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Compatible Polyethylene/Polyvinyl Chloride Particle Hybrids Prepared by *in-situ* Polymerization

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NOTE

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Polyethylene/polyvinyl chloride (PE/PVC) hybrids were successfully prepared by a polymerization-filling method. The catalyst for ethylene polymerization was supported on PVC particles, and ethylene was then polymerized in-situ on the surface of the activated PVC. PVC particles could be well segmented and dispersed during in-situ polymerization, and the prepared hybrids had an additional tangent peak between the glass transitions of polyethylene and PVC, indicating the formation of a compatible interlayer between nascent polyethylene and PVC during polymerization.

Keywords hybrid, *in-situ* polymerization, compatibility, immiscible polymers

Introduction

Polymer hybrids are of both commercial and theoretical importance because they offer properties or a balance of properties not available in a single polymer. A compatible hybrid has better properties than the average of its polymeric components. The morphology and interface conditions play an important role in the performance of the hybrids. However, most polymer pairs are immiscible and will form large dispersed domains with poor interface adhesion. A third polymeric ingredient, which is compatible with both polymer components, is often introduced into their physical mixing to improve compatibility. Other methods include reactive blending and the addition of monomeric

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Address correspondence to Joong-Hee Lee, Polymer BIN Fusion Research Team, Department of Polymer Science and Technology, Chonbuk National University, Duckjin-dong, 1Ga 664-14, Jeonju, Jeonbuk, South Korea. Tel.: 82-63-270-2342; Fax: 82-63-270-2341; E-mail: jhl@chonbuk.ac.kr reactants (1–3). However, it is still difficult to manufacture practical hybrids of polymers with large differences in polarity and crystallinity, for example the hybrid of polyethylene (PE) and polyvinyl chloride (PVC).

Polymerization-filling is a particular method (4–7) which introduces a second phase into a polyolefin matrix during the polymerization of olefin monomers. A Ziegler-Natta catalyst system for olefin polymerization is deposited on the surfaces of supporting particles, and polyolefin-particle hybrids with varied filling degrees and properties can be prepared by regulating the polymerization conditions. In our previous work, polyethylene/kaolin composites were prepared and systematically investigated. The composites were characterized by their excellent properties, especially improved rheological and anti-wear behaviors (8, 9). Despite the large polarity difference, the composites had a homogeneous dispersion of kaolin particles and a strong interfacial interaction. The interface adhesion between polyethylene and kaolin particles could not be destroyed by solvent extraction, and the glass transition temperature of the polyethylene was noticeably influenced by the presence of kaolin. The *in-situ* polymerization of ethylene monomer on the surface of kaolin overcame the difference in polarity, which suggested that polymerization-filling was also a suitable method for manufacturing hybrids of immiscible polymers. Here, we present the preparation of PE/PVC hybrids by *in-situ* polymerization and a comparison of their structures and properties with those of counterparts prepared by mechanical melt mixing.

Experimental

Preparation of PE/PVCH Hybrids by in-situ Polymerization

Heptane (dried over 4A molecular sieves) was used as the solvent for both the activation of PVC and the polymerization of ethylene. Polymerization grade ethylene gas, provided by Beijing Yanshan Petrochemical Corp., was used as monomer without further purification. All operations were carried out under a dry nitrogen atmosphere.

Activation of PVC Particles

PVC (5 g; XJ-4 type, Tianjin Chemical Co., China) was dried at 50°C for 4 h to remove moisture and then swelled in a mixture of 20 ml chlorobenzene and 80 ml heptane at 80°C for 2 h. $TiCl_4$ (30 ml) was added dropwise into the solution, and stirring was maintained for 24 h. After filtration and thorough washing with hexane, the residue was dried in vacuum to give activated PVC particles. The concentration of Ti in the activated PVC particles was 1.4×10^{-5} mol/g, as measured by spectrophotometer.

