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# Influences of Mineral Filler Content and Surface Treatment on the Properties of Polyethylene Blend Nanocomposites

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## ABSTRACT

To study the effect of mineral filler (nano-calcium carbonate, nCC) on the mechanical and crystallization behavior of high-density polyethylene (HDPE)/low-density polyethylene (LDPE) blends involving HDPE/LDPE (40/60 wt%) without and with malonic acid (MA; 5 wt%) and different amounts (1-5 wt%) of nCC were prepared through melt blending technique followed by compression molding. The mechanical tests indicate that HDPE/LDPE/nCC nanocomposite with 3 wt% nCC is higher than that of HDPE/LDPE (denoted as HL). In addition, inclusion of MA further increased the mechanical properties of the nanocomposites. This improvement in the mechanical properties was attributed to good interfacial adhesion between the fillers and matrix, as evidenced by scanning electron microscopy (SEM) examination. With the addition of MA into HL/nCC induces the great change of crystallization behavior of HL matrix. Improved distribution of nCC, enhanced crystallization temperature is achieved for HL/modified-nCC samples.

Keywords: HDPE/LDPE blend, Nano-$CaCO_3$, malonic acid, Mechanical and Thermal properties

## 1. Introduction

Polymer nanocomposites have attracted much attention from both industry applications and academic research fields due to their remarkable properties, such as mechanical properties, thermal properties, electrical properties, and rheological behavior (Nurhajati et al., 2014; Yin et al., 2009). It is well known that nanoparticles performance a vital role in their application to polymer nanocomposites. Polymer-based nanocomposites have been expansively considered in research and application because the inclusion of the nanoparticles delivers an improved toughness, stiffness, dimensional stability, gas barrier properties, and/or flame retardancy. Within the polymer nanocomposites, those based on polyethylene (PE) have deliberated significant attention because of its relatively high mechanical properties, great recyclability, good processability, low cost and widely used in the manufacturing of electrical insulation systems. 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 (Hossen et al., 2016). When HDPE blended with LDPE, then it can increase the susceptibility to bubble instabilities and may reason melt fracture. This mixture may deliver a capacity to tailor the material to convention the specific end-use, cost performance and so on to produce the materials for packaging films having the combined properties of HDPE and LDPE. Due to the excellent processability, elasticity, and extensibility of high-density polyethylene (HDPE) and advantageous mechanical performances of low-density polyethylene (LDPE), a number of studies on the property/structure of HDPE/LDPE blends have been conducted. The addition of peroxide to blends of polyolefin-rubber combinations has been used to improve the mechanical properties (Hejna et al., 2019). 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 (Pourrahimi et al., 2016). Polymeric nanocomposites prepared by

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dispersive mixing processes have been reported to exhibit markedly improved mechanical properties over pure polymers and polymeric composites filled with micron size particles (Zhang et al., 2010b). 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 (Lin et al., 2020). 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 (Agarwal et al., 2020; Huang et al., 2020). 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 (Lee et al., 2020). 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 (Liu et al., 2020). Some researcher's reports (Chow et al., 2016; Liang et al., 2008; Zhang et al., 2010a), 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 malonic acid. 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.

## 2. Experimental

### *2.1 Materials*

High density PE, DGDA6098 was from Qilu Petrochemical Co. (Zibo, China). Low-density polyethylene (LDPE) was purchased from Aldrich, density: 0.925 g/cm3, melt index: 25 g/10 min (190°C/2.16 kg); impact strength: 45.4 J/m (Izod, ASTM D 256, −50°C). CaCO3 nanoparticles were supplied by Shiraishi Kogyo Kaisha Ltd (Japan) and had a density of 2.7 g/cm3 and a diameter of 60–80 nm. Malonic acid (analytical reagent, and identified as MA), and ethanol (analytical reagent) were commercially available and used as received.

### *2.2 Methods*

#### *Surface treatment of $CaCO_3$ particles*

Three hundred grams of nano-$CaCO_3$ was put into a 1000 mL three-necked flask equipped with a mechanical stirrer. Subsequently a solution of 3 g MA in 500 mL ethanol was also added. The mixture reacted for 1 h at 80°C under vigorous stirring. Then the ethanol was distilled out and the MA treated nano-$CaCO_3$ was dried to constant weight at 100°C.

