

Effect of Nano-Calcite on Polyethylene Blend and its Nanocomposites: A Study of Mechanical and Thermal Characterization

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Abstract: The effect of nano-calcite (nano-calcium carbonate, nCC) on the mechanical and crystallization behavior of high-density polyethylene (HDPE)/low-density polyethylene (LDPE) (50/50 wt%) blends with and without titanate coupling agent (isopropyl tri-(dioctylpyrophosphato) titanate (JN114)) and different amounts of nCC were prepared through melt blending. The mechanical tests indicate that HDPE/LDPE/nCC composite with 10 wt% nCC is higher than that of HDPE/LDPE. In addition, incorporation of JN114 further increased the mechanical properties of the composites. This improvement in the mechanical properties was attributed to good interfacial adhesion between the fillers and matrix, as evidenced by scanning electron microscopy examination. The addition of small amounts of JN114 into HDPE/LDPE/nCC induces the great change of crystallization behavior of HDPE/LDPE matrix. Improved distribution of nCC, enhanced crystallization temperature is achieved for HDPE/LDPE/modified-nCC samples.

Key words: HDPE-LDPE blend; Nano-CaCO₃; Titanate coupling agent; Mechanical and Thermal properties.

I. INTRODUCTION

Thermoplastic polymers are produced and consumed to day in vast quantities. High density polyethylene (HDPE) and low density polyethylene (LDPE) blends have been attracting a lot of attention because of various reasons. One of the reasons is the cost-effectiveness of these blends in industrial and commercial usage. Low density polyethylene (LDPE) has a wide application in industry. Because of the suitable properties, it can be processed easily and used in different materials. Polyethylene has excellent chemical resistance and is not affected by acids, bases, or salts [1]. The addition of peroxide to blends of polyolefin-rubber combinations has been used to improve the mechanical properties [2]. However, these materials are seldom used as neat polymers; they are usually compounded with mineral fillers. The literature shows that interactions between polymer molecules and inorganic fillers may affect their properties on microscopic (conformation, crystallinity, molecular dynamics) and macroscopic (stiffness, hardness, toughness) levels. The effects of inorganic fillers on the microstructure and mechanical properties of polyethylene composites depend strongly on the particle shape and size distribution, aggregate size, surface characteristics, the fraction of filler, and the degree of dispersion [3, 4]. Polymeric nanocomposites

prepared by dispersive mixing processes have been reported to exhibit markedly improved mechanical properties over pure polymers and polymeric composites filled with micron size particles [5]. The outstanding properties of nanocomposites are attributed to small particle size, large interfacial area and high surface energy of the nanoparticle fillers, which lead to strong interfacial adhesion between the fillers and the polymer matrix. Extensive research work has been carried out to correlate the reinforcing ability of composites with the strength of interfacial adhesion [6, 7]. It is thought that inorganic filler could enhance the mechanical performance of polyethylene. Various inorganic fillers such as talc, mica, clay, and calcium carbonate (CaCO₃) and fiber reinforcements such as glass fibers are commonly incorporated into thermoplastic polymers. Recently, natural fibers such as sisal, wood, and cellulose also have been used to reinforce thermoplastics [8, 9]. These composites generally exhibit superior stiffness, strength, and heat distortion temperatures with respect to unreinforced polymers. However, reinforcing materials such as glass fibers, carbon fibers, and aramide fibers are not biodegradable. Among the various reinforcing materials, CaCO₃ is attractive because of its low cost [10, 11]. Another advantage of CaCO₃ is derived from its hydrophilic behavior, that is, its water adsorption characteristics. It is anticipated that the incorporation of CaCO₃ can improve the water adsorption of a composite, thereby accelerating the biodegradation process of polyethylene polymers containing ester bonds. CaCO₃ in the form of chalk, whiting, and limestone is perhaps the most widely available and used mineral in the world to be used as an additive today. Because CaCO₃ can be processed in a wide range of particle sizes, the resulting products function as low-cost fillers that are added to extend and cheapen the application of polymeric systems [12]. Some researcher's reports [13-15], the influences of various additives on the morphological, crystallization behavior and thermal properties of polyethylene compounds were revealed. So far, most research on the quantitative characterization of interfacial interaction has been concentrated on micron-size-particle-filled composites with polyethylene (PE) or polypropylene (PP) matrix. However, there is still no report on mechanical properties and crystallization behavior of inorganic particulate-filled HDPE/LDPE composites modified with titanate coupling agent. The present study sought to the

