

Preparation and Characterization of Calcium Carbonate/Low-Density-Polyethylene Nanocomposites

Wen-Yi Wang,¹ Xiao-Fei Zeng,¹ Guo-Quan Wang,² Jian-Feng Chen^{1,3}

¹Key Laboratory for Nanomaterials, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

²Institute of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

³Research Center of the Ministry of Education for High Gravity Engineering and Technology, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

Received 11 December 2006; accepted 2 April 2007

DOI 10.1002/app.26833

Published online 20 July 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Calcium carbonate/low-density-polyethylene (LDPE) nanocomposites have been prepared by melting blend with twin-screw extruder. The mechanical properties of composites and the dispersion of the nanoparticles were studied. The reinforcement mechanism was discussed. The results show that not only the tensile property but also the flexural modulus of the system have been evidently increased by the addition of calcium carbonate. The calcium carbonate particles have been dispersed in the matrix in the nanometer scale. The reinforcement mecha-

nism of the calcium carbonate lies on that the calcium carbonate particles, acting as hetero-nuclei, can induce higher crystallinity at the matrix-particle interface compared to regions away from the interface. Consequently, in the process of the tensile test, the nanocomposites have better tensile yield strength. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1932–1938, 2007

Key words: nano-CaCO₃ particles; LDPE; nanocomposites; reinforcement

INTRODUCTION

Thermoplastic materials are being increasingly considered in agriculture, automotive, aerospace, and electronic. Thermoplastics such as polypropylene and polyethylene have excellent chemical resistance and have emerged as ideal materials for automobile and consumer products. However, they are seldom used as neat polymers and are usually compounded with mineral fillers. Initially, fillers were used as “extenders” for polymers to reduce cost but as the cost of polymer and the requirements of modern applications increased, attention has been more and more focused on functionality enhancement.^{1–3} Nowadays, “functional fillers” find application in the polymer industrial most exclusively, for example, to improve stiffness, toughness, dimensional-stability, electric-insulation, or to decrease the dielectric loss. A prerequisite for functional fillers is full dispersion (break-up of agglomerates in to their primary particles) and uniform spatial distribution in the polymer matrix because agglomerates entrap air and act as sites for fracture initiation, thus leading to premature material failure.^{4,5}

The traditional successful toughening method is the elastomer toughening the plastic.^{6–8} Recently, in the mechanism for rubber toughening in noncrazing polymers, it shows that these particles can facilitate the development of microvoids and activate dilatational yielding in the deformed zone close to the fracture surface.

Similar to the requirement of void creation via cavitation in the rubber-toughening mechanism, which is proposed for the toughening to occur in rigid filler systems, the particles must debond from the matrix, creating voids around the particles, and allowing the interparticle ligaments to deform plastically. In fact, the stretching of the matrix ligaments between cavitated or debonded particles is the main adsorbing energy mechanism. On the other hand, voids reduce the macroscopic plastic resistance of the material and void coalescence also potentially decreases the fracture strain and the overall toughness achievable by the material. Ideally, the voids should not form immediately upon the application of stress as this may reduce the elastic modulus.

On improving the toughness, it is necessary to obtain a low particle matrix adhesion, at the same time, it is also necessary to prevent particle agglomeration and void coalescence. The two conditions are often contradictory. When the adhesion between a second phase particle and the matrix is weak, agglomeration is most often observed, while a strong

Correspondence to: J.-F. Chen (chenjf@mail.buct.edu.cn).

adhesion, although enabling to achieve a uniform dispersion, almost inevitably leads to a lack of debonding and brittle behavior. The problem is even more difficult to be solved since, for these reasons, to get different purposes, different surface agents can be used.⁹⁻¹¹

In this study, the mechanical and thermal properties of LDPE composites filled with nano-calcium carbonate (nano-CaCO₃) were investigated. Dispersion of nano-CaCO₃ was investigated by means of TEM. Strength enhancing of the nanocomposites was tested by SEM. The approach followed is that of trying to elucidate the effects of interfacial interactions on physical and mechanical properties of the composites. The mechanisms of crystallinity and spacious superficial interface in calcium carbonate-reinforced polyethylene are investigated as an important constituent of deformation behavior, and compared with neat polyethylene processed under identical conditions. The differences in the deformation behavior of the two materials are discussed in terms of modulus and crystallinity.