#### *Preparation of blends*

Prior to melt mixing, HDPE, LDPE, and nCC were dried in a vacuum oven at 70°C for 6h to remove water and then cooled down to room temperature. The materials were deposited in a desiccator earlier to processing. All the materials were instantaneously added into the extruder after earlier mixing. The contents of nCC and HDPE/LDPE (denoted as HL) were maintained at 1, 3, and 5 wt% and 40/60 wt%, respectively. Blending with various unmodified and modified filler contents was carried out in a twin-screw extruder (L/D = 40, model ZSK25 manufactured in Werner & Pfleiderer, Germany). The processing temperature, rotor speed, and blending time were set at 180°C, 60 r/min, and 10 min, respectively. The resultant blend was compression-molded in a hot press at 190°C for 5 min between two steel plates under a pressure of 10 MPa. Lastly, the pressure was freed and the mold withdrawn from the plates. The resulting sheets were quenched immediately to room temperature in air compression. The desired samples were cut into standard shapes and sizes for testing mechanical and thermal properties. There were four nanocomposites, HL/1nCC, HL/3nCC, HL/5nCC and HL/3nCCM, in this experiment, and the MA concentration was 5 wt%, respectively. The concentration of HL was 100 wt%, when the concentration of nCC was 0%.

#### *Filler dispersion analysis*

Studies on the morphology of fractured surfaces of samples were performed using an SEM, model JEOL JSM-5900LV. All samples were dipped into liquid nitrogen for 0.5 h. Then, the samples were fractured. The fracture ends of the samples were placed on aluminum stubs and sputter coated with a thin layer of gold to avoid electrostatic charging during investigation and observed at an accelerating voltage of 10 kV.

#### *Mechanical properties evaluation*

The influences of unmodified and surface modified nCC on HDPE/LDPE (40/60 wt%) blends were evaluated through the mechanical properties, such as tensile strength, tensile modulus and impact strength. Standard samples were tested 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 prior to subjecting to tensile testing. Tensile testing was carried out with 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 attained by a computer. All tests were carried out according to the ASTMD-638-91 standard, and five replicates were tested for each sample to get an average value. Izod impact strength for the samples having dimensions 63.5 × 12.7 × 3 $mm^3$ was performed with a pendulum apparatus (DTI-602, Dae-Kyung Technology, Incheon, South Korea) using acutely notched specimens (notch depth: 2 mm) according to ASTM D 25622 at room temperature.

### *Crystallization studies*

DSC (Q20, TA, USA) was used to examine the melting properties and crystallization behaviors of HL, HL/nCC and HL/modified nCC specimens purged with nitrogen. The specimens about 5-8 mg were rapidly heated to 220°C from room temperature (25°C), held for 5 min to eliminate previous thermal and stress histories. Then, the samples were cooled to 25°C and then heated to 220°C at a cooling/heating rate of 10°C/min to obtain their crystallization and melting behaviors. The relative crystallinity of each component in the various HL blends was calculated by the following equations:

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

Where $\Delta H_m^0$ is the melting enthalpy of the 100% crystalline form of PE ($279Jg^{-1}$) (Alamo et al., 1997).

## 3. Results and Discussion

### *3.1 Dispersion of nano-CaCO$_3$ (nCC) particles in polyethylene matrix*

It's done extensively adopted that the delivery of nCC is one of the most vital factors which determines its reinforcement and toughening influences in matrix, particularly for the use of nCC (Gatos et al., 2007) owing to its huge definite surface area and elevated surface energy. When nano-particles are used, the dispersion becomes an intense problem, as nanoparticles have a strong tendency to agglomerate. Therefore, homogeneous dispersion of the nanoparticles in the PE matrix is a hard process. A proper dispersion can be attained by surface modification of the filler particles and suitable treatment conditions. Figure 1 (a- d) illustrates the morphology of the impact-fracture surface of HL/1nCC, HL/3nCC and HL/modified-3nCC nanocomposites, respectively.

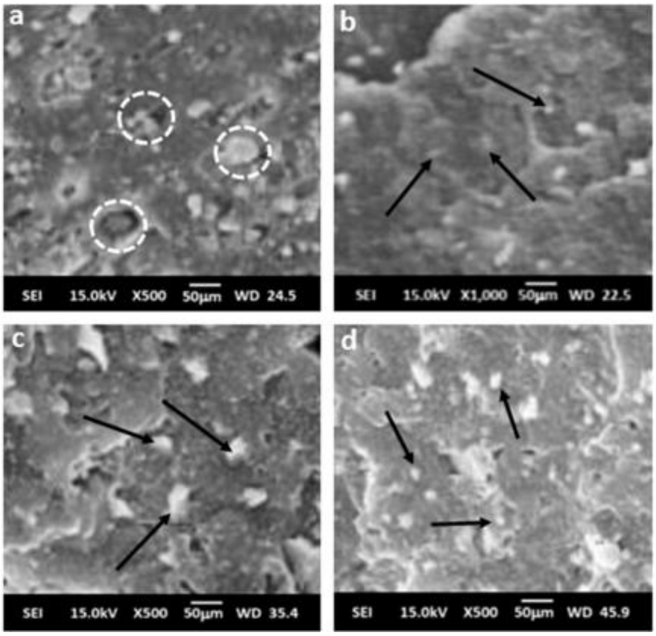

**Fig. 1- SEM micrographs of impact-fractured surfaces of (a) HL/1nCC, (b) HL/3nCC, (c) HL/5nCC, and (c) HL/3nCCM nanocomposites.**