Ethylene Polymerization on the Surface of PVC

The polymerization of ethylene was carried out in a 500 ml three-necked flask at 60°C under a total pressure of 1.067×10^5 Pa, with $AlEt_2Cl/MgPh_2$ as a co-catalyst (molar ratios: $Al/Ti = 30$, $Al/Mg = 2$). A prescribed amount of activated PVC in heptane (100 ml) was added to the flask which had been flushed with ethylene. The polymerization started following the injection of the co-catalyst. The polymerization was terminated using anhydrous alcohol after a certain polymerization time. Samples with different compositions were obtained by regulating the duration of polymerization.

Preparation of PE/PVC Hybrids by Melt Mixing

PVC powders were high-speed kneaded with adequate amounts of thermal stabilizers (tribasic lead sulfate, dibasic lead phosphate, lead stearate, and stearic acid) and then melt mixed with HDPE (5000s type, Beijing Yanshan Petrochemical Corp., China) at 180°C using a Haake mixer. The blends were sheeted in a flat high press for further measurements.

X-Ray Photo-electron Spectrum of Activated PVC

The electron binding energies of titanium and chlorine elements in the activated PVC were measured with an ES-300 spectrometer (UK).

Scanning Electron Microscopy Investigation

The PE/PVC hybrids prepared by polymerization-filling and melt mixing were cryo-fractured using liquid nitrogen. After gold-layer sputtering, we studied the morphology of the fractured surfaces, as well as the nascent PE/PVC hybrid particles, using a Hitachi Jeol scanning electron microscope.

Mechanical Properties

Dynamic mechanical measurements were carried out with a Perkin-Elmer DMA-7 using a heating rate of 5°C/min and a frequency of 1 Hz. The specimens were rectangular bars (20 mm × 3 mm × 1 mm) cut from the compression molded samples.

Results and Discussions

In-situ Polymerization

During the adsorption of $TiCl_4$, the PVC particles changed color from white to brown. The activated PVC contained 1.4×10^{-5} mol/g titanium after rinsing with hexane, indicating

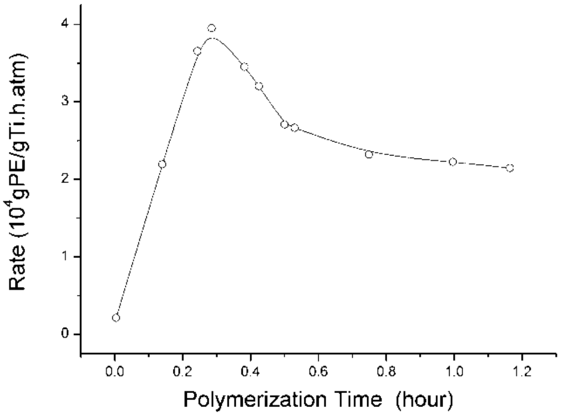

Figure 1. Kinetic curves of ethylene polymerization with activated PVC.

a firm anchoring of titanium onto the surface of the PVC. X-ray photoelectron spectroscopy (XPS) also revealed a 1ev decrease in the binding energy of the 2p electron of chlorine after PVC was activated with $TiCl_4$.

The kinetic behavior of the activated PVC during ethylene polymerization is shown in Figure 1. The activated PVC exhibited an appropriate catalytic ability during a polymerization reaction of more than 1 h. The nascent particles prepared with different polymerization durations had coarse surfaces similar to those of the activated PVC, while their sizes increased with the polymerization time. The similarity between the shapes of the activated PVC and nascent particles is a result of a "copying" phenomenon in polyolefin synthesis using a supported catalyst. As shown in Figure 2, the ethylene that polymerized onto the surface of the activated PVC and the PVC particles were surrounded by the polyethylene layers formed *in-situ*.