EXPERIMENTAL

Materials

Low-density-polyethylene (LDPE, 1F7B), the nominal melting index of which is about 7 g/10 min at 190/2.16 (i.e., at 190°C and 2.16-kg piston force), was supplied as pellets by Yanshan Petrochemical Company, China.

The nanosized precipitated calcium carbonate (cubic shape; an average primary particle size of 40 nm) is prepared by our research center, which was coated with stearic acid to increase dispersion and compatibility with the polymer matrix. It was designed to be a reinforcing additive to improve the various properties of plastic materials.

The preparation of nano-calcium carbonate dispersed in LDPE

To get a good dispersibility of the calcium carbonate particles, masterbatch is prepared. LDPE was melt-mixed with calcium carbonate particles using a twin-screw extruder (PE-20, Keya Company Limited, Nanjing, Jiangsu Province, China). The temperatures of the extruder are ordinal 120, 145, 175, and 170°C. The mixing weight ratio of LDPE and nano-CaCO₃ is 3 : 7.

The preparation of calcium carbonate /LDPE nanocomposites

The pellets of calcium carbonate/LDPE composites were prepared by the twin-screw extruder. The

TABLE I
Compositions of the LDPE and the Masterbatch

Sample	LDPE (wt %)	Masterbatch (wt %)
1	100	0
2	90	10
3	80	20
4	70	30
5	50	50
6	30	70

LDPE and the masterbatch were mixed as pro-ratio. Table I showed the mixing weight ratio of LDPE to masterbatch. The nanocomposites were prepared by the injection-molding machine (JN88-E, Chen Hsong Machinery, China), the temperatures of which were ordinal 145, 185, and 185°C.

Mechanical properties of the nanocomposites

The impact strength of the nanocomposites was measured by Charpy pendulum impact testing machines (XJJ-5, ChengDe Jinjian Testing Machine Company, Hebei Province, China) at room temperature and -20°C. The tensile (testing speed: 50 mm/min) and the flexural (testing speed: 10 mm/min) properties were recorded by Instron universal testing machine (Instron 1185, Instron Company, England) 20°C (293 K).

Microstructure microscopy of the fracture section of the composites

The microstructure microscopy of the fracture section of the composites was evaluated by scanning electron microscopy (SEM). The surfaces prepared by tensile testing machine were platinum/palladium sputter coated. SEM images were obtained by (Cambridge-S250MK3, England).

Thermal stability

The samples were analyzed by thermogravimetric analysis (TGA), using a Netzsch STA-449c Thermal Analyzer (Netzsch Company, Germany) under nitrogen flow from 50 to 800°C at the rate of 10.00°C/min. The TG curves were shown in Figure 5. The 5% loss temperature ($T_{5\%}$), the maximum weight loss temperatures (T_{max}), and char residue at 800°C are listed in Table IV.

Crystallinity of the matrix

The samples were analyzed by the differential scanning calorimeter (DSC) using a DSC-2 (PerkinElmer Company, America) under nitrogen heat and hold for 5 min at 150°C and then cooled from 150 to 30°C

TABLE II
Values of T_c , T_{onset} , and ΔH_c for Neat LDPE
and CaCO₃/LDPE Composites

Sample	LDPE	LDPE/CaCO ₃ (7 wt %)	LDPE/CaCO ₃ (21 wt %)
T_p (°C)	92.24	93.98	96.90
T_{onset} (°C)	95.57	97.31	100.01
ΔH_c (J/g)	-77.09	-74.72	-74.11

at the rate of 10.00°C /min to get crystallization curve. The crystallinity properties are shown in Table II.

Evaluation of dispersibility of the nanoparticles in LDPE matrix

The dispersion of the calcium carbonate was evaluated by transmission electron microscopy (TEM). TEM specimens were cut at -90°C using an ultramicrotome (LKB-5, Switzerland) with a diamond knife. TEM images were obtained by Hitachi H-800 (Japan) with the acceleration voltage of 200 kV.

