An Investigation About Solid Equal Channel Angular Extrusion on Polypropylene/Organic Montmorillonite Composite

Hong Li,[1] Xun Huang,[2] Chengya Huang,[3] Yaoming Zhao[3]

[1]*Faculty of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510090, People's Republic of China*
[2]*School of Chemistry and Chemical Engineering, Sun-Yat Sen University, Guangzhou 510275, People's Republic of China*
[3]*College of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, People's Republic of China*

Received 18 May 2010; accepted 24 April 2011
DOI 10.1002/app.34739
Published online 23 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The solid equal channel angular extrusion (ECAE) process on polypropylene (PP)/organic montmorillonite (OMMT) was carried out. Scanning electron microscopy, polarized optical microscopy, transmission electron microscopy, and X-ray diffraction were used to observe and characterize the samples structures. Experimental results show that both PP spherulites and OMMT particles were significantly deformed and orientated toward the shearing direction, and OMMT agglomeration particles were broken into needle-like primary particles, some even exfoliated into nanosilicate layers after twice ECAE processes due to the immense solid shear force. This solid process approach introduces a new way to prepare PP/OMMT nanocomposites. The mechanism of exfoliation between PP and OMMT was also discussed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2222–2227, 2012

Key words: polypropylene; organic montmorillonite; equal channel angular extrusion; exfoliation; nanocomposite

INTRODUCTION

Organic montmorillonite (OMMT) was first used as reinforcing filler in polymer/clay hybrid by Usuki et al.[1] OMMT was exfoliated and dispersed in Nylon-6 matrix after the intercalation, and the formed Nylon-6/OMMT composite, which was called polymer/clay nanocomposite, showed great improvement in the heat distortion temperature of Nylon-6. The modulus of Nylon-6/OMMT composite approximately doubled when the content of OMMT was only 4.5 wt %.[1] Since then, polymer/clay nanocomposite has attracted wide attention in the world.

Polypropylene (PP) is one of most widely used polymer materials, various PP/OMMT nanocomposites have also been prepared by different stragtegies,[2–7] including fusion intercalation, solution intercalation, and monomer *in situ* reaction. Fusion intercalation refers to mixing PP with OMMT in an extruder above the melting point of PP, to exfoliate and disperse the OMMT in PP matrix. Solution intercalation refers to dissolving PP and modified MMT in specific solute and then evaporating the solution to form an exfoliated PP/OMMT nanocomposite. The affinity of OMMT for PP is much weaker than for Nylon, the exfoliation and the dispersion of OMMT in PP is rather difficult because of the weak polarity of PP, therefore, the reinforcement of PP depends on the increasing shearing force during the blending of PP with OMMT. The viscosity of PP in solid state is several million times larger than that of PP in molten state,[8] if a solid extrusion is conducted after mixing OMMT with PP, the exfoliation and dispersion of OMMT will be improved greatly. In this paper, the solid extrusion of PP/OMMT complex was investigated, and the exfoliation and dispersion of OMMT in PP matrix were observed.

Equal channel angular extrusion (ECAE) is a newly developed technique for processing solid polymer materials.[9–14] This processing method consists of extruding a sample through a die with two channels of equal cross-section. A huge shearing force is occurred in the crossing plane of two channels and leads to plastic deformation. Because the cross-section of solid processed sample is same as that before extrusion, the solid extrusion of the samples can be processed repeatedly.

EXPERIMENTAL

Materials

PP F401, with melt flow index of 2.5 g/10 min, was produced by Sinopec™. OMMT, primer particle size 100–160 nm and agglomeration size 5–10 μm, was

Correspondence to: H. Li (lihong@gdut.edu.cn).

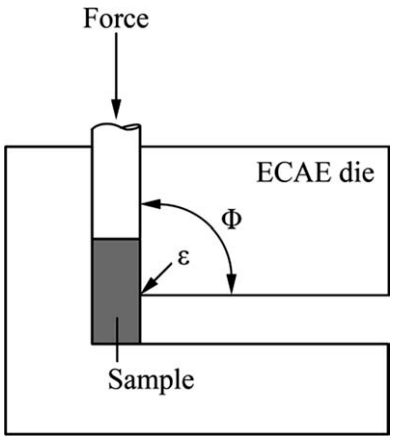

Figure 1 Schematic illustration of ECAE process.

produced by Institute of Shanxi Minerals and Chemical Industry.