Figure 1(a) shows that the nCC particles were dispersed in HL unevenly, and some big aggregates were revealed on the fracture surface, with a particle size greater than 3 μm, meaning that the compatibility between the HL and nCC was poor. The aggregated unmodified nCC particles have a poor compatibility with HL matrix as of their hydrophilic surfaces, which conduct to voids in the matrix and interface debonding. The inhomogeneous dispersion of fillers can reduce the mechanical strength of nanocomposites significantly. However, when the nCC amount was raised to 3%, a homogeneous dispersion of finer reinforcing particles can be observed (Figure 1 (b)). Furthermore, when the nCC amount was raised to 5%, some protuberances were observed on the surface, which were assumed to be agglomerations of the nCC particles (Figure 1(c)). These 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 significantly. Moreover, more homogeneous distribution of nCC has been achieved in HL/modified-3nCC nanocomposite (Figure 1(d)) compared to HL/3nCC nanocomposite (Figure 1(b)), there were no aggregates and the average particle size was smaller than that of HL/3nCC. Additionally, nCC particles disperse more uniformly and finely in polymer matrix than that of HL/3nCC nanocomposite and the cohesive force between them was stronger and the agglomeration was weakened. There are many fine cavities around nCC and HL. Those fine inorganic particles and cavities could induce large-scale plastic deformation of the matrix, leading to improved fracture toughness.

### *3.2 Mechanical properties of the nanocomposites*

Mechanical properties of all specimens were relatively investigated through the measurements of tensile and impact testing. Mechanical property tests were performed on HDPE/LDPE (HL), HL/1nCC, HL/3nCC and HL/5nCC unmodified nanocomposites with nCC loadings varying from 1 to 5 wt% and modified with 5 wt% malonic acid (MA). Figure 2 presents the effects of unmodified-nCC and modified-nCC on the tensile strength and tensile modulus of the nanocomposites. It was reported (Chan et al., 2002) that the mechanical properties of composites depend on the characteristics and interaction between the composition components. It can be observed that the tensile strength decreased with increasing amount of nCC particles, while the tensile modulus and impact strength was significantly enhanced with increasing nCC particles content up to 3 wt% of nCC and then decreased. The tensile strength of unmodified and modified nanocomposites against nCC content is shown in Figure 2(a). It is well known that the tensile strength of nanocomposites is influenced by the filler content and the interfacial adhesion between particles and matrix. With increasing concentration of nCC particles, owing to the tendency of agglomeration of nanoparticles poorly interfacial adhesion existed between the HL matrix and the nanoparticles, and hereafter the load-bearing capacity of cross-sectional area of nanocomposites reduced, and only a small amount of stress could be shifted from the matrix to inorganic particles, hence tensile strength displayed decrease in the magnitude; in this case agglomerated particles smoothly debonded from the matrix and could not allow any fraction of exterior load eventually reducing the tensile strength. Hence, the tensile strength of the nanocomposites reduced with an increase in the content of nCC particles. These outcomes were compatible with the results of the research study performed by Zaman et al (Zaman et al., 2013). To develop the dispersion of the filler in the HL matrix and improve in the interfacial adhesion between filler and matrix, MA is led to modify HL/nCC nanocomposites. The addition of MA into HL/nCC blends considerably developed the interfacial adhesion between the filler and the matrix than those of HL/nCC nanocomposites. The maximum tensile strength of HL/3nCCM nanocomposites was 26.9 MPa and about 36% higher than that of the HL matrix. As narrated above, MA developed the compatibility of HL matrix and nCC. At the same time, nCC reacted with MA to form calcium malonate on its surface. It is well known that MA can coat or pack nanoparticles, thus decrease the surface energy of nanoparticles and develop the dispersion of nCC in HL. In addition, as a reactive polar small molecule, MA is inclined to diffuse into the agglomerates of nanoparticles and hinders them from agglomerating. With the action of high temperature and shear stress during the procedure, MA can homopolymerize or graft to HL, thus progressing the interfacial action between the nanoparticles and the matrix and improvement the mechanical properties of the nanocomposites.

