PREPARATION OF ORGANICALLY MODIFIED CACO$_3$ AND ITS USE IN THE MANUFACTURE OF POLYPROPYLENE COMPOSITES

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Abstract

The most common filler used in plastics is CaCO$_3$ due to its abundance and low cost. Usually dispersion of particles in a polymer is difficult due to strong tendency of the fine particles to agglomerate. Surface treatment of fillers is a way to modify the interfacial adhesion.
In this work, various organic modification agents for CaCO$_3$ are used to provide a hydrophobic surface and, to increase the interfacial adhesion. For this purpose, stearic acid, vinyl acetate, maleic anhydride, paraffin, EVA are used in different combinations and ratios. CaCO$_3$ particles are modified with different ratios of coatings. Appropriate samples are selected for blending and molding with PP. Thermal analysis measurements, surface tension analysis and mechanical test techniques were used to determine the best coating agent.
Results indicate that modification of inorganic CaCO$_3$ particles with EVA is a successful way to achieve better dispersion. This enables usage of more inorganic filler in PP without sacrificing the mechanical properties.

1   Introduction

Polypropylene (PP) has been widely used as an engineering thermoplastic and has a variety of applications including packaging, textiles, stationery, containers laboratory equipments and automotive components. PP has good resistance to many chemical solvents, bases and acids, and fatigue. It is reasonably economical, easy to process, and appropriate to treat with conventional fillers.

Calcium carbonate (CaCO$_3$) is the most popular filler used in PP. It is inexpensive and can be used at high loadings.[1,2] Polypropylene compounds usually are filled with CaCO$_3$ to increase rigidity. The surface of CaCO$_3$ filler is usually treated with fatty acids such as stearic acid to modify the filler surface to become hydrophobic for improving dispersibility of the polar filler when incorporated into nonpolar PP melts, for any improvement in mechanical properties of the composite structure. [3]

In the study, we aimed to increase the interfacial adhesion between PP and CaCO$_3$ by various organic modification for CaCO$_3$ prior to its use in the composite structure. Influence of the surface coating with various polymeric coating materials on the surface and morphological properties as well as mechanical, and thermal properties of the PP composites was investigated.   Paraffin, ethylene-vinylacetate (EVA), styrene-maleic anhydride (S-MA), styrene-vinylacetate (S-VAc) polymers and co-polymers were used as surface modifier or compatibilizer for CaCO$_3$. To improve the compatibility between filler CaCO$_3$ and PP matrix,

calcium carbonate particles were coated with a thin layer of the polymers from their dilute solution and then incorporated into the PP matrix where the filler amounts were taken as 30, 40 and 50 wt-% in those composites.

Surface coating of $CaCO_3$ particles and its uniformity were characterized by attenuated total reflectance-Fourier transform infrared spectroscopy (FTIR-ATR) and scanning electron microscopy (SEM). Effect of the type of coating materials on mechanical properties were determined by stress-strain tests, dynamic mechanical analysis (DMA), and the thermal properties of the samples were tested by thermogravimetry (TG). The change of surface free energy of composites with type of coating materials was determined by contact angle measurements, and the surface free energy components of the composites were determined using van Oss-Good methodology. FT-IR, TGA and SEM measurements revealed that the $CaCO_3$ particles were uniformly covered by coating materials and had a good dispersion in matrix. In conformity with SEM observations, the DMA and stres-strain tests revealed the EVA coated $CaCO_3$ particles showed better dispersibility in PP matrix resulting in better mechanical properties and higher tensile modulus. It was found that the surface free energy of the PP matrices varied with the type of coating materials and filler content.

Results indicate that modification of inorganic $CaCO_3$ particles in organic polymers is a successful way to achieve better dispersion in PP matrix. This enables the usage of more inorganic filler in polymers without sacrificing the mechanical properties, which gives an advantage gained in price, volume and performance relations, in addition to the decrease in usage of non-renewable, non-biodegradable petroleum based polymers such as PP in their composites.

2 **Materials and testing methods**

2.1 Materials

The raw materials used for this work are as follows. The PP homopolymer, used a s matrix phase in this study, was Polypro HJ4012 in a pellet form (Yuhwa Korea Pertochemical). Calcium carbonate was generously supplied by Novaplast Ltd., and used as inorganic filler for polymer composites. PMMA was supplied by Rainbow Polymers (India), and used as coating agent of CaCO3. EVA was supplied by Polisan Turkey, as the grade Evatane, and used as coating agent of CaCO3. Paraffin in block form was purchased from merck. Vinyl acetate (VAc), maleic anhydride (MA) and Styrene (S) monomers were purchased from Merck, and used as coating agent raw materials of CaCO3. Styren-Vinyl acetate and Styrene-Maleic anhydride copolymers were synthesized.