Sample preparation

PP and OMMT were blended by open mill at 180°C for 10 min. Then, the molten mixture was compressed into a 125 × 100 × 10 mm^3 plate sample mold, cooled down to the room temperature. PP/OMMT sample plates were prepared and then cut into sample bars with cross-sections of 25 × 10 mm^2.

Solid extrusion

The ECAE process was schematically shown in Figure 1. An internal angle of 90° between two channels with cross-section dimensions of 25 × 10 mm^2 was adopted. When a sample passes through the ECAE die, the plastic shear strain assigned to the sample can be given by the following theoretical expression[15]:

$$\varepsilon = \frac{2}{\sqrt{3}} \cot\left(\frac{\emptyset}{2}\right) \quad (1)$$

In our case, $\phi = 90°$, eq. (1) gives a plastic shear strain $\varepsilon = 1.15$.

Solid extrusion was conducted at room temperature (about 25°C) with constant ram speed of 3 mm/min. Because ECAE processing speed was very slow, PP sample had little temperature change when processing through ECAE channel. When ram speed was 3 mm/min, temperature change of PP sample in ECAE processing is shown in Figure 2.

The sample ECAE-PP/OMMT was extruded once, whereas the sample ECAE-PP/OMMT-A was extruded twice without changing direction as illustrated in Figure 3.

Analysis equipment

The samples observed were cut with the microtome into an ultrathin cross-section of 10–20 μm. The sample spherulites were observed with a JNOEC™ Nikon™-YS2 polarized optical microscopy (POM) equipped with a Nikon™ 4500 digital camera. A JSM-5910 scanning electron microscopy (SEM) was used to observe the sample cryogenic breaking surface. Before observation, these samples were treated first with an etching agent[16,17] (a solution of 1.3 g/100 g $KMnO_4$, 65.8 g/100 g H_2SO_4, and 32.9 g/100 g H_3PO_4) for 24–48 h, then washed out the etching agent thoroughly and dried at room temperature, and then sprayed with a layer of Au in vacuum. X-ray diffraction (XRD) measurements were performed using a *D*/max-IIIA, with a Cu tube source ($\lambda = 0.154$ nm).

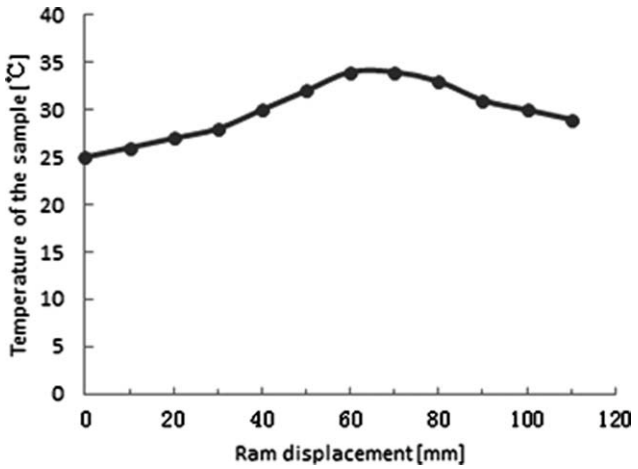

Figure 2 Temperature change of PP sample in ECAE process.

RESULTS AND DISCUSSION

Effect of ECAE process on the morphology of PP crystallite

A series of PP/OMMT complex (OMMT content: 1 wt %, 2 wt %, and 5 wt %) were adopted to examine the effect of the ECAE process. The large spherulite in neat PP sample was observed [Fig. 4(a)]. After adding OMMT, the spherulite size decreased drastically, and there was a reductive tendency in spherulite size with the increasing content of OMMT in the sample [Fig. 4(b,d,f)]. This might be attributed to the heterogeneous nucleation induced by OMMT

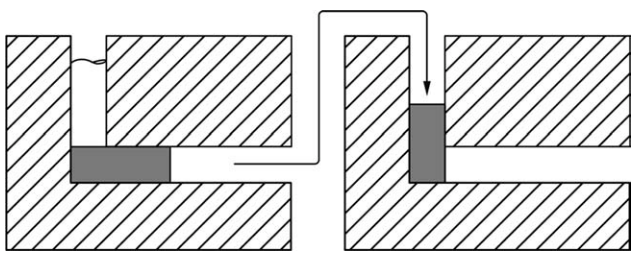

Figure 3 Schematic illustration of twice ECAE processes.

