Thermal and Mechanical Properties of Modified $CaCO_3$/PP Nanocomposites

A. Buasri, N. Chaiyut, K. Borvornchettanuwat, N. Chantanachai and K. Thonglor

Abstract**—**Inorganic nanoparticles filled polymer composites have extended their multiple functionalities to various applications, including mechanical reinforcement, gas barrier, dimensional stability, heat distortion temperature, flame-retardant, and thermal conductivity. Sodium stearate-modified calcium carbonate ($CaCO_3$) nanoparticles were prepared using surface modification method. The results showed that sodium stearate attached to the surface of $CaCO_3$ nanoparticles with the chemical bond. The effect of modified $CaCO_3$ nanoparticles on thermal properties of polypropylene (PP) was studied by means of differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA). It was found that $CaCO_3$ significantly affected the crystallization temperature and crystallization degree of PP. Effect of the modified $CaCO_3$ content on mechanical properties of PP/$CaCO_3$ nanocomposites was also studied. The results showed that the modified $CaCO_3$ can effectively improve the mechanical properties of PP. In comparison with PP, the impact strength of PP/$CaCO_3$ nanocomposites increased by about 65% and the hardness increased by about 5%.

Keywords**—**Polypropylene Nanocomposites, Modified Calcium Carbonate, Sodium Stearate, Surface Treatment

I. Introduction

POLYMER nanocomposites have attracted increasing attentions in recent years because of their significant improvement in mechanical performance, thermal stability and/or electrical properties over the matrix polymers [1]. The effects of filler nanoparticles on these properties have been extensively investigated. It has been found that the addition of a few percent by weight of these nanoparticles can result in significant improvement in physical and chemical properties [2]. However, these advantages can only be exploited if filler nanoparticles are distributed homogenously and do not form aggregates in the polymer matrix. Particle aggregation, which is often detected in particulate filled polymers, can result in a number of problems, including deteriorated mechanical properties and poor aesthetics [3]. One of the most efficient ways to hinder aggregate formation is the surface coating of the filler with a surfactant. Surface treatment leads to the decrease of both particle/particle and matrix/filler interaction. As a consequence, surface coated fillers are used practically always for the production of particulate filled thermoplastic products [4]-[5].

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Several researchers attempted to modify polymeric materials by filling with nanometer inorganic rigid particles, and discussed the dispersion property as well as its mechanisms, such as mica, talcum powder, rectorite, organoclay, carbon nanotube, bentonite, and so on, [6]-[7]. Among these fillers, calcium carbonate ($CaCO_3$) is one of the most commonly used inorganic fillers in polymer. It based fillers have extensively been used because of their low-cost and availability. Its composites find a wide range of application like sewer pipes, garden furniture, breathable films, etc. It has been reported that the addition of $CaCO_3$ nanoparticles could improve the thermal and mechanical properties of polypropylene (PP) [8]. The surface of $CaCO_3$ nanoparticles also is usually modified in order to prevent agglomeration of the particles. In this study, we modified the surface of $CaCO_3$ nanoparticles using sodium stearate to disperse them into the PP matrices without aggregation, and investigated the thermal and mechanical properties of nanocomposites.

II. Experimental Methods

A. Materials

PP pellet (homopolymer) was purchased from Liack Seng Trading Co., Ltd. under the trade name HP500N (6331); the density was 0.946 g/cm^3 and the melt flow index was 12.0 g/10 min. Nano-precipitated $CaCO_3$ (NPCC 101) were supplied by Behn Meyer Chemical (T) Co., Ltd. and had a density of 2.5-2.6 g/cm^3 and a diameter mean (d) of 40 nm. Sodium stearate was supplied by Sigma-Aldrich. All chemicals used were analytical grade reagents.

B. Surface Modification of $CaCO_3$ Nanoparticles

The $CaCO_3$ nanoparticles were surface modified using sodium stearate prior to melt blending with PP. $CaCO_3$ 300 g was dried at 120 ^oC for 4 h and was dissolved in 1.2 l solution mixture of water and ethanol (the volume ratio between water and ethanol was 2:1) and the suspension was stirred for 2 h. The temperature of the mixture was increased up to 80 ^oC, and sodium stearate was added drop by drop. The mixture was further stirred at 300 rpm for 2 h. At last, the modified $CaCO_3$ nanoparticles were rinsed with deionized water and dried at 120 ^oC for 12 h in an oven [9].

C. Preparation of $CaCO_3$/PP Nanocomposites

All samples were prepared by twin screw extruder and injection molding machine. The weight content of fillers varied from 3 to 7% w/w. The melt blending of fillers and PP pellets were carried out on a co-rotating twin screw extruder (HAAKE, Germany) with the setting temperatures of 170-195 ^oC from hopper to die and the screw speed of 100 rpm. Then, the pellets were injection-molded and the standard specimens for mechanical and thermal properties measurements were prepared using an injection molding machine (Battenfeld Model : BA 250 CDC, Germany). The melt temperatures from hopper to nozzle were set as 175-210 ^oC, and the mould pressure was 40 bar.