RESULTS AND DISCUSSION

Mechanical properties of calcium carbonate/LDPE nanocomposites

As structure materials, mechanical properties are very important. So, these properties are tested in this study. When impacted at the room temperature, the samples of the neat LDPE and the nanocomposites do not break, which is difficult to distinguish which is better, and so the impact property is gotten at -20°C.

Figure 1 is the curve of the impact properties and the flexural modulus of the nanocomposites changed by the addition of the calcium carbonate particles. It shows that when calcium carbonate particles are added, the impact strength of the nanocomposites have a descending trend.

From the SEM images, it is clear that there is better adhesion between particles and matrix, so that the particles could not create the void and allow the interparticle ligaments to deform plastically, which induce that nanocomposites have a low toughness. At the same time, the intermolecular distance of LDPE increases because of the particles addition, which decreased the interaction of the macromolecule chain. When the composites are impacted, it is easy to create crack rapidly and only adsorb little energy, which reduce the toughness of the composites. Moreover, the bad influence is added along with the content addition of calcium carbonate.

However, the flexural modulus has evidently increased. The flexural modulus of neat LDPE is 106 MPa. When calcium carbonate particles were added

35 wt %, the flexural modulus of nanocomposite reaches 186 MPa, which is 1.75 times than that of neat LDPE.

From Figure 1, the curve of the flexural modulus shows that the flexural modulus increases more and more evidently along with the content addition of calcium carbonate. The reason is that in low particle content, the particles have better dispersion and large distance between them, which affect flexural modulus independently. However, in large particle content, the range interval of the particles decreases, and so the effect of flexural modulus has a superposed filed, which lead to the flexural modulus increasing evidently.

When calcium carbonate particles was added 49 wt %, the flexural modulus of nanocomposite reaches 328 MPa, which is 3.09 times higher than that of neat LDPE, nevertheless the composite has a bad toughness and a bad rate of elongation at break, which has not a better-applied field.

The engineering stress-strain plots for neat polyethylene, 7, 14, 21, 35, and 49% calcium carbonate-reinforced polyethylene at a rate of 50 mm/min exhibiting elastic and plastic deformation regions are presented in Figure 2. The regions of significance are elastic region, yielding, cold drawing, and fracture.

Figure 2 shows that the reinforcement of neat polyethylene with calcium carbonate decreases fracture strain. It is expected that at a constant displacement rate of tensile test, the fracture strain would decrease with increase in the percent reinforcement.

In the inorganic-particle/semicrystalline polymer composites, the inorganic particles have two functions. First, the particles can act as hetero-nuclei inducing the semicrystalline polymers to crystallization, which is equal to immobilize the macromolecules. Table II shows the crystallinity properties of the nanocomposites and the neat LDPE. It shows

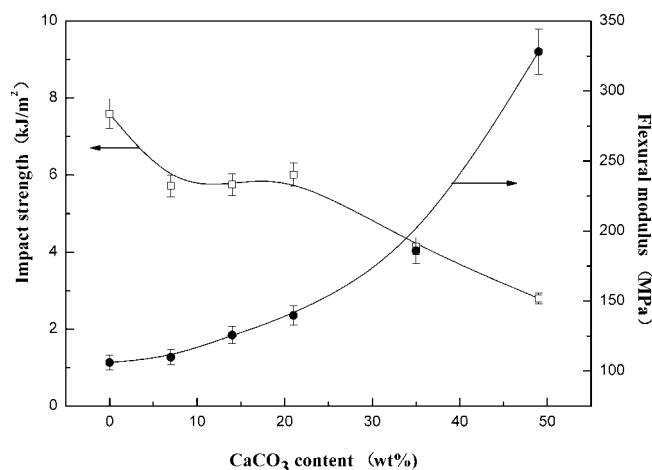


Figure 1 Impact strength and flexural modulus of neat LDPE and CaCO₃/LDPE composites.