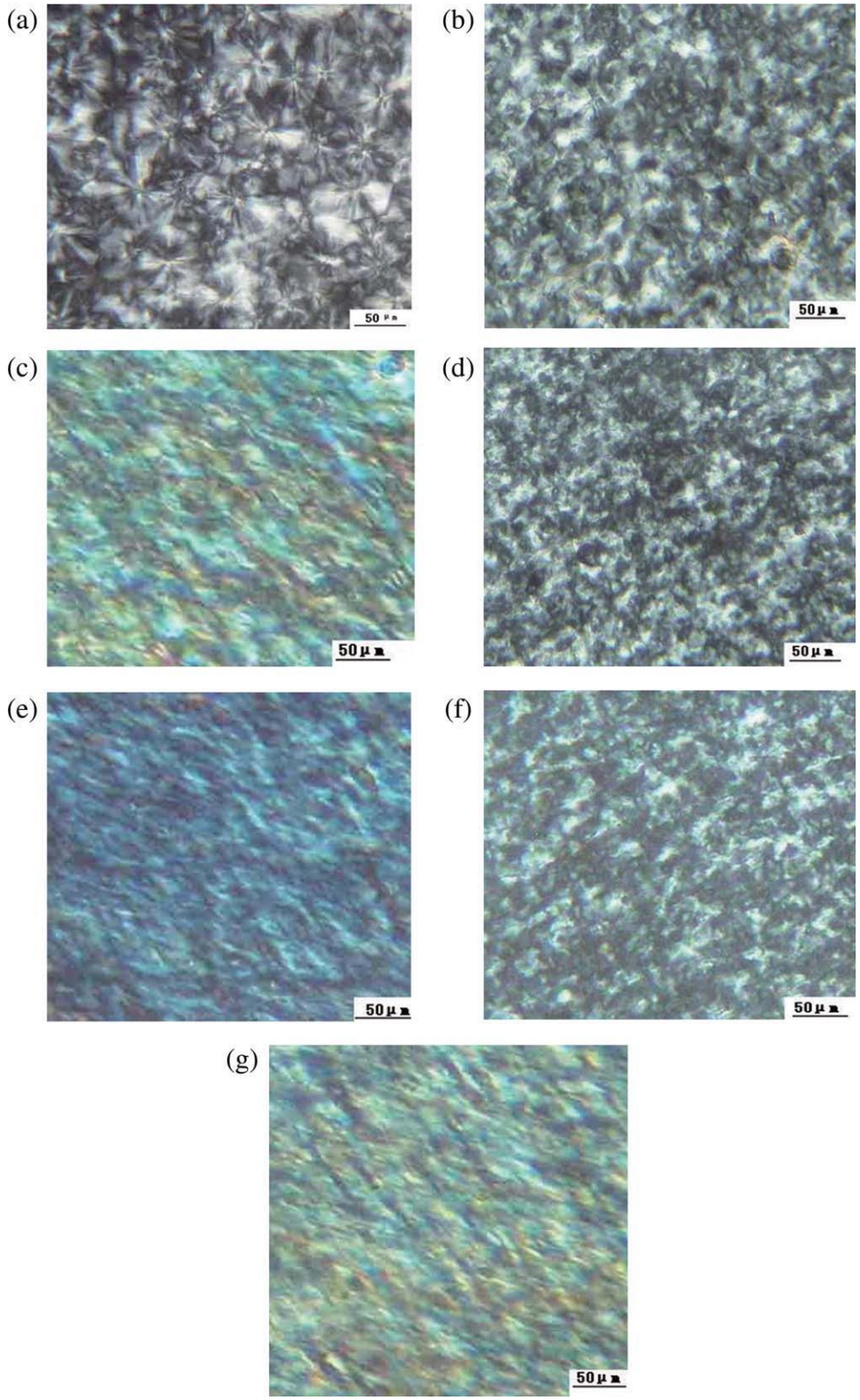

Figure 4 Polarized optical micrographs of PP and PP/OMMT composites before and after ECAE. (a) PP; (b) PP/1 wt % OMMT; (c) ECAE-PP/1 wt % OMMT; (d) PP/2 wt % OMMT; (e) ECAE-PP/2 wt % OMMT; (f) PP/5 wt % OMMT; and (g) ECAE-PP/5 wt % OMMT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

particles.[18] The large size crystal was hard to form possibly because of the OMMT particle's interfering with the spherulite growth of PP. Through once ECAE process, the orientation arrangement of elongated spherulite was observed in ECAE-PP/OMMT complex [Fig. 4(c,e,g)]. With the increase of OMMT

content, there was not an obvious effect on elongated crystallite after ECAE process.