effect of unmodified and modified nCC particles on the mechanical and crystallization behavior of polyethylene-based melt-compounded composites.

II. EXPERIMENTAL

A. Materials

Polyolefin's used in this study are HDPE (density = 0.954g/cm³, MI = 0.8 g/10min) and LDPE (density = 0.918 g/cm³, MI = 3 g/10min) supplied by polyolefin Company Ltd. Singapore. Nano-sized CaCO₃ with an average diameter of 40 nm was obtained from Keli New Materials Co, Ltd (Henan, China). Titanate-coupling agent, including isopropyl tri-(dioctylpyrophosphato) titanate (JN114) was provided by Changzhou City Jinai Co., Ltd (Jiangsu Province, China).

B. Methods

Surface Treatment of CaCO₃ Particles

One hundred grams of nCC particles and 400 g of ethanol (water) were added to a high-speed dispersion machine filled with zirconium oxide beads and ground for 1-2 h at a speed of 400 rpm. After the ground nano-particles were filtered to remove the zirconium oxide beads, the titanate coupling agent (0.5 wt % with respect to the filler) was introduced. The mixture was kept at 78°C for 2 h and was then filtered to remove the solvent. The mixture was further dried at 120°C for 2 h to remove the residual solvent. After being ground by air current, treated nCC particles were prepared.

Preparation of Blends

Before melt mixing, HDPE, LDPE, nCC were dried in a vacuum oven at 80°C for 6h and then cooled down to room temperature. The materials were stored in a desiccator prior to processing. All the materials were simultaneously added into the extruder after previous mixing. High density polyethylene-low density polyethylene (HDPE/LDPE) blends involving (HDPE/LDPE; 50/50 wt%) with different amounts (5, 10 and 15 wt%) of calcium carbonate (CaCO₃) was prepared by melting-blend with a twin-screw extruder (Brabender Plasticorder, model PLE-331). The blends were prepared by melting the mixed components in extruder, which was set at the temperature: 180°C, rotor speed: 60 rpm, blending time: 10min. The resultant mixture was compression-molded in a hot press at 190°C for 5 min between two steel plates under a pressure of 10 MPa. Finally, the pressure was released and the mold removed from the plates. This was followed by cooling to room temperature between two thick-metal blocks kept at room temperature. A template frame was used to ensure a constant film thickness (1mm). The samples were cut into standard shapes and sizes (according to the ASTM D 638-91 standard) for testing the mechanical properties. The specimens were then sealed in plastic bags as they waited the processing and analysis. The compositions of tested materials and their codes were listed in Table 1.

Filler Dispersion Analysis

Scanning Electron Microscopy (SEM; JEOL, Japan JSM-6360 LV at an accelerating voltage of 10 kV) was employed to study fracture surfaces of all tested samples. The SEM samples were held in liquid nitrogen for 30 min and then broken into two pieces. The fractured surfaces of the specimen were coated with a thin layer (10–20 nm) of gold palladium.

Mechanical Properties Evaluation

Mechanical properties of HDPE/LDPE and HDPE/LDPE/nCC nanocomposites were studied in both tensile and impact tests. Standard specimens were sampled from the compression molded sheet and then conditioned at the temperature of (25 ± 2)°C and the relative humidity of 50 ± 5% for 24 h. Tensile testing was performed on a screw-driven universal testing machine (Instron 4466) equipped with a 10 kN electronic load cell and mechanical grips. The tests were conducted at a crosshead speed of 30 mm/min and data was acquired by a computer. All tests were carried out according to the ASTM D-638-91 standard, and five replicates were tested for each sample to get an average value. Izod impact tests of notched samples were carried out according to ASTM D256-93a standard, the instruments was Ceast pendulum impact tester (Model 6545/000). The dimension of the specimens (length × width × thickness) was 63.50 × 13 × 3.20 mm³. All measurements were performed 5 times to take an average value.