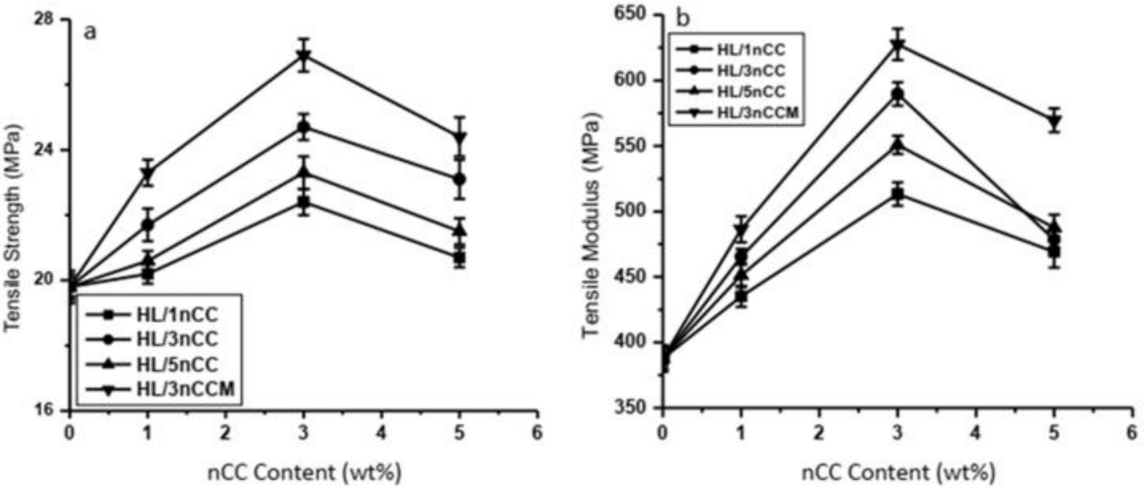

**Fig. 2- Effect of nCC content on (a) Tensile strength and (b) tensile modulus of HL/nCC nanocomposites**

Figure 2(b) shows that tensile modulus of the composites with nCC content. It can be seen that the tensile modulus increased first and then decreased with increasing nCC content. The maximum tensile modulus was obtained at nCC content of 3 wt%. The maximum tensile modulus of the HL/nCC nanocomposites was found to be 627.5 MPa. At this stage, the tensile modulus value of the HL/nCC nanocomposite was about 62% higher than that of

HL. It is well known that the addition of any rigid filler to a polymer matrix increases its modulus. According to the trend of the modulus variant, the HL/3nCCM nanocomposite increased more evidently than HL/nCC nanocomposite. The increase in modulus suggests an efficient stress transfer from polymer matrix to inorganic fillers. An important increase in the modulus was performed for 3 wt% nCC; and beyond 3% nCC, the values started to decrease. The decrease was related to the weak bond strength, adhesion, or lower molecular interaction caused by the higher content of the nCC in the HL matrix (Zaman et al., 2014). The inclusion of more than 3% nCC not only developed stress but also developed microcracks and delivered weak adhesion between the filler and matrix. Particularly when the nCC content was greater than 3%, the modulus decreased.

Impact strength is a vital characteristic for impact toughness of materials. Figure 2(c) illustrates the relationship between the Izod impact strength and the content of nCC. 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 3 wt%. According to the trend of the impact strength variation, the HL/3nCCM nanocomposite increased more obviously than HL/3nCC. The maximum impact strength of HL/3nCCM was 6.2 kJ/m$^2$, about 195% than that of HL. 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 MA-treated nCC particles, the agglomeration reduces the effective number of nanoparticles, which would absorb the impact energy. In the case of the MA-treated HL/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.