Effect of ECAE process on the morphology of OMMT particles

After chemical etching, the samples were subjected to further investigation by SEM. The OMMT particles dispersed in PP/OMMT complex were existed mostly in the form of agglomeration with the size of 5–10 μm [Fig. 5(a)]. Through ECAE process, the particle agglomeration deformation took place and an orientation which was roughly parallel to the shearing force was observed [Fig. 5(b)]. Through solid extrusion, a tremendous shear force changed the sphere agglomerative particles into the rod-like particles with an aspect ratio about 5–10. Further, the once extrusion sample continued to process a secondary solid extrusion (sample ECAE-PP/2 wt % OMMT-A), the agglomeration OMMT particles were not observed [Fig. 5(c)], instead, the needle-like OMMT fine particles dispersed were observed. This phenomenon indicated that the solid extrusion had a significant effect on OMMT agglomeration to disperse in solid state and should result in well OMMT particle's dispersion.

Effect of repeat ECAE process on the morphology of OMMT particles

Without ECAE process, PP/2 wt % OMMT sample showed that OMMT agglomeration particles dispersed in PP matrix through the observation of transmission electron microscopy (TEM), the primary particle layer thickness was about 5 μm [Fig. 6(a)]. After once ECAE process, OMMT particles in PP matrix were deformed into the rod-like agglomerates, partial primary crystal layers were broken (exfoliated), the primary layer thickness reduced to about 0.5 μm [Fig. 6(b)]. After twice ECAE processes (ECAE-PP/2 wt % OMMT-A), OMMT primary particles were further exfoliated into a thinner layer, with thickness about 50–100 nm [Fig. 6(c,d)]. These exfoliated OMMT layers dispersed in PP matrix, forming PP/OMMT nanocomposites.

XRD was applied to measure the distance between the OMMT layers to characterize the exfoliation of OMMT layers ulteriorly. The XRD patterns in Figure 7 show the effects of ECAE process on the exfoliation of the OMMT layers. The diffraction peaks of the [0 0 1][19] of pure OMMT [Fig. 7(a)] and PP/2% OMMT [Fig. 7(b)] were, respectively, at $2\theta = 2.86^\circ$ and $2\theta = 2.70^\circ$. Correspondingly, the distances of OMMT layers, $d_{001} = 3.08$ nm and $d_{001} = 3.21$ nm, were calculated using Bragg's Law: $2d \sin \theta = \lambda$. The diffraction peak of the [0 0 1] of ECAE-PP/2% OMMT sample after once ECAE process was $2\theta =$ 2.14° [Fig. 7(b)], moving toward small angle, while the distance of OMMT layers, $d_{001} = 4.05$ nm, indicating that the space of OMMT layers expanded to a certain extent due to ECAE process, leading the exfoliation of OMMT layers. ECAE-PP/2%OMMT-A