Crystallization Studies

The melting and crystalline behaviors of HDPE/LDPE (HDPLDP) and samples were measured with a Perkin Elmer DSC-7 (Perkin Elmer, Inc., Wellesley, MA, USA). First, HDPLDP and samples were heated from 25 to 250°C during 10 min to eliminate all of the thermal history in the materials. Then, the samples were cooled to 25°C at a cooling rate (R) of 10°C/min to obtain their crystalline characteristics. Last, the samples were heated to 250°C at a heating rate of 10°C/min to obtain their melting characteristics. All measurements were carried out under the nitrogen atmosphere environment. The sample weight was in the range 5–8 mg. Degree of crystallinity (X_c%) was calculated using melting enthalpy of the samples according to the following equation:

$$X_c\% = \frac{\Delta H_m}{\Delta H_m^0} \times 100$$

Where ΔH_m^0 is the melting enthalpy of the 100% crystalline form of PE (279Jg⁻¹) [16].

III. RESULTS AND DISCUSSION

A. Dispersion of Nano-CaCO₃ (nCC) Particles in Polyethylene Matrix

It has been widely accepted that the distribution of CaCO₃ is one of the most important factors which determines its

reinforcement and toughening effects in matrix, especially for the use of nano- CaCO_3 [17] due to its large specific surface area and high surface energy. Figure 1 (a, b) illustrates the morphology of the impact-fracture surface of HDPLDP/nCC10 and HDPLDP/modified-nCC10 composites, respectively. In the former composite, CaCO_3 tends to form some aggregates with the size of about 200-500 nm, about the aggregation of 2-5 CaCO_3 particles. Many cavities between the particles and the matrix were observed, which suggests that the interfacial adhesion between the two phases was poor (Fig. 1a). The untreated nCC particles agglomerated in the matrix owing to their larger specific surface area and high polar surface energy. The aggregated nCC particles had poor compatibility with the matrix because of their hydrophilic surface, which led to interface debond. The inhomogeneous dispersion of fillers can degrade the mechanical strength of composites considerably. When the PE matrix was filled with the nCC particles treated with JN114, the nanoparticles were homogeneously dispersed in the PE matrix and aggregates of the nanoparticles were hardly observed; the diameters of the particles were almost below 100 nm (Fig. 2b). The interfacial contact between the nanoparticles and PE matrix was good. There is a strong polar-polar interaction between nonpolar polyethylene matrix and treated nCC particles. As a result, a good compatibility was obtained, thereby resulting in an excellent interfacial adhesion between the nCC particles and the matrix. The good compatibility also improved the dispersion and reduced the aggregates of nCC particles in the PE matrix.

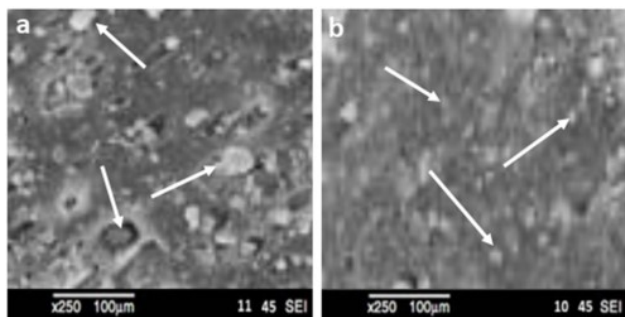


Fig. 1 SEM micrographs of impact-fractured surfaces of (a) HDPLDP, (b) HDPLDP/nCC10, and (c) HDPLDP/nCC10T composites

