 3 SEM micrographs of HDPE/$CaCO_3$ (30%) blends fractured under liquid nitrogen: (a) unmilled blends and (b) milled blends.

for milled blends, the temperature at which γ relaxation occurred was higher than that for unmilled blends. This may be due to the limitation of molecular movement resulted from stronger interfacial interaction between HDPE and $CaCO_3$ fillers in milled systems.

Effect of Pan-Milling on Rheological Properties of Blends

Figure 6 shows the apparent shear viscosity curves of HDPE/$CaCO_3$ blends. The apparent shear viscosity for milled HDPE/$CaCO_3$ blends is



(a) Unmilled blends (b) Milled blends

Figure 4 SEM micrographs of tensile fractured surfaces of HDPE/$CaCO_3$ (30%) blends: (a) unmilled blends and (b) milled blends.

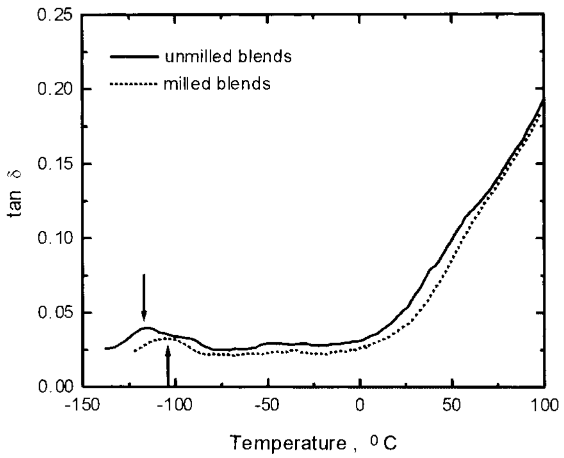


Figure 5 DMTA curves of unmilled and milled HDPE/CaCO$_3$ (30%) blends.

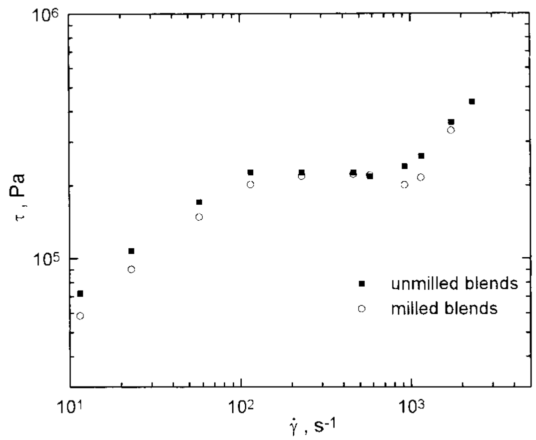


Figure 7 Apparent shear stress versus apparent shear rate curves of unmilled and milled HDPE/CaCO$_3$ (30%) blends (220°C).

significantly lower than that of unmilled blends. Similar results were obtained for apparent shear stress, as shown in Figure 7. These indicate that pan milling can improve the processing properties of HDPE/CaCO$_3$ blends.

Effect of Pan-Milling on Mechanical Properties of Blends

The tensile properties of various HDPE/CaCO$_3$ blends were shown in Figures 8 and 9. While tensile strength increased slightly, modulus of milled blends showed a minor reduction compared to that of unmilled blends (Fig. 8). Elongation at the break of milled HDPE/CaCO$_3$ blends was greatly improved over that of unmilled HDPE/CaCO$_3$ blends, particularly when CaCO$_3$ concentration was high (Fig. 9). At a CaCO$_3$ concentration of 30%, the elongation at the break of milled HDPE/CaCO$_3$ blends was 18-fold higher over that of unmilled HDPE/CaCO$_3$ blends. This is probably because of the improved interfacial interaction between HDPE and the filler as shown in earlier evidences.

CONCLUSIONS

1. Milling of HDPE in the presence of CaCO$_3$ greatly reduced the time required for each milling cycle and the particle size of HDPE during pan-milling.
2. Oxygen-containing groups introduced onto

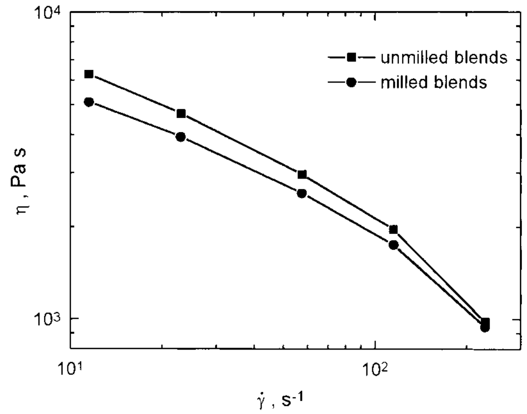


Figure 6 Apparent shear viscosity versus apparent shear rate curves of unmilled and milled HDPE/CaCO$_3$ (30%) blends (220°C).

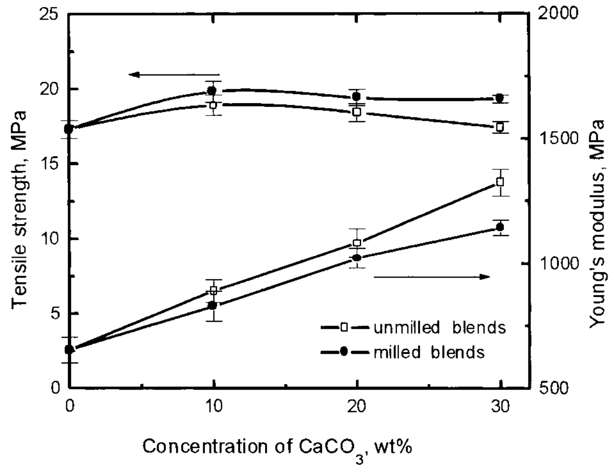


Figure 8 Tensile strength and Young's modulus of unmilled and milled HDPE/CaCO$_3$ blends.

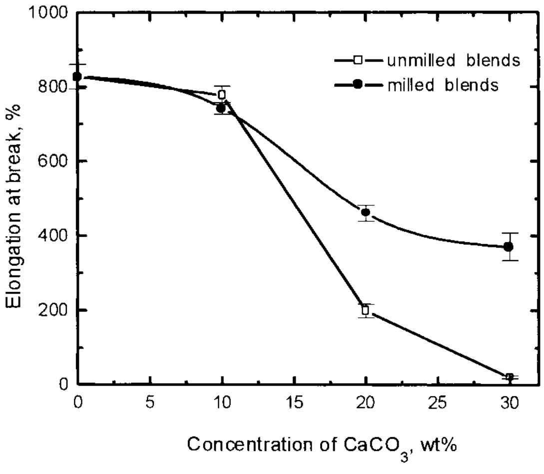


Figure 9 Elongation at the break of unmilled and milled HDPE/$CaCO_3$ blends.

HDPE chains during pan-milling increased interfacial interactions and improved the dispersion and distribution of calcium carbonate particles in HDPE/$CaCO_3$ blends.

3. Rheological, thermal and mechanical properties are improved. The elongation at break of HDPE/$CaCO_3$ blends with high concentrations of calcium carbonate are much higher than that of unmilled blends.

The author acknowledges the financial support of this project by the National Science Foundation of China and the State Education Commission of China.

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