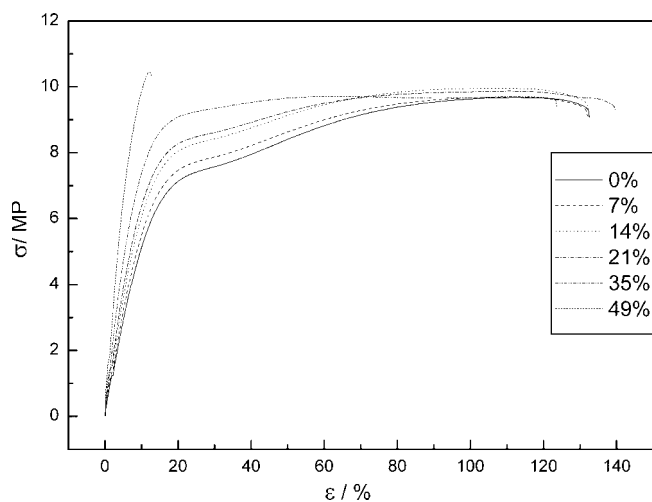


Figure 2 Stress–strain curves of neat LDPE and CaCO_3 /LDPE composites.

that the beginning crystallizing temperature and the peak temperature of the nanocomposites have been higher than those of the neat LDPE. The ΔH of the nanocomposites has been decreased a little, which means that the crystallinity of the nanocomposites is lower than that of the neat LDPE.

It can be explained that the nanoparticles acting as heterogeneous nucleating agent during crystallization of LDPE from melt are inclined to absorb macromolecule segments, owing to nanoparticles have spacious superficial area, consequently whose movement were constrained and initiate to crystallize. The acceleration of the crystallization and the higher crystallizing point induce the lower crystallinity. These reasons induce higher crystallinity at the matrix-particle interface compared to regions away from the interface.

Atomic force microscopy can also indicate higher crystallinity at the matrix-particle interface compared to regions away from the interface, which recently proposed by Misra and coworkers,¹² using atomic force microscopy. For this reason, the nanocomposites have higher yield strength than the neat polymer matrix. However, this immobilization has a limitation, with increase in stress, greater stress relaxation occurred quickly and the plastic deformation has entered the cold-drawing regions. Second, the matrix-particle interface will provide a potential site for crack nucleation and the failure initiates when the particles are debonded from the matrix such that the fracture strain has a value that is intermediate between the mineral and the polymer matrix.

In the anaphase of the cold drawing, the stresses of the neat polymer and the nanocomposites are equaled by and large, which show that the stresses of resisting exogenic force are supplied by the macromolecule chain and the nanoparticles have less

effects. Ulteriorly, the addition of the nano- CaCO_3 goes beyond the limit will induce the decrease of the tensile properties. For example, added 49 wt % nano- CaCO_3 , the nanocomposite becomes a brittle material.

Two aspects may be noted from Figure 2. First, with the increase in percent reinforcement, the region of cold drawing was maintained and the higher yield strength was gotten. Second, adding nano- CaCO_3 beyond the limit, the composites changed to brittle.

Table III shows the tensile properties of the nanocomposites and the neat LDPE. It shows that added the proper quantities of the calcium carbonate particles, the tensile strength and the elongation at break of nanocomposites are maintained and the tensile yield strength of nanocomposites increased evidently.

Microstructure microscopy of the fracture section of the composites

When the ductile polymer materials are tensioned, the fracture section of the matrix can have roughness and the sections with a bigger deformation are changed form translucent to opaque as the stress whitening set in. However, when the brittle polymer materials are tensioned, the sample will be broken quickly and the fracture section of the matrix is relatively flat and smooth.

The final fracture surface of the nanocomposite was presented in Figure 3 (SEM image). From Figure 3(a), it is clear that the fracture section of the nanocomposite has extensive plastic deformation characterizing ductile fracture, which means that the matrix has absorbed energy through the consequence of stress relaxation.