Dispersion of PVC and Interface Adhesion

In our previous study (10, 11) on polyethylene/kaolin composites, the aggregates of kaolin were broken up and dispersed by the polyethylene molecular chains during *in-situ*

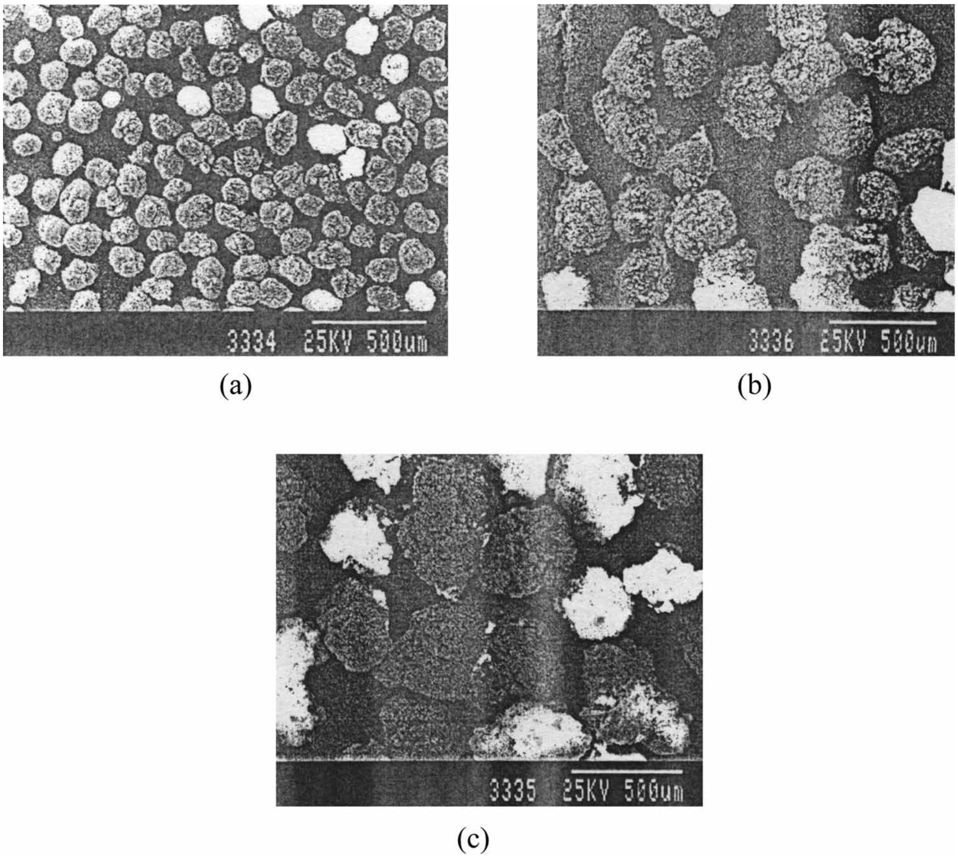

Figure 2. SEM photographs of (a) activated PVC and PE/PVC hybrids prepared with different polymerization durations: (b) 30 min and (c) 70 min.

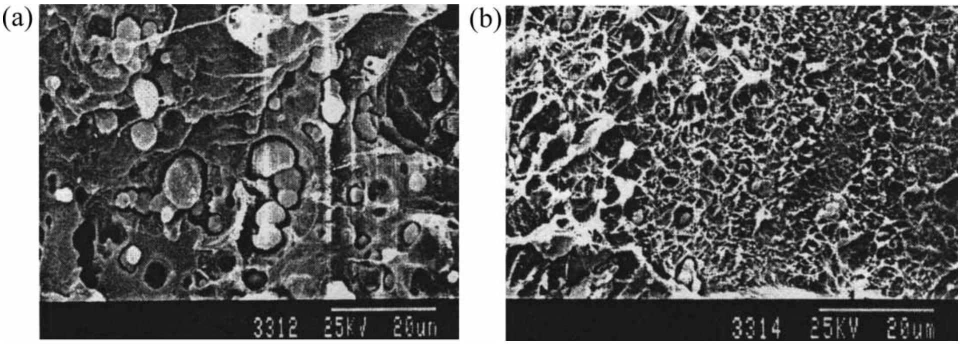

Figure 3. SEM photographs of cryo-fractured surfaces of PE/PVC hybrids prepared with (a) melt mixing and (b) *in-situ* polymerization.