D. Characterization

A differential scanning calorimetry (DSC) equipment Perkin Elmer Model: Pyris 1 (USA) was used to study the crystallization and melting behaviors of the samples. DSC scanning program was set as follows: firstly, the sample was heated from -10 to 300 ^oC at the heating rate of 10 ^oC/min and maintained at 300 ^oC for 5 min to erase the thermal history; secondly, the sample was cooled down to -10 ^oC at the cooling rate of 10 ^oC/min. For the annealed specimens, the sample was directly heated from -10 to 300 ^oC at the heating rate of 10 ^oC/min. Thermogravimetric analysis (TGA) equipment Perkin Elmer Model : TGA 7 HT (USA) was employed to examine the thermal degradation of the samples. The weight of each sample was about 7 mg. Experiments were carried out from 50 to 600 ^oC with a heating rate of 10 ^oC/min.

Scanning electron microscopy (SEM) was performed to investigate the impact fracture surfaces of the nanocomposites by a Camscan-MX 2000 (England) equipped with an energy dispersive spectroscope (EDS) to observe the interfacial morphology and the dispersion of the nanoparticles in the PP matrix. The specimens were gold coated before SEM examination.

Tensile tests were performed in a Universal Testing Machine LR 50 K (England) at a crosshead speed of 150 mm/min. Samples for tensile tests conformed to ASTM D638 dumb-bell geometry. The impact test was run using Pendulum Impact Tester Zwick I (USA). The dimension of specimens followed ASTM D256. The Shore D hardness test was carried on a Hardness Tester PTC (USA) according to ASTM D2240 standard. The mechanical properties reported hereinafter are the average of eight successful tests.

III. Results and Discussion

A. Thermal Properties

PP is a kind of typical semi-crystalline polymers, and the crystallization behavior of PP significantly influences its mechanical properties. Thus, investigation of the thermal properties is significant both from the theoretical and practical points of view [7]. The thermal properties of PP/$CaCO_3$ nanocomposites such as crystallization temperature (T_c), melting temperature (T_m), the degree of crystallinity (X_c), initial degradation temperatures (T_d) and char residue obtained from the DSC and TGA studies are summarized in Table I. Generally, $CaCO_3$ has a weak α-nucleation for PP crystallization and that with highly efficiency β-nucleation has not been reported [8]. It can be seen that the T_c and T_m of neat PP were 117.56 ^oC and 164.75 ^oC. The T_c of $CaCO_3$ filled PP slightly decreased with the increasing of the mass ratio of $CaCO_3$/PP.

The results of DSC tests show that PP and PP/$CaCO_3$ nanocomposites has similar T_m. Indeed, T_m is affected by flexibility of chains. It is clear that the presence of nanosized $CaCO_3$ that causes to lessen the flexibility of chains and leads to increase the T_m [10]. The addition of $CaCO_3$ to PP matrix causes a decrease the values of fusion heats. Decreasing of fusion heat can be mainly attributed to substitution of PP by nanosized $CaCO_3$. Since the main consumption part of fusion heat relates to change of crystal domain to amorphous structure, thus it may be concluded that the presence of nanosized of $CaCO_3$ in matrix has a great effect on decreasing of crystal domain. As a matter of fact the effect can be attributed to the fact that nanoparticles place in amorphous region and prevent the nucleation and growth of crystal domain [11].

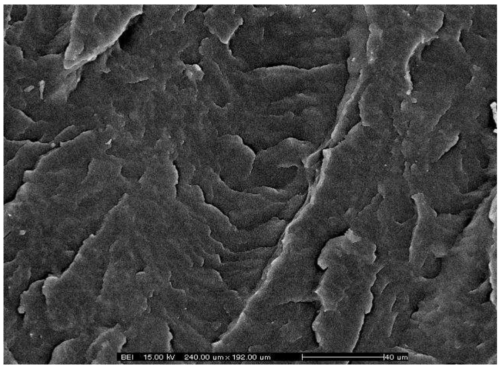
Table I shows TGA data of PP/$CaCO_3$ nanocomposites in pure nitrogen environment. It is found that pure PP showed the lowest thermal stability, based upon T_d, 270.01 ^oC. PP/$CaCO_3$ nanocomposites have higher T_d and char residue compared with neat PP.

TABLE I
THERMAL PROPERTIES OF NEAT PP AND PP/$CaCO_3$ NANOCOMPOSITES

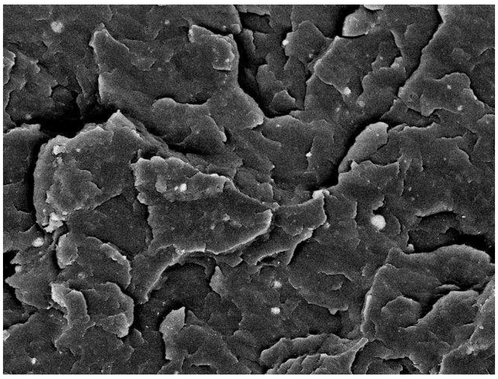
Materials	T_c [^oC]	T_m [^oC]	X_c [%]	T_d [^oC]	Char Residue [%]
Neat PP	117.56	164.75	60.27	270.01	1.70
PP/3% $CaCO_3$	113.88	162.37	45.40	370.11	40.95
PP/5% $CaCO_3$	114.40	165.08	41.07	451.21	60.51
PP/7% $CaCO_3$	115.39	165.28	23.32	386.88	68.00