In Figure 3(b–e), paralleled to the tensile axis, the assemblages of the macromolecule chains have orientated as fibrillated structure (fibrillated structure is characterized by severely deformed lamellae with enhanced plastic flow in cold-drawing process). So, the fracture is characterized by severely deformed fibrils. This type of deformation was

TABLE III
Tensile Properties of Neat LDPE
and CaCO_3 /LDPE Composites

Samples	Tensile strength (MPa)	Tensile yield strength (MPa)	Elongation at break (%)
1	9.7 ± 0.29	7.35 ± 0.20	132.6 ± 4.2
2	9.69 ± 0.28	7.62 ± 0.25	132.0 ± 4.6
3	9.80 ± 0.4	8.27 ± 0.18	132.4 ± 4.8
4	9.87 ± 0.31	8.34 ± 0.21	139.6 ± 6.0
5	9.76 ± 0.28	9.13 ± 0.18	123.6 ± 5.2
6	10.34 ± 0.37	10.34 ± 0.30	12.6 ± 2.0

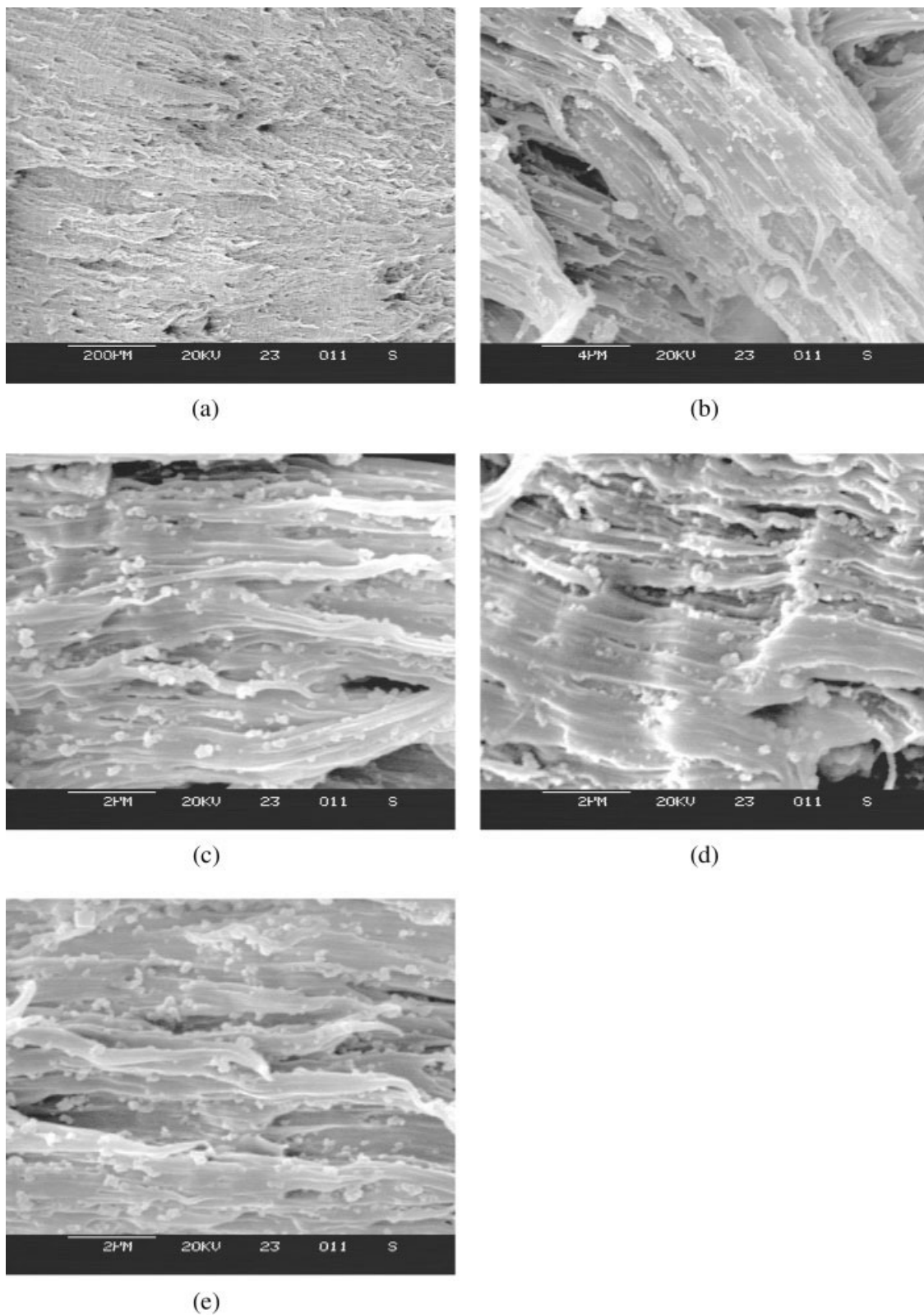


Figure 3 SEM images of the composite filled with 21 wt % nano- CaCO_3 .

defined as fibrillated deformation. Also, from Figure 3(b–e), it shows that on the surface of the fibrils, the nanoparticles have a strong interaction with the matrix.