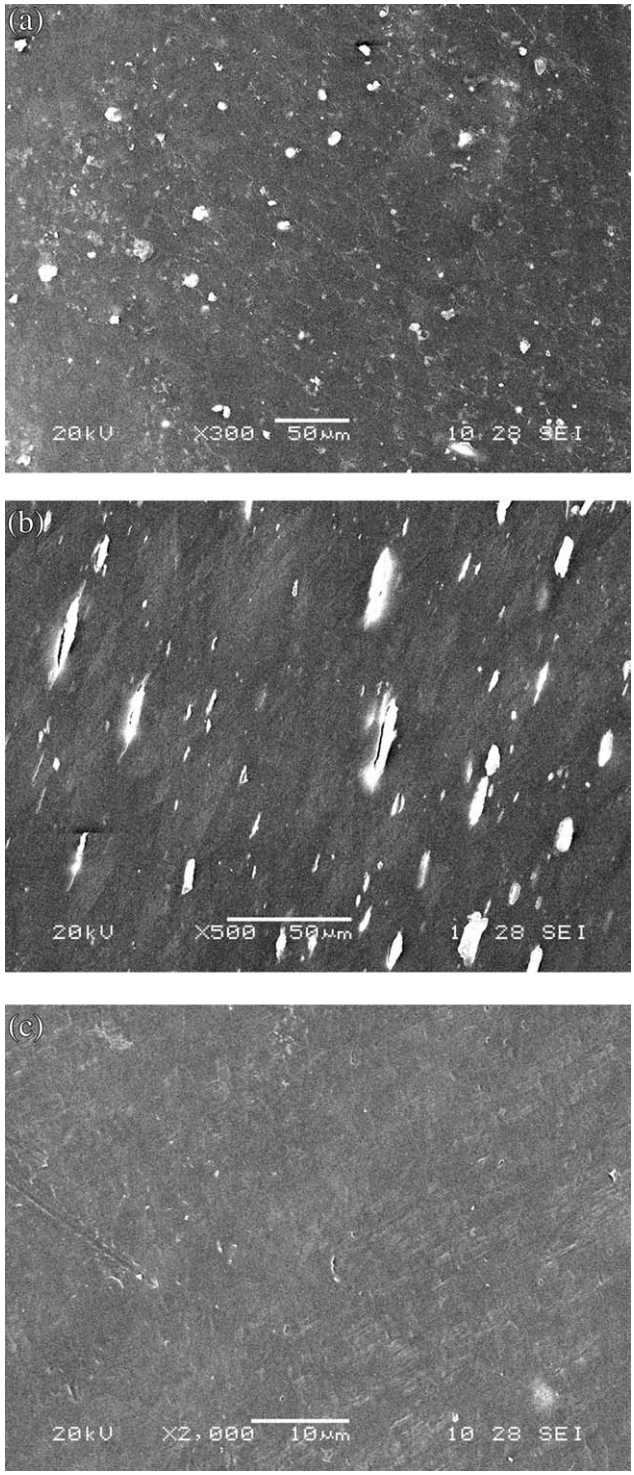

Figure 5 SEM of PP/2 wt % OMMT sample before and after once and twice ECAE process. (a) PP/2 wt % OMMT; (b) ECAE-PP/2 wt % OMMT; and (c) ECAE-PP/2 wt % OMMT-A.

