Partial Exfoliation and Layer Expansion of Vermiculite Layer in Solid State by Solid State Shear Milling (S³M) Method

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ABSTRACT: A new method, solid state shear milling (S³M), was reported for realizing the exfoliation and layer expansion of vermiculite layer in solid state by using pan-mill equipment, which can exert fairly strong squeezing force and shearing force on milled materials. The mecha- nism was discussed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1806–1809, 2006

Key words: morphology; polypropylene; vermiculite; solid state shear milling (S³M); TEM

INTRODUCTION

Polymer-layered silicate nanocomposites have be- come an important area of polymer composite re- search since the polyamide 6/clay-intercalated nano- composites were first reported by Okada et al.[1] Poly- mer/clay nanocomposites have shown dramatic improvements in mechanical,[2–4] thermal,[5] and barrier properties.[6,7] At present, there are three principal methods for preparation of polymer/clay nanocom- posites: (a) in situ polymerization, (b) solution inter- calation, and (c) melt compounding. A majority of current nanocomposites research have focused on the understanding of how superior nanocomposites are formed, especially for melt compounding method be- cause of its convenience for preparation of polymer/ clay nanocomposites. In general speaking, there are four factors influencing the preparation of polymer/ clay nanocomposites: (a) the compatibility between polymer and clay;[8] (b) some properties of polymer, such as molecular weