

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 homogeneously 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 $2.5\text{--}2.6 \text{ g/cm}^3$ 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°C 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°C , 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°C 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 $170\text{--}195^\circ\text{C}$ 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 °C, 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 °C at the heating rate of 10 °C/min and maintained at 300 °C for 5 min to erase the thermal history; secondly, the sample was cooled down to -10 °C at the cooling rate of 10 °C/min. For the annealed specimens, the sample was directly heated from -10 to 300 °C at the heating rate of 10 °C/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 °C with a heating rate of 10 °C/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/CaCO₃ 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, CaCO₃ 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 °C and 164.75 °C. The T_c of CaCO₃ filled PP slightly decreased with the increasing of the mass ratio of CaCO₃/PP.

The results of DSC tests show that PP and PP/CaCO₃ nanocomposites has similar T_m . Indeed, T_m is affected by flexibility of chains. It is clear that the presence of nanosized CaCO₃ that causes to lessen the flexibility of chains and leads to increase the T_m [10]. The addition of CaCO₃ 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 CaCO₃. 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 CaCO₃ 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].

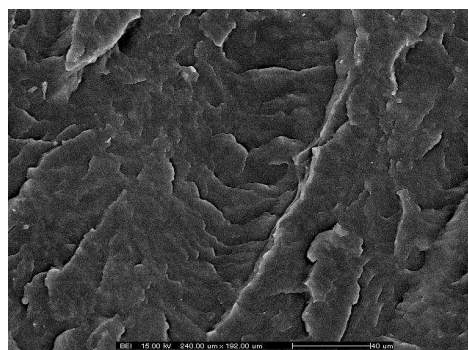
Table I shows TGA data of PP/CaCO₃ nanocomposites in pure nitrogen environment. It is found that pure PP showed the lowest thermal stability, based upon T_d , 270.01 °C. PP/CaCO₃ nanocomposites have higher T_d and char residue compared with neat PP.

TABLE I
THERMAL PROPERTIES OF NEAT PP AND PP/CaCO₃ NANOCOMPOSITES

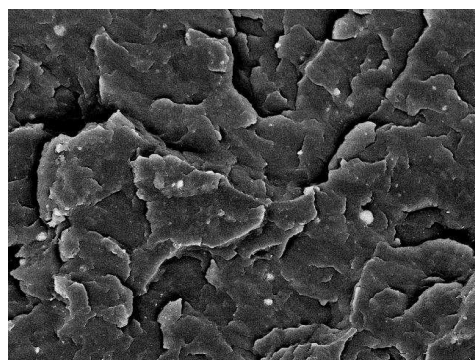
Materials	T_c [°C]	T_m [°C]	X_c [%]	T_d [°C]	Char Residue [%]
Neat PP	117.56	164.75	60.27	270.01	1.70
PP/3% CaCO ₃	113.88	162.37	45.40	370.11	40.95
PP/5% CaCO ₃	114.40	165.08	41.07	451.21	60.51
PP/7% CaCO ₃	115.39	165.28	23.32	386.88	68.00

B. Surface Morphology

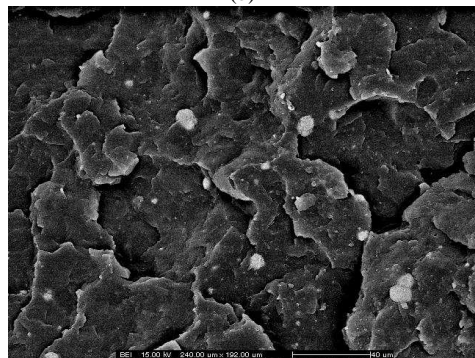
The dispersion of the nanoparticles will have a significant effect on the mechanical properties of the nanocomposites. The morphology of nanocomposites was evaluated by SEM to observe the distribution of nanoparticles within the materials. Fig. 1 shows micrographs of a fractured surface of the nanocomposites. 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 CaCO₃ 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].



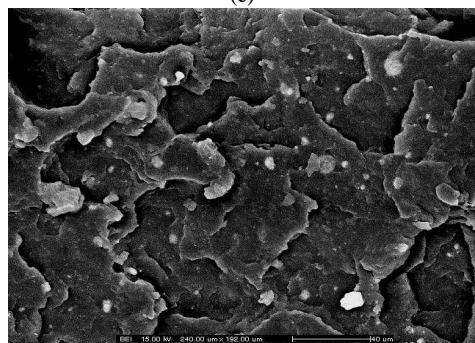
(a)



(b)



(c)



(d)

Fig. 1 SEM images of materials (a) Neat PP (b) PP/3% CaCO₃ (c) PP/5% CaCO₃ (d) PP/7% CaCO₃

C. Mechanical Properties

The effects of CaCO₃ 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 CaCO₃ 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/m² and 66.7, respectively. The impact strength and hardness of PP increased to 4.72 kJ/m² and 68.7 with adding 3 wt% of CaCO₃ nanoparticles. In comparison with PP, the impact strength of PP/CaCO₃ nanocomposites increased by about 65% and the hardness increased by about 3%. In summary, the results showed that the modified CaCO₃ can effectively improve the mechanical properties of PP.

TABLE II
MECHANICAL PROPERTIES OF NEAT PP AND PP/CaCO₃ 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/CaCO₃ 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 CaCO₃ 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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REFERENCES

- [1] Y. Lin, H. Chen, C.M. Chan, J. Wu, "Nucleating effect of calcium stearate coated CaCO₃ nanoparticles on polypropylene," *J. Colloid Interface Sci.*, 354 (2), pp. 570–576, 2011.
- [2] S. Karamipour, H. Ebadi-Dehaghani, D. Ashouri, S. Mousavian, "Effect of nano-CaCO₃ on rheological and dynamic mechanical properties of polypropylene: Experiments and models," *Polym. Test.*, 30, pp. 110–117, 2011.
- [3] A. Kiss, E. Fekete, B. Pukánszky, "Aggregation of CaCO₃ particles in polypropylene composites: Effect of surface coating," *Compos. Sci. Technol.*, 67, pp. 1574–1583, 2007.
- [4] R.G. Raj, B.V. Kokta, F. Dembele, B. Sanschagrin, "Compounding of cellulose fibres with polypropylene: Effect of fibre treatment on dispersion in the polymer matrix," *J. Appl. Polym. Sci.*, 38 (11), pp. 1987–1996, 1989.

- [5] P. Mareri, S. Bastide, N. Binda, A. Crespy, "Mechanical behaviour of polypropylene composites containing fine mineral filler: Effect of filler surface treatment," *Compos. Sci. Technol.*, 58, pp. 747–752, 1998.
- [6] J.Z. Liang, "Evaluation of dispersion of nano-CaCO₃ particles in polypropylene matrix based on fractal method," *Compos. Part A: Appl. Sci. Manuf.*, 38 (6), pp. 1502–1506, 2007.
- [7] B. Shentu, J. Li, Z. Weng, "Effect of oleic acid-modified nano-CaCO₃ on the crystallization behavior and mechanical properties of polypropylene," *Chinese J. Chem. Eng.*, 14, pp. 814–818, 2006.
- [8] Z. Zhang, C. Wang, Y. Meng, K. Mai, "Synergistic effects of toughening of nano-CaCO₃ and toughness of β -polypropylene," *Compos. Part A: Appl. Sci. Manuf.*, 43 (1), 189–197, 2012.
- [9] L. Han, X. Li, Y. Li, T. Huang, Y. Wang, J. Wu, F. Xiang, "Influence of annealing on microstructure and physical properties of isotactic polypropylene/calcium carbonate composites with β -phase nucleating agent," *Mater. Sci. Eng. A*, 527, pp. 3176–3185, 2010.
- [10] S.S. Saghi, S.M. Zebarjad, J.V. Khaki, S.A. Sajjadi, "The effect of nano-sized calcium carbonate on thermodynamic parameters of HDPE," *J. Mater. Process. Technol.*, 209, pp. 1310–1317, 2009.
- [11] S.M. Zebarjad, M. Tahani, S.A. Sajjadi, "Influence of filler particles on deformation and fracture mechanism of isotactic polypropylene," *J. Mater. Process. Technol.*, 155–156, pp. 1459–1464, 2004.
- [12] C.M. Chan, J. Wu, J.X. Li, Y.K. Cheung, "Polypropylene/calcium carbonate nanocomposites," *Polymer*, 43, pp. 2981–2992, 2002.

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