B. Mechanical Properties of the Nanocomposites

The mechanical properties of all samples were comparatively investigated through the measurements of tensile and impact testing. Mechanical property tests were performed on HDPE/LDPE (HDPLDP), HDPLDP/nCC unmodified with nCC loadings varying from 5 to 15 wt% and modified with 0.5 wt% titanate coupling agent. Table 1 presents the effects of unmodified-nCC and modified-nCC on the tensile strength and notched Izod impact strength of HDPLDP/nCC and HDPLDP/modified-nCC, respectively. It has been reported [18] that the mechanical properties of composites depend on the characteristics and interaction between the composition components. It can be seen that the addition nCC particles

gave rise to a decrease in tensile strength of the composites while the impact strength was significantly enhanced with increasing nCC particles content. With the increase in the filler concentration, the notched Izod impact strength of all composites increased and then decreased. The maximum impact strength was achieved at a loading of 10 wt%. According to the trend of the impact strength variation, the HDPLDP/modified-nCC composite increased more obviously than HDPLDP/nCC. The maximum impact strength of HDPLDP/modified-nCC was 3.7 kJ/m^2 , about 164% of that of HDPLDP. When the nCC particles are dispersed in the matrix, the particles act as the concentration of stress which leads to the formation of cracks in the matrix. However, the cracks would be effectively stopped when they propagate to the surface of particles. Thus if a large amount of cracks are created in the composite, which absorb the impact energy, the toughness of composites would be improved. However, if the interfacial adhesion between the particles and matrix is too weak, the micro-cracks would propagate along the interface between the matrix and the nCC particles and the capability of inorganic particles to terminate the crack propagation would be weakened. Therefore, the interfacial adhesion between the nCC particles and the matrix also plays an important role in enhancing the impact strength of the composites. If the nCC particles disperse unevenly in the matrix and severe aggregates occur in the matrix, as was found in the composites filled with the untreated and JN114-treated nCC particles, the agglomeration reduces the effective number of nanoparticles, which would absorb the impact energy. In the case of the JN114-treated HDPLDP/nCC composite, the excellent adhesion of particles with the matrix and their good dispersion in the matrix were responsible for this composite having the best impact strength. It is known that the tensile strength of composites is influenced by the filler fraction and the interfacial adhesion between particles and matrix. With the addition of the nCC particles, the cross-section area of composites to bear load decreased, and only a small amount of stress could be transferred from the matrix to inorganic particles if a weak interfacial adhesion existed between the matrix and particles. Thus, the tensile strength of the HDPLDP/nCC composites decreased with increasing content of nCC particles. These results are consistent with the results of the research study carried out by Teixeira et al. [19]. The interfacial adhesion plays a crucial role in improving the tensile strength of the composites. The stronger the interfacial adhesion the composite has, the larger the stress that can be transferred to inorganic particles from the matrix, which leads to higher tensile strength. The treatment of nCC particles with JN114 significantly improved the interfacial adhesion of the corresponding composite, and it thus had the highest tensile strength among the other composites. The composite filled with the untreated-nCC particles had relatively poor interfacial adhesion, and had the lowest tensile strength. The mechanical property results were consistent with the SEM observations, as shown in Figure 1.

Table1: Compositions and mechanical properties of polyethylene blends and its nanocomposites

Sample code	HDPLDP (50/50 wt%)	CaCO ₃ (wt %)	JN114 (wt%)	Tensile strength (MPa)	Impact strength (kJ/m ²)
HDPLDP	100	-	-	19.2 ± 0.8	1.4 ± 0.05
nCC5	5	95	-	18.7 ± 1.2	1.9 ± 0.07
nCC10	10	90	-	17.3 ± 0.9	2.8 ± 0.06
nCC15	15	85	-	16.6 ± 0.7	2.6 ± 0.05
nCC5T	5	95	0.5	21.9 ± 1.1	3.5 ± 0.07
nCC10T	10	90	0.5	20.8 ± 0.9	3.7 ± 0.04
nCC15T	15	85	0.5	19.2 ± 1.3	3.2 ± 0.06

HDPLDP: High-density polyethylene (HDPE)/low density polyethylene (LDPE); nCC: nano-calcium carbonate; CaCO₃: calcium carbonate; JN114: Titanate coupling agent.

