Preparation of PET Nanocomposites: Dispersion of Nanoparticles and Thermal Properties

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The development of polymer/inorganic nanocomposites has attracted a great deal of interest due to the improved hybrid properties derived from the two different components. Various nanoscale fillers have been used to enhance polymer mechanical and thermal properties, such as toughness, stiffness, and heat resistance. The effects of the filler on the final properties of the nanocomposites are highly dependent on the filler shape, particle size, aggregate size, surface characteristics, polymer/inorganic interactions, and degree of dispersion.

In this paper, we describe the influence of different $CaCO_3$ dispersion methods on the thermal properties of polyethylene terephthalate (PET)/$CaCO_3$ composites: i.e., the adsorption of $CaCO_3$ on the modified PET surface, and the hydrophobic modification of the hydrophilic $CaCO_3$ surface. We prepared PET/$CaCO_3$ nanocomposites using a twin-screw extruder, and investigated their thermal properties and morphology.

NOMENCLATURE

PET = Polyethylene terephthalate
PCC = precipitated calcium carbonate
SEM = scanning electron microscopy
TGA = thermogravimetric analysis
TMA = thermo mechanical analyzer
HDT = heat distortion temperature

1. Introduction

Nanocomposites are widely used in electronics, transportation, construction, and consumer products due to the surface modification and dispersion of nanoparticles.[1-4] The nature of the fillers used, including their composition, dimensions, and homogeneity of dispersion and adhesion level in a polymeric matrix, is important for the bulk properties of the composites. Nanoparticles have attracted interest as fillers for polymeric matrices. Nanocomposites are defined as having at least one dimension of the particle size in the dispersed phase less than 102 nm.[5] Due to the nanoscale dimensions, nanocomposites possess superior physical and mechanical properties compared to more conventional microcomposites, and therefore offer new technology opportunities.

This report deals with nanocomposites composed of calcium carbonate ($CaCO_3$) nanoparticles dispersed in polyethylene terephthalate (PET). The aim of this study was to analyze the effects of different $CaCO_3$ dispersion methods on the thermal properties of PET/$CaCO_3$ nanocomposites.

2. Experimental

2.1 Materials

The homo-polyester grade PET used in this study was supplied by Huvis (Seoul, Korea). The precipitated calcium carbonate (PCC) used in this study was supplied by NanoMaterials Technology (Singapore). Two grades of $CaCO_3$ nanoparticles were used: NPCC-111 and NPCC-201. These two grades share certain characteristics: density = 2.5 g/cm^3, average (primary) particle size = 40 nm, BET surface area = 40 m^2/g, purity (unmodified basis) $\geq$ 97%, and cubic particle shape.[6] The main difference between the two grades is that the surface of the NPCC-201 grade is partially modified with stearic acid to facilitate particle dispersion and distribution within the matrix, while that of NPCC-111 grade was untreated.

2.2 Dispersion of $CaCO_3$ using surface modification

Two different methods were used to improve the dispersibility of $CaCO_3$ in the PET matrix. The first is the hydrophobic modification of the hydrophilic surface of $CaCO_3$ to achieve good compatibility with the hydrophobic polymer matrix.[7,8] The NPCC-201 used in this method was treated with stearic acid. The second method is the adsorption of $CaCO_3$ on the modified PET surface. The hydrophilic

modification of the PET surface was achieved by hydrolysis.[9-11] Figure 1 shows the different methods of surface modification of both filler and matrix.