Thermal degradation

Thermal stability is an important property for which the nanocomposite morphology plays an important

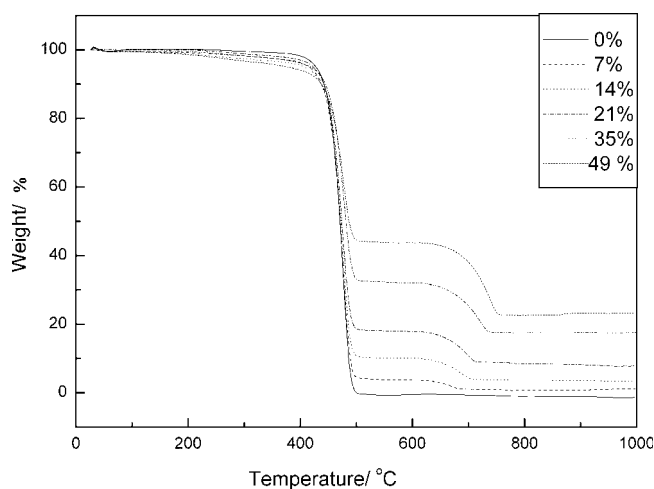


Figure 4 TG curves for neat LDPE and CaCO₃/LDPE composites.

role. The calcium carbonate/LDPE hybrids were analyzed by TGA. The TG curves were shown in Figure 4. The onset loss temperature (T_{onset}), the 5% loss temperature ($T_{5\%}$), the maximum weight loss temperatures (T_{max}), and char residue at 800°C were listed in Table IV. Figure 4 shows that the thermal stability of nanocomposites is about equal to that of the neat LDPE.

In Figure 4, the nanocomposites have two degradation steps: the first degradation step is polymer degradation; the second degradation step is calcium carbonate particles degradation, which is different to the degradation of neat LDPE that has one degradation step. The results show that calcium carbonate particles stabilize LDPE a little. The curve slope of the polymer degradation step (the maximum degradation velocity) in nanocomposites is less than that of neat LDPE. The probable reasons may be that in nanocomposites, along with the degradation proceeding, the content of the calcium carbonate particles has increased, which induced the assembling of the calcium carbonate particles, which may occur on the surface of the nanocomposites creating a physical protective barrier on the surface of the material.

Table IV reveals that the calcium carbonate/LDPE nanocomposites show a less thermal stability. Filled calcium carbonate, the thermal gravimetric loss temperature of nanocomposites was almost equal to that of the neat LDPE, which is different to the organo-montmorillonite-filled polymer matrix.^{13–15}

In Table IV, the char residue of nanocomposites tends to increase compared with that of polymer matrix. The char residue of neat LDPE is 0.53 wt %, because the condition is under the nitrogen, which leads to part of the polymer carbonized.

Dispersibility of the calcium carbonate particles in LDPE matrix

The better the inorganic particles disperse in the polymer matrix, the better the mechanical or other properties of the nanocomposites will be. However, the dispersion of the inorganic particles in a thermoplastic is not easy because of two reasons. First, the surface of the nano-CaCO₃ particles has the hydrophilic groups; second, the nanoparticles have a strong tendency to agglomerate, because the nano-CaCO₃ particles have small radius and has a large surface energy. To have a good dispersion, the surface modification must be done.