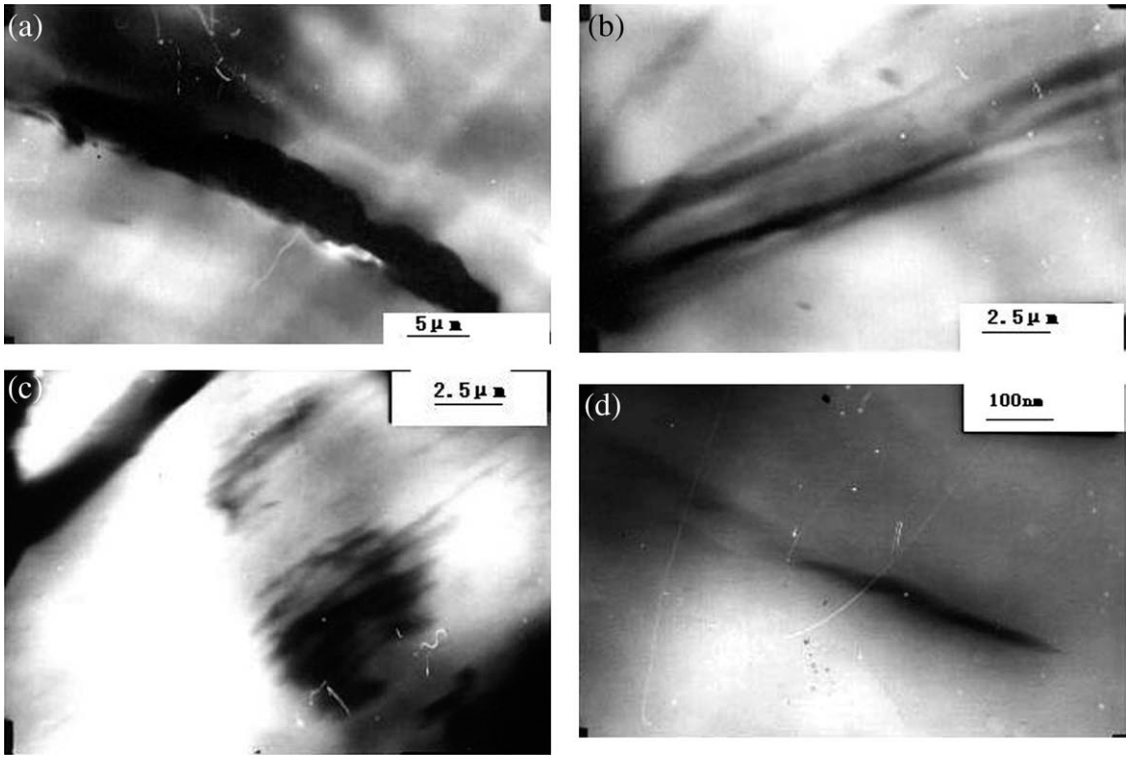

Figure 6 TEM micrographs of PP/2% OMMT, ECAE-PP/2% OMMT, ECAE-PP/2% OMMT-A. (a) PP/2 wt % OMMT; (b) ECAEPP/2 wt % OMMT; (c) ECAEPP/2 wt % OMMT-A; and (d) ECAEPP/2 wt % OMMT-A.

sample after twice ECAE processes did not show the diffraction peak of the [0 0 1], which indicated that the distance of OMMT layers was too large to detect. As the XRD applied in the experiment has an angular range of $2\theta > 1.02^\circ$, the maximum distance of OMMT layers detected is 8.65 nm accordingly. Therefore, the distance of OMMT layers in ECAE-PP/2%OMMT-A sample exceeded 8.65 nm, which is 2.5 times larger than the thickness of the pure OMMT layers. In this case, it can be considered that OMMT particles were completely exfoliated and dispersed in PP matrix in the form of the independent nanolayers to form PP/OMMT nanocomposites. The results of XRD further supported the conclusion of TEM, that is, OMMT nanolayer structure can be formed in PP effectively because of tremendous shear force produced by ECAE process. In the experiment, the best exfoliation of OMMT took place in ECAE-PP/2%MMT-A.

Mechanism of exfoliation of montmorillonite in ECAE process

Montmorillonite is a layer silicate structure of the microscopic crystals.[19,20] Its chemical formula is $M_x(Al_{4-x}Mg)Si_8O_{20}(OH)_4$. The structure of MMT crystal consists of SiO_4 tetrahedral layers and AlO_6 octahedral layers in 2 : 1 proportion, forming the double-layer complex, which is parallel each other. Usually, the OMMT particles are 5–10 μm

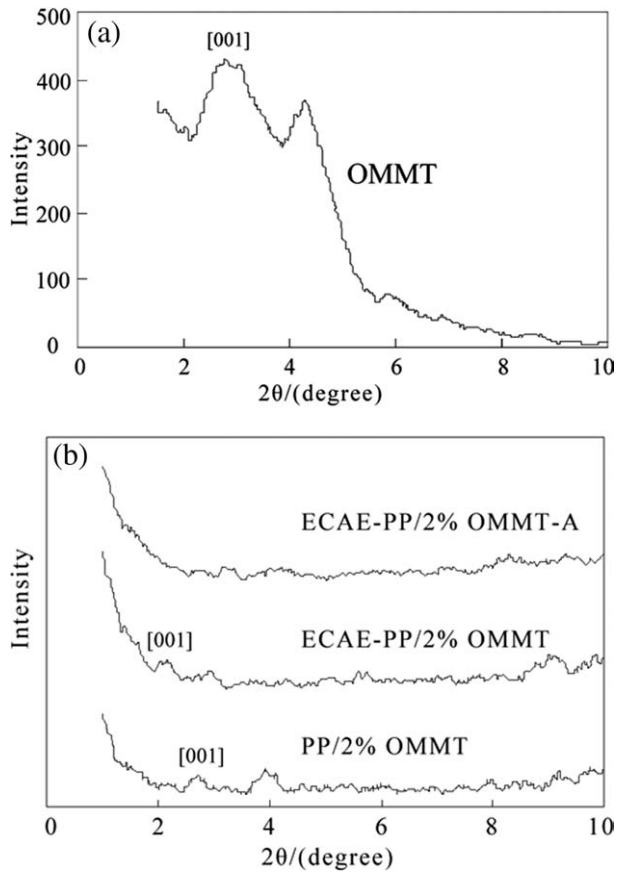

Figure 7 XRD patterns of (a) OMMT and (b) PP/2% OMMT, ECAE-PP/2% OMMT, ECAE-PP/2% OMMT-A.