C. Melting and Crystallization Behaviors

The crystallization and melting behaviors of HDPLDP, HDPLDP/unmodified-nCC10 (nCC10), and HDPLDP/modified-nCC10 (nCC10T) composites are shown in Figure 2. It can be seen from Figure 2(a) that the crystallization peak temperature (T_c) is enhanced from 115.3°C of HDPLDP to 120.1°C of nCC10 composite. It is interesting to observe that the T_c of nCC10T is increased up to 122.2°C, much higher than that of HDPLDP, and even higher than that of nCC10 composite. This means that there is a synergistic effect of JN114 and CaCO₃ in HDPLDP crystallization process possibly due to that, CaCO₃ increases the viscosity of HDPLDP melt, leading to the increase of local shear stress and making more homogeneous network structure formation of JN114 in nCC10T. Furthermore, the melt temperature (T_m) of HDPLDP matrix has not been influenced by the addition of CaCO₃ and/or JN114 apparently [Figure 2 (b)]. Considering the nucleation effect of JN114 in HDPLDP, one can believe that the crystallization of HDPLDP in nCC10T is mainly determined by JN114 rather than by nCC. Figure 2 (c) shows the values of crystallinity. The crystallinity of the polymer matrix shows an increase after the introduction of nCC particles and the sample with surface-treated nCC shows the highest value of crystallinity.

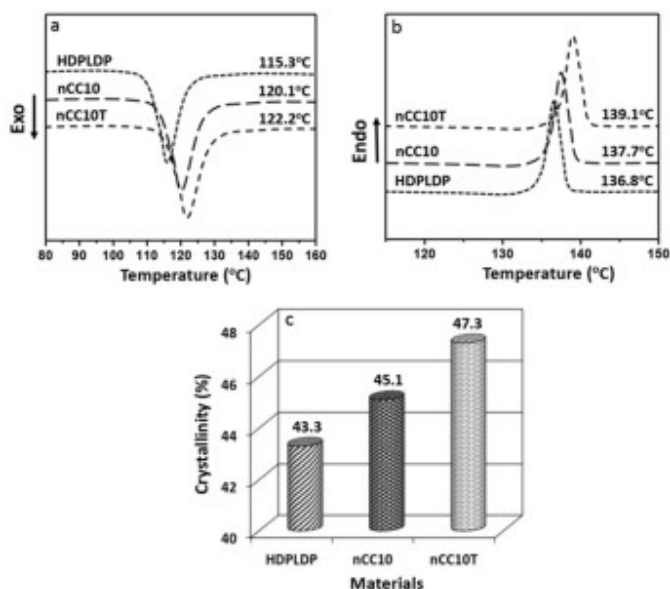


Fig. 2 DSC cooling curves of (a) HDPLDP, nCC10 and nCC10T composites and heating curves of (b) HDPLDP, nCC10 and nCC10T composites.

III. CONCLUSIONS

In this study, the effects of nCC on the mechanical properties, such as tensile strength, and impact strength with and without JN114 of HDPLDP blends were investigated. The following results were obtained:

- SEM analysis clearly indicated that the addition of JN114 into HDPLDP/nCC10, nCC particles were homogeneously dispersed in HDPLDP blends, and their interfacial adhesion with the matrix was superior to those of the HDPLDP/nCC10 without JN114.
- The impact strength of the HDPLDP/nCC composites were obviously increased as the nCC content increased but the tensile strength decreased gradually as the nCC content increased. The addition of JN114 increased the mechanical properties of the nanocomposites.
- DSC measurements showed that the addition of JN114 led to a higher crystallization temperature and nucleation were improved at the same time. The crystallization temperature of nCC10T is much higher than that of nCC10 and even higher than that of HDPLDP.

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