2.2 Copolymer Synthesis

Copolymers having Styrene/Maleic anhydride and Styrene/ Vinyl Acetate ratios of ½ were prepared.

2.3 Surface Coatings of CaCO3 with Polymers

All the coatings were applied for 100 g CaCO3 and 0.25 g coating agent.

2.4 Blend Preparation

The blends were prepared in a Thermo Haake Polylab OS model mixer at a temperature of 200°C. Test samples were prepared by compression molding in a temperature and pressure controlled hot-press. Test specimens were compressed between 2 mm thick flat sheets for 30 seconds holding time.

2.5 Mechanical Characterization

Effect of the coating materials on PP-$CaCO_3$ composites were evaluated through the mechanical properties. Mechanical properties such as yield stress, tensile stress, elastic modulus, storage modulus, loss modulus and phase angles were determined by stress-strain tests and DMA. Glass transition temperatures and miscibility of the combinations were evaluated with a Perkin-Elmer Pyris Diamond DMA. Storage modulus (E'), loss modulus (E'')

and loss tangent (tanδ) of each sample were recorded in multi-frequency mode at at 0.5, 1.0, 2.0, 5.0 and 10.0 Hz.

Dynamic mechanical analysis allows us to examine polymer/filler miscibility in polymer blends and also determine the complex (dynamic) modulus and the glass transition temperatures (Tg) of polymers. The complex modulus is composed of the storage modulus E´ and the loss modulus E´´. These are dynamic elastic characteristics results of DMA add information about the behaviour of the blends and phase morphology.

Figure 1 shows the plot of the storage modulus versus temperature for pure PP and PP composites at different polymer/filler ratios (30 wt-% uncoated CaCO3, 30 wt-% EVA coated CaCO3, 30 wt-% Paraffin coated CaCO3, 30 wt-% S-MA coated CaCO3, 30 wt-% S-VAc coated CaCO3). The value of storage modulus signifies the stiffness of the material. The effects of temperature and coating material on the loss modulus, E" of the samples at a frequency of 2 Hz are given in the Figure 2. The loss modulus measures the energy dissipated as heat. It is seen from Figures 1 and 2 that according to the E' and E'', at each temperature, coated composites have higher tensile storage modulus and tensile loss modulus than that of uncoated composites. That means coated CaCO3 brings in higher elastic response to deformation by applied force.

Generally for incompatible system, the tanδ versus temperature curve shows two damping peaks corresponding to the glass transition temperatures of individual polymers [4]. When blend omponents are compatible, a single peak is found for the combined processes [5]. Figure 3 shows the variation of loss tangent (tanδ) with temperature for the pure and composite PP. As the temperature increases, damping goes through a maximum near Tg in the transition region, and then a minimum in the rubbery region. The damping is low below Tg because thermal energy is insufficient to cause rotational and transnational motions of the segments [6]. As a result of this, the chain segments are frozen in. So, below Tg, the molecular slip resulting in viscous flow is low. Above Tg also the damping is low because molecular segments are very free to move about and there is little resistance for their flow.
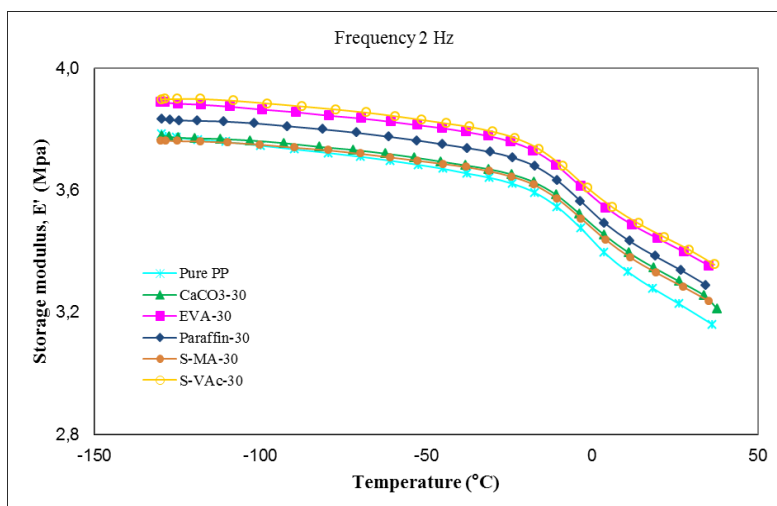
Figure 1 Storage modulus (E´) curves as function of temperature for PP composites at a frequency of 2 Hz.