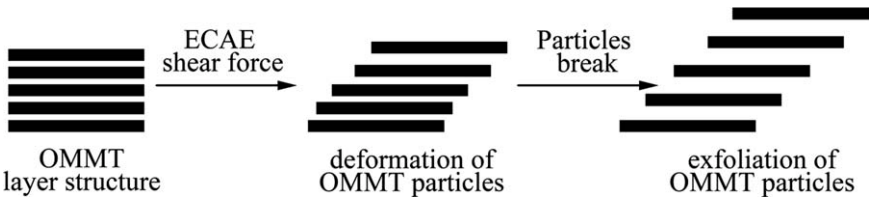

Figure 8 Schematic of OMMT layers exfoliated by the shear force in ECAE process.

agglomerates, which are assembled with 0.5–3 μm primary particles. Each primary particle consists of hundreds of OMMT crystal layer, which can be exfoliated under certain conditions. When blending PP with OMMT by an open mill, the shearing force is too small to overcome the interlayer attraction force, thus OMMT particles can only disperse as primary or agglomeration particles in PP matrix. By ECAE process, PP/OMMT composites are subjected to much larger simple shear force in the ECAE die, which compels both PP spherulite and OMMT agglomeration deformation or break. By twice ECAE processes, OMMT primary layers can even be exfoliated. As we know, the viscosity of PP in solid state is several million times larger than that of PP in molten state, which means that the exfoliation of OMMT primary particles is possible with ECAE process. The exfoliation mechanism of OMMT primary particles is shown in Figure 8.

CONCLUSIONS

The solid state ECAE process is an effective method to prepare PP/OMMT nanocomposites. Through TEM, SEM, POM, and XRD observation of ECAE-PP/OMMT sample, ECAE process can produce the immense solid shear force, which is enough to stretch, deform, tear, or break both PP spherulite and OMMT agglomerated particles. The once ECAE process can deform agglomerated OMMT particles from sphere- to rod-like bar with an aspect ratio 5–10. The twice ECAE processes further tear or break these rod-like OMMT particles into needle-like primary particles or even exfoliate a primary particle to silicate nanolayers, which disperse in PP matrix and will endow PP great reinforcement.

References

1. Usuki, A.; Kojima, Y.; Kawasui, M. Polym Prepr 1987, 28, 447.
2. Kato, M.; Usuki, A.; Okada, A. J Appl Polym Sci 1997, 66, 1781.
3. Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. Macromolecules 1997, 30, 6333.
4. Usuki, A.; Kato, M.; Okada, A.; Kurauchi, T. J Appl Polym Sci 1997, 63, 137.
5. Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, A.; Okada, A. J Appl Polym Sci 1998, 67, 87.
6. Alexandre, M.; Dubois, P. Mater Sci Eng R-Rep 2000, 28, 1.
7. Ray, S. S.; Okamoto, M. Prog Polym Sci 2003, 28, 1539.
8. Karger-Kocsis, J. Polypropylene Structure, Blends and Composites, Vol. 1 Structure and Morphology, Chapman & Hall, London 1995; p 289.
9. Hung-Jue, S.; Li, C. K. Y. J Mater Sci Lett 1998, 17, 853.
10. Sue, H. J.; Dilan, H.; Li, C. K. Y. Polym Eng Sci 1999, 39, 2505.
11. Li, C. K. Y.; Xia, Z. Y.; Sue, H. J. Polymer 2000, 41, 6285.
12. Xia, Z. Y.; Sue, H. J.; Hsieh, A. J. J Appl Polym Sci 2001, 79, 2060.
13. Xia, Z. Y.; Sue, H. J.; Hsieh, A. J.; Huang, J. W. L. J Polym Sci Part B: Polym Phys 2001, 39, 1394.
14. Boulahia, R.; Gloaguen, J. M.; Zairi, F.; Nait-Abdelaziz, M.; Seguela, R.; Boukharouba, T.; Lefebvre, J. M. Polymer 2009, 50, 5508.
15. Segal, V. M. Mater Sci Eng A 1995, 197, 157.
16. Bassett, D. C.; Olley, R. H. Polymer 1984, 25, 935.
17. Akinay, A. E.; Tincer, T. J Appl Polym Sci 1999, 74, 866.
18. Xu, W., Ge, M, He, P. J Polym Sci Part B: Polym Phys 2002, 40, 408.
19. Chitnis, S. R.; Sharma, M. M. React Funct Polym 1997, 32, 93.
20. Manias, E.; Touny, A.; Wu, L.; Strawhecker, K.; Lu, B.; Chung, T. C. Chem Mater 2001, 13, 3516.