The dispersion of the nano-CaCO₃ particles in LDPE matrix is shown in Figure 5. Figure 5(a,b) is filled with 21 wt % calcium carbonate; Figure 5(c–e) is filled with 55 wt % nano-CaCO₃. Figure 5(a,c) is magnified 10k times; Figure 5(b,d,e) is magnified 50k times. Figure 5(a,c) shows that the calcium carbonate has been dispersed in the polymer matrix in the nanometer scale. Because the dispersion only occurred in the twin-screw extruder and the blending time was transitory, some of the calcium carbonate particles were existed as aggregates. Comparing Figure 5(a) with Figure 5(c), with the addition of the nano-CaCO₃, the distance between the nanoparticles was smaller, the reuniting chance of the nanoparticles was added, which leads the dispersion of the calcium carbonate particles decreased, which is clearly in Figure 5(e) that the aggregate is bigger with a large content of the nano-CaCO₃.

Figure 5(b,d) shows that most of the nano-CaCO₃ particles are dispersed well and existed in the polymer matrix in a primary particles state. Even in the aggregate, the calcium carbonate particles were not connected tightly, which were aggregated unconsolidated.

CONCLUSION

LDPE-based nanocomposites were prepared by melting blend with twin-screw extruder. The calcium carbonate particles added to the thermoplastics can evidently increase flexural modulus and the yield strength of the composites at the same time. The

TABLE IV
Thermal Properties of Neat LDPE and CaCO₃/LDPE Composites

Sample	T_{onset} (°C)	$T_{5\%}$ (°C)	T_{max} (°C)	Char residue at 800°C (wt %)
1	441.7	426.7	481.7	0.56
2	439.5	412.5	477.5	0.67
3	437.3	402.3	477.2	3.64
4	441.7	421.7	476.5	8.47
5	443.1	418.2	483.1	17.51
6	437.1	380.5	481.1	22.55