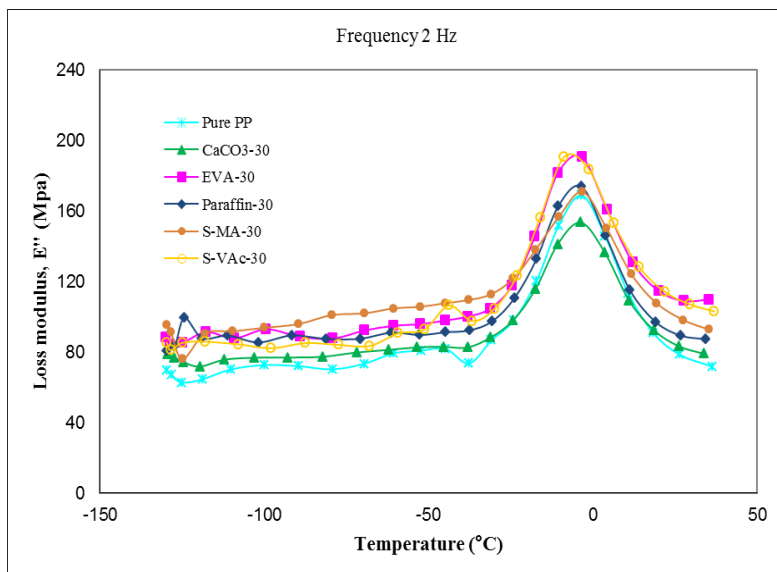**Figure 3** *Loss modulus (E´´) curves as function of temperature for PP composites at a frequency of 2 Hz.*
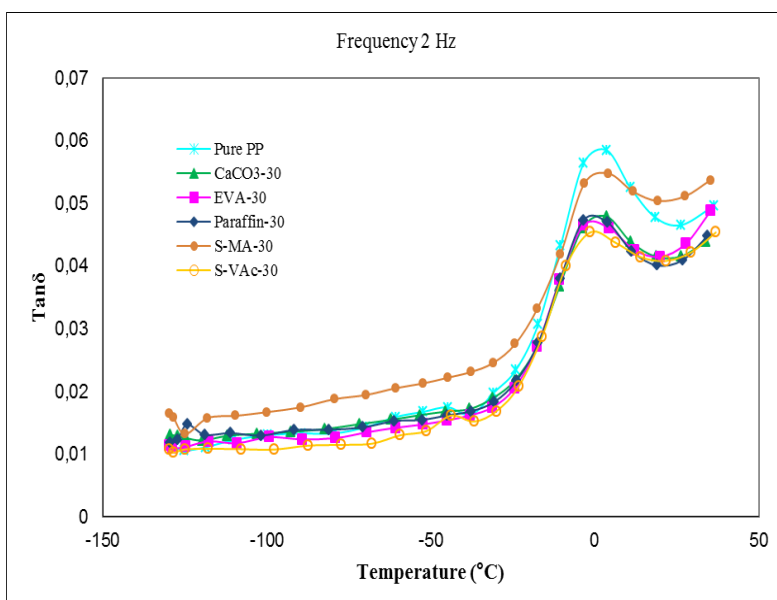

Figure 4 *Loss tangent (Tan δ) curves as function of temperature for PP composites at a frequency of 2 Hz.*

2.6 Scanning electron microscopy (SEM)

The fracture surfaces of stress strain test specimens were evaluated with Jeol SEM (5910LV, JSM).

To determine if there were any agglomeration and incompatibility between the coating materials and $CaCO_3$, Scanning Electron Microscopy (SEM) micrographs of coated particles were obtained. In Figure 4 (a), irregular particles of uncoated $CaCO_3$ can easily be seen. Figure 4 (b) and (c) show Paraffin coated $CaCO3$ surfaces (polymer/coating material ratio is 100/0.25). The irregular $CaCO_3$ particles can clearly be seen and the coated small particles are visible. However, surface of the coated particles are nearly the same as that of the core sample.