(a)

(b)

Hydrophilic PET surface

(c)

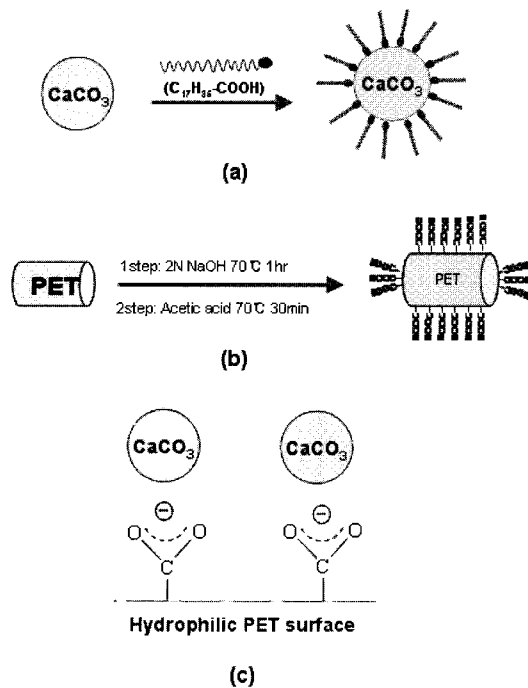Fig. 1 Different dispersion methods by surface modification: (a) Hydrophobic modification of CaCO₃ surface. (b) Hydrophilic modification of the PET surface for adsorption. (c) CaCO₃ adsorption on the hydrophilic surface of PET.

2.3 Preparation of PET/CaCO₃ nanocomposite

Both PET and CaCO₃ were dried in a vacuum oven at 80°C for 24 h to remove any moisture. A Bautech twin-screw extruder (19-mm barrel diameter, L/D ratio of 40) was used to compound the CaCO₃ and PET homogeneously. The extruded strand was guided through a water bath for solidification, and then granulated using a pelletizer. The compounding temperature was 270°C and the screw speed was 200 rpm.

2.4 Characterization

The heat distortion temperature (HDT) was measured using a thermo mechanical analyzer (TMA-7; PerkinElmer, Boston, MA) for a temperature range of 30–120°C, a heating rate of 2°C/min, and a static force of 880 mN.[12]

The thermal stability and filler content of the samples were determined by thermogravimetric analysis (TGA) (TGA7 device; TA Instruments, New Castle, DE), by recording the weight loss as a function of temperature. Each sample was heated from 30–700°C at a scanning rate of 10°C/min in an atmosphere of N₂.

The crystallization properties were measured using a differential scanning calorimeter (DSC) (DSC-7 device; PerkinElmer) over the temperature range of 50–270°C. Cooling scans were obtained down to 50°C at a cooling rate of 10°C/min.

The samples were fractured in liquid nitrogen for morphological analysis. The fracture surfaces were coated and examined by scanning electron microscopy (SEM).

2.5 Results

The morphological analysis showed good dispersion for both NPCC-111 and NPCC-201. Figure 2 shows SEM images of the fracture surfaces of the PET/NPCC-201 nanocomposite and the adsorption surfaces of the modified PET/NPCC-111 nanocomposite. The darker gray area is the PET matrix, and light gray spherical shapes are the dispersed CaCO₃.

The good dispersion of PET/NPCC-201 shown in Fig. 2(a) is due

to the hydrophobic characteristics of the CaCO₃ coated with stearic acid.[13,14] The homogeneous adsorption of CaCO₃ on the modified PET shown in Fig. 2(b) is due to the hydrophilic surface of the PET caused by hydrolysis.
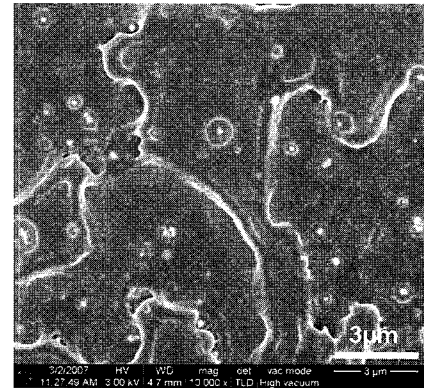
(a) Hydrophobic modified CaCO₃ (NPCC-201) in PET
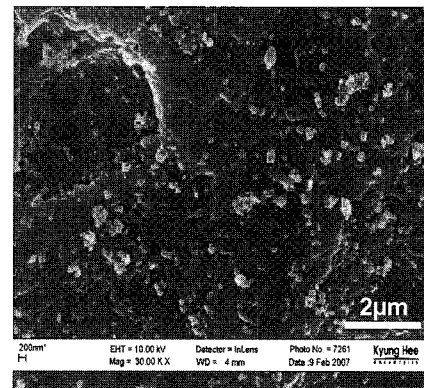
(b) CaCO₃ (NPCC-111) absorption on hydrophilic modified PET