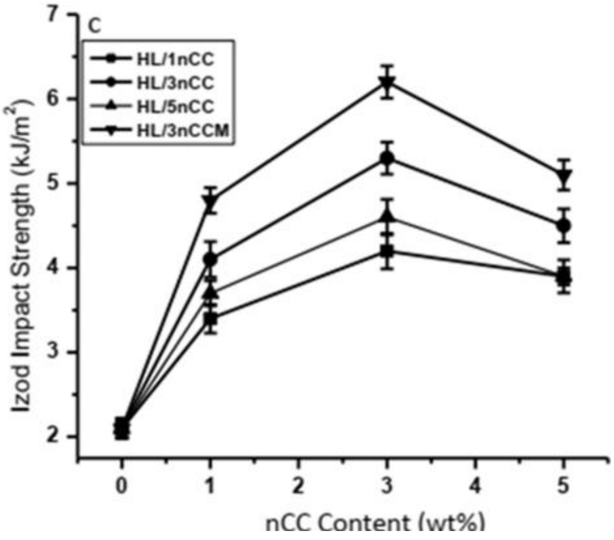

**Fig. 3- Effect of nCC content on Izod impact strength of HL/nCC nanocomposites.**

### *3.3 Melting and crystallization behaviors*

The crystallization and melting behaviors of HL, HL/3nCC and HL/3nCCM nanocomposites are shown in Figure 4. It can be seen from Figure 4(a) that the crystallization peak temperature ($T_c$) is enhanced from 115.9°C of HL to 120.1°C of HL/3nCC nanocomposite. It is remarkable to observe that the $T_c$ of HL/3nCCM is increased up to 123.5°C, much higher than that of HL, and even higher than that of HL/3nCC nanocomposite. This means that there is a synergistic effect of MA and nCC in HL crystallization process possibly due to that, nCC increases the viscosity of HL melt, leading to the increase of local shear stress and making more homogeneous network structure formation of MA in HL/3nCCM. Furthermore, the melt temperature ($T_m$) of HL matrix slightly influenced by the addition of nCC and/or MA apparently [Figure 4 (b)]. Considering the nucleation effect of MA in HL, one can believe that the crystallization of HL in HL/3nCCM is mainly determined by MA rather than by nCC. Figure 4(c) shows the values of crystallinity of the samples. 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. It can be seen that MA induces the great enhancement of Xc (%) in HL/3nCCM sample.

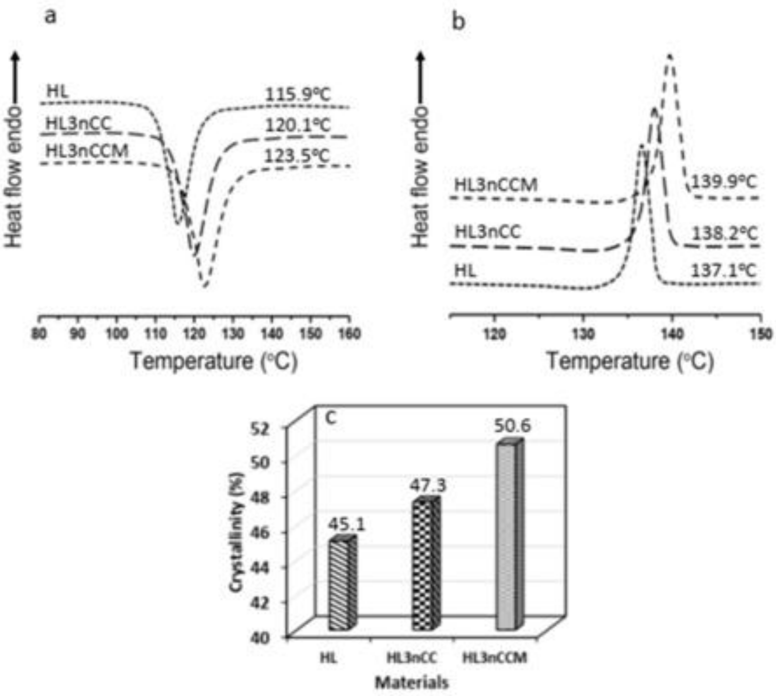

**Fig. 4- DSC cooling curves of (a) HL, HL3nCC and HL3nCCM composites and heating curves of (b) HL, HL3nCC and HL3nCCM composites.**

## 4. Conclusions

This study obviously demonstrated that the incorporation of the malonic acid (MA) to nCC modifies the mechanical properties such as tensile strength, tensile modulus and impact strength of the HL/nCC nanocomposites. When nCC was at 3 wt%, the tensile strength, tensile modulus and impact strength of these nanocomposites reaches maximal values, the increase of them is more than 36%. Relatively, when the surface of the nCC particles is pretreated with MA, the compatibility between the particles and the matrix, and the uniformity of the dispersion and distribution of the fillers in the matrix and the interfacial morphology between them could be improved better than those of the HL/3nCC nanocomposite system. SEM analysis clearly showed that the addition of MA into HL/3nCC, nCC particles were homogeneously dispersed in HL blends, and their interfacial adhesion with the matrix was superior to those of the HL/3nCC without MA. DSC measurements displayed that the addition of MA led to a higher crystallization temperature and nucleation were improved at the same time. The crystallization temperature of HL/3nCCM is much higher than that of HL/3nCC and even higher than that of HL.

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