(a)   (b)   (c)
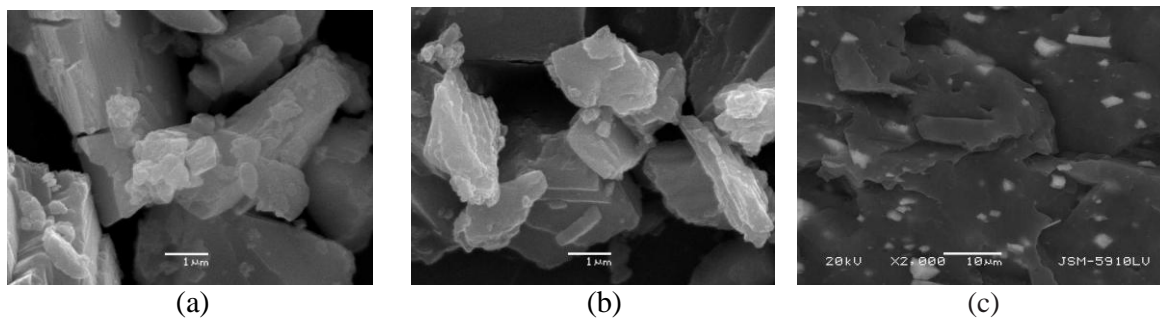
Figure 5 SEM micrographs of CaCO3 particles (a): uncoated CaCO3 (1µm), (b): paraffin coated CaCO3 (1µm), (c): fractured surface of paraffin coated CaCO3 (10µm).

2.7 Particle Size Analysis

Particle size distributions of surface modified and unmodified CaCO3 particles were analyzed and the effect of surface modification of CaCO3 was determined.

In Figure 6, particle size distribution of CaCO3 is shown. Avarage particle size of CaCO3 is 0.38µm and the distribution is between 0.3-2 µm, which mean CaCO3 used as filler for PP matrice was produced by grinding and size distribution is wide.
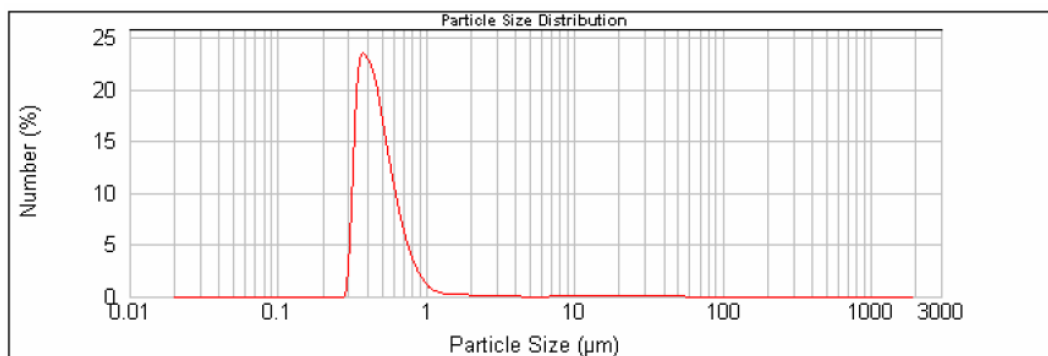
Figure 6 PSD of untreated CaCO3

In Figure 7, particle size distribution of CaCO3 coated with 0.25% Paraffin by weight is shown. Avarage particle size of surface modified CaCO3 is 0.40µm and the distribution is between 0.3-2 µm. Apparently, dispersion of particles is homogeneous and no agglomeration of surface modified CaCO3 particles or modification agents took place.
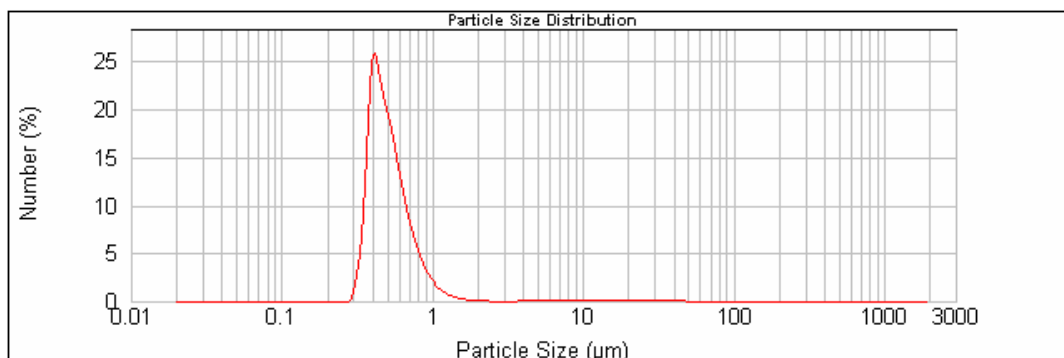
Figure 7 PSD of 0.25% by weight Paraffin coated CaCO3

It was found that the surface free energy of the PP matrices varied with the type of coating materials and filler content.

Results indicate that modification of inorganic CaCO$_3$ particles in organic polymers is a successful way to achieve better dispersion in PP matrix. This enables the usage of more inorganic filler in polymers without sacrificing the mechanical properties, which gives an advantage gained in price, volume and performance relations, in addition to the decrease in usage of non-renewable, non-biodegradable petroleum based polymers such as PP in their composites.

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