B. Surface Morphology

The dispersion of the nanoparticles will have a significant effect on the mechanical properties of the nanocomposites. The morphology of nanocomposites was evaluated by SEM to observe the distribution of nanoparticles within the materials. Fig. 1 shows micrographs of a fractured surface of the nanocomposites. The fracture surface of the pure PP was smooth and featureless, but fairly good nanoparticle dispersion is seen in these micrographs [12]. The dispersion is found to be better for nanocomposites containing 3% w/w $CaCO_3$ nanoparticles. At filler content of 7% w/w, aggregates of nanoparticles are found. However, in spite of using sodium stearate for preventing the coalescence of nanoparticles, partial coalescence was unavoidable, especially at higher nanoparticle content [2].



(a)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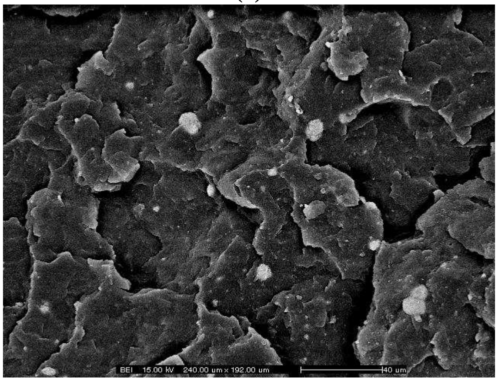
(c)

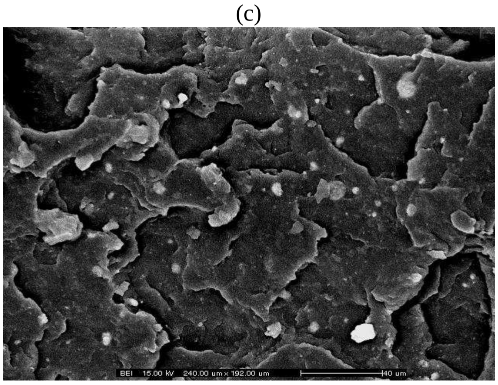
(d)

Fig. 1 SEM images of materials (a) Neat PP (b) PP/3% $CaCO_3$ (c) PP/5% $CaCO_3$ (d) PP/7% $CaCO_3$

C. Mechanical Properties

The effects of $CaCO_3$ nanoparticles content on mechanical properties of PP matrix were presented in Table II. The results show that the tensile strength of PP slightly decreases with increasing content of fillers. With the filler content of 3% w/w, the tensile strength and tensile modulus were 31.06 MPa and 1.12 GPa, respectively. Hence, the significantly increase in the modulus must be caused by the strong interaction between the polymer and filler, because of the large interfacial area between them [12]. The value of elongation at break obtained at 3-7 wt% of $CaCO_3$ nanoparticles content is higher than that of pure PP sample. The high tensile modulus but and elongation at break, compared with pure PP sample, indicates that this material exhibits ductile behavior. In addition, at higher filler content, aggregates of nanoparticles are found. This may also accounts for the superior mechanical properties of the nanocomposites containing the lower wt% of filler.

The notched impact strength and Shore D hardness were listed in Table II. It can be seen that the impact strength and hardness of PP were 2.85 kJ/m^2 and 66.7, respectively. The impact strength and hardness of PP increased to 4.72 kJ/m^2 and 68.7 with adding 3 wt% of $CaCO_3$ nanoparticles. In comparison with PP, the impact strength of PP/$CaCO_3$ nanocomposites increased by about 65% and the hardness increased by about 3%. In summary, the results showed that the modified $CaCO_3$ can effectively improve the mechanical properties of PP.

TABLE II
MECHANICAL PROPERTIES OF NEAT PP AND PP/$CaCO_3$ NANOCOMPOSITES

Materials	Tensile Strength [MPa]	Young's Modulus [GPa]	Elongation at Break [%]	Impact Strength [kJ/m^2]	Shore D Hardness [-]
Neat PP	33.26	1.06	37.14	2.85	66.7
PP/3% $CaCO_3$	31.06	1.12	80.79	4.72	68.7
PP/5% $CaCO_3$	30.51	1.08	68.91	4.69	69.9
PP/7% $CaCO_3$	29.78	1.11	56.07	4.17	70.3

IV. CONCLUSION

PP/$CaCO_3$ nanocomposites with different filler content have been developed. Effect of surface treatment on the mechanical and thermal properties of composites has been studied. The treatment of filler increased the interfacial bonding strength and the wettability of the filler by PP matrix leading to the enhancement in mechanical properties of the composites. The results of TGA and DSC experiments indicated that the addition of filler enhanced the thermal stability of the composites. In addition, it was found that $CaCO_3$ significantly affected the crystallization temperature and crystallization degree of PP. The morphology, evaluated by scanning electron microscopy (SEM), indicated that a uniform dispersion of fiber in the PLA matrix existed.

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