Fig. 2 Dispersion of CaCO₃ with different modification methods

Table 1 HDT of the PET/CaCO₃ nanocomposites for different dispersion methods with a CaCO₃ content of 7 wt%

specimen size	5.08 × 3.2 ×1.0 mm		
sample	pure PET	NPCC-111/PET	NPCC-201/PET
HDT (°C)	83.2	91.5	86.9

The results of thermal analysis also showed that the PET/CaCO₃ nanocomposites had superior properties to those of pure PET. Table 1 shows the HDT of the PET/CaCO₃ nanocomposites.

In general, the thermal properties of polymers improve with increasing inorganic filler content.[15] The TGA results shown in Fig. 3(a) indicate the CaCO₃ contents in the nanocomposites. Both the PET/NPCC-201 nanocomposite and the modified PET/NPCC-111 nanocomposite have the same filler content (7 wt%) but different HDT.

The difference in HDT was due to the crystallinity of the composites. Figure 3(b) shows the cold crystallization curve of PET/CaCO₃ nanocomposites. In this DSC curve, the crystallization peak of the modified PET/NPCC-111 nanocomposite occurred earlier than the others. In addition, the peak area of the modified PET/NPCC-111 nanocomposite was wider than the others. These results suggest that NPCC-111 is more effective than NPCC-201 at improving the crystallinity.

3. Conclusions

We successfully prepared PET/CaCO₃ nanocomposites using different dispersion methods. The first was the adsorption method on the modified PET surface of CaCO₃ (NPCC-111). The second was the

hydrophobic modification (NPCC-201) of the hydrophilic surface of CaCO₃. SEM images of the fracture surfaces of the PET/NPCC-201 and adsorption surfaces of the modified PET/NPCC-111 show a good CaCO₃ dispersion.

In addition, thermal analysis showed superior properties of both PET/NPCC-201 and modified PET/NPCC-111 nanocomposites compared to pure PET. In particular, the HDT of the modified PET/NPCC-111 was significantly better than that of PET/NPCC-201. This difference in HDT was due to the different crystallinities of the composites. The DSC results suggested that NPCC-111 is more effective than NPCC-201 for improving the crystallinity.
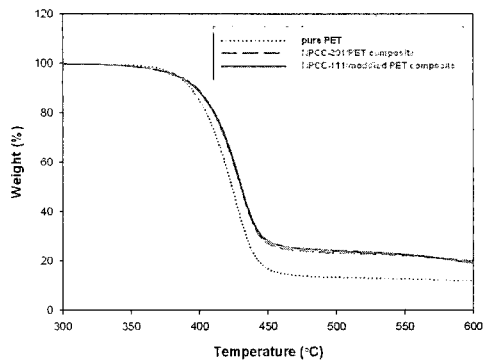
(a) TGA curve
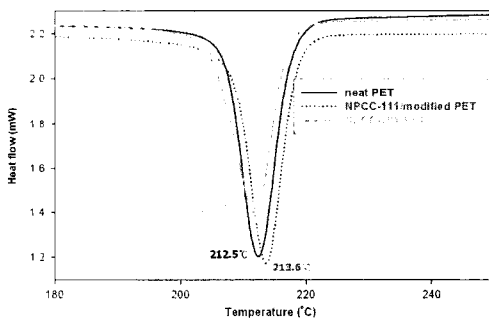
(b) DSC cooling curve for PET/CaCO₃ nanocomposites

Fig. 3 Thermal properties of the PET/CaCO₃ nanocomposites

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