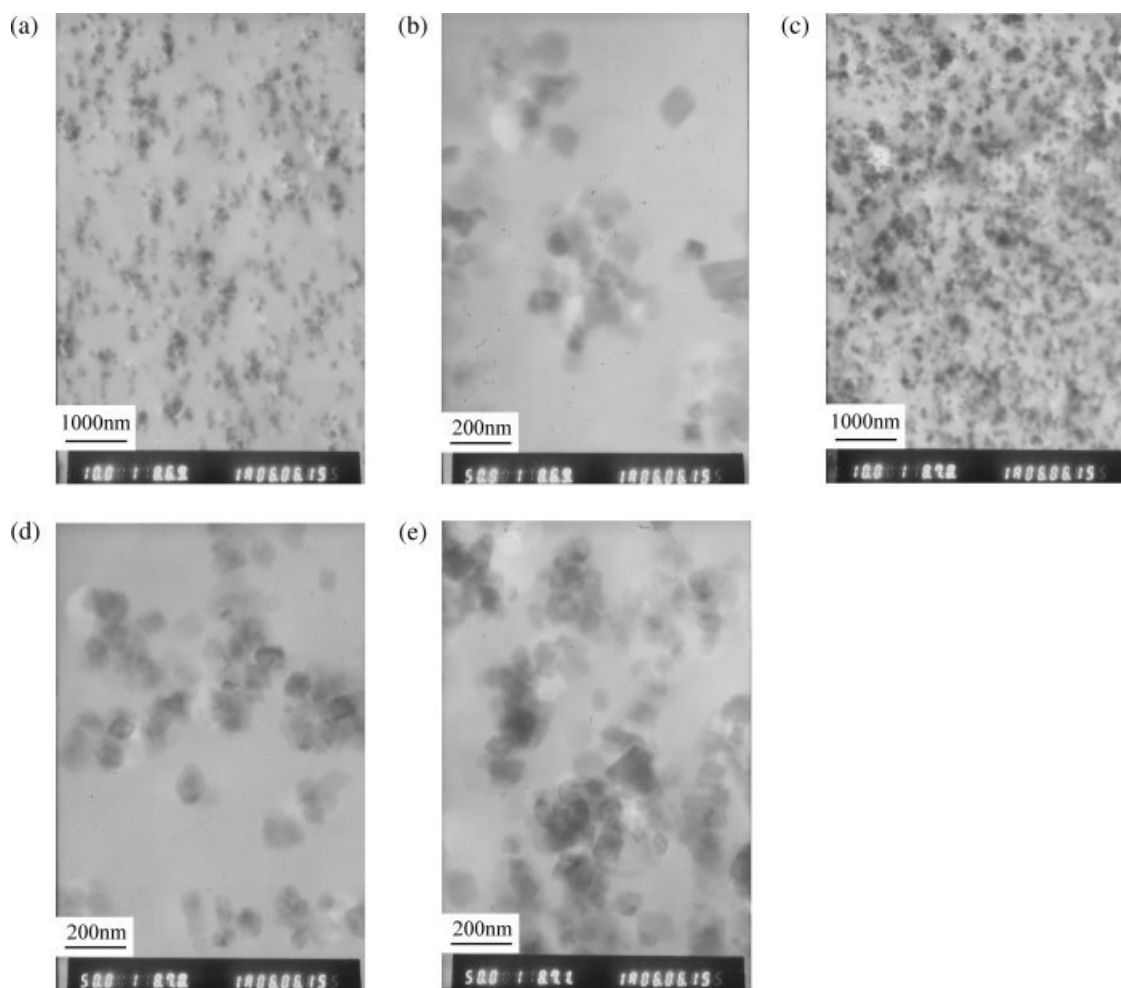


Figure 5 TEM images of the composite: (a) and (b) filled with 21 wt % nano-CaCO₃; (c), (d), and (e) filled with 35 wt % nano-CaCO₃.

DSC results show that the calcium carbonate particles act as heterogeneous nucleating agent during the crystallization of LDPE because of the spacious superficial area. From the TGA, the calcium carbonate particles have no effect on the matrix. The nanocomposites structure is demonstrated by SEM and TEM. This work also shows that calcium carbonate/LDPE nanocomposites can be prepared in ordinary machines, which provide a general concept for manufacturing polymer nanocomposites by direct melting blending.

References

- Almeras, X.; Le Bras, M.; Hornsby, P.; Bourbigot, S.; Marosi, Gy.; Keszei, S.; Poutch, F. *Polym Degrad Stab* 2003, 82, 325.
- Leong, Y. W.; Abu Bakar, M. B.; Mohd Ishak, Z. A.; Ariffin, A. *Polym Degrad Stab* 2004, 83, 411.
- Tang, Y.; Hu, Y.; Song, L.; Zong, R.; Gui, Z.; Chen, Z.; Fan, W. *Polym Degrad Stab* 2003, 82, 127.
- Zebarjad, S. M.; Tahani, M.; Sajjadi, S. A. *J Mater Process Technol* 2004, 155, 1459.
- Li, Y.; Fang, Q. F.; Yi, Z. G.; Zheng, K. *Mater Sci Eng A* 2004, 370, 238.
- Tam, W. Y.; Cheung, T.; Li, R. K. Y. *Polym Test* 1993, 15, 333.
- da Silva, A. L. N.; Coutinho, F. M. B. *Polym Test* 1993, 15, 45.
- Yang, J.; Zhang, Y.; Zhang, Y. *Polymer* 2003, 44, 5047.
- Xu, W.; Liang, G.; Zhai, H.; Tang, S.; Hang, G.; Pan, W.-P. *Eur Polym J* 2003, 39, 1437.
- Yu, Y.-H.; Lin, C.-Y.; Yeh, J.-M. *Polymer* 2003, 44, 3553.
- Tanniru, M.; Misra, R. D. K.; Berbrand, K.; Murphy, D. *Mater Sci Eng A* 2005, 404, 208.
- Dasari, A.; Misra, R. D. K. *Acta Mater* 2004, 52, 1383.
- Wenyi, W.; Xiaofei, Z.; Guoquan, W.; Jianfeng, C. *J Appl Polym Sci* 2003, 100, 2875.
- Tang, Y.; Hua, Y.; Zhang, R.; Gui, Z.; Wang, Z.; Chen, Z.; Fan, W. *Polymer* 2004, 45, 5317.
- Chow, W. S.; Mohd Ishak, Z. A.; Karger-Kocsis, J.; Apostolov, A. A.; Ishiaku, U. S. *Polymer* 2003, 44, 7427.