polymerization. Here, the activated PVC particles are in fact agglomerates of primary PVC particles, which can also be separated from each other by the growing polyethylene molecular chains. In Figure 3, the SEM images of the cryo-fractured surfaces of the hybrids revealed the dispersion of PVC in the polyethylene matrix. In PE/PVC hybrids prepared with polymerization-filling, the PVC was dispersed in small particles about 1 micron in size; the hybrids prepared by melt mixing had dispersed PVC particles ranging from 1 to 10 microns in size. A series of SEM images of hybrids with various PVC dispersion contents (not shown), having been prepared at different polymerization durations, indicated an effective segmentation and dispersion of the original PVC particles during the polymerization-filling. By contrast, the counterparts prepared by melt-mixing contained an almost unchanged dispersion of PVC particles.

The dynamic mechanical analysis (DMA) curves in Figure 4 show a new tangent peak for the PE/PVC hybrid prepared by *in-situ* polymerization. The hybrid counterpart prepared

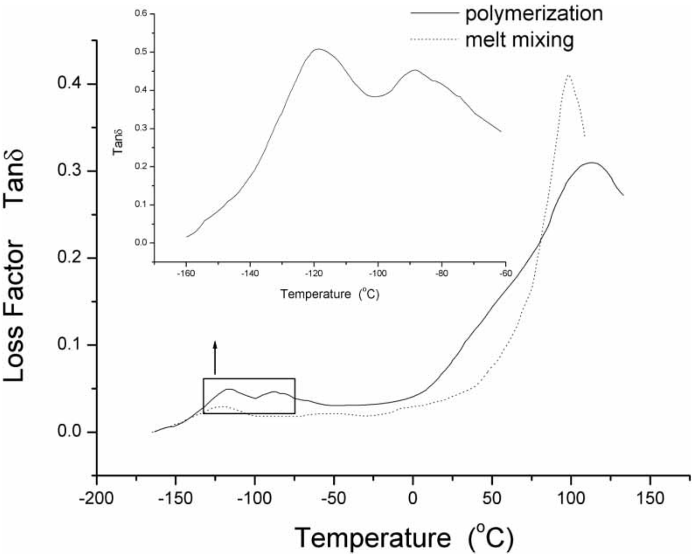

Figure 4. DMA loss factor of PE/PVC hybrids as the function of temperature.

by melt mixing had two peaks, corresponding to the glass transition (T_g) of polyethylene at low temperature and the (T_g) of PVC at high temperature, respectively. The hybrids with the same composition prepared by *in-situ* polymerization had a broader PVC (T_g) region and an additional peak at −84.5°C. As is well accepted, the polymeric hybrid should be regarded as a mixture of polymeric solutions with various compositions, so the broader (T_g) region revealed a better miscibility between polyethylene and PVC in the hybrid prepared by polymerization-filling. The new peak between the (T_g) of polyethylene and PVC represents the compatible interface layer formed during polymerization. The *in-situ* synthesis of ethylene on the surface of PVC provided a good interface adhesion between the nascent polyethylene and the activated PVC, and this interlayer acted as the third composition of the hybrid, exhibiting a quite different molecular mobility from polyethylene and PVC. The hybrid with PE/PVC = 79.6/20.4 also had an additional peak at about −40°C. The higher temperature clearly indicated the influence of the higher PVC content in the interlayer.

The formation mechanism of the compatible interlayer, and whether it is a graft structure from the chemical linkage between polyethylene and PVC or a simple molecular homogeneous layer owing to *in-situ* polymerization overcoming the polarity difference, will be further investigated, as well as its influence on the mechanical properties of the hybrids.

Conclusions

This paper presents a promising method for preparing compatible PE/PVC hybrids by the *in-situ* polymerization of ethylene on the surface of PVC. PVC particles could be well segmented and dispersed during the *in-situ* polymerization. The presence of a new tangent peak in the DMA curves indicated the formation of a compatible interlayer between the nascent polyethylene and the PVC.

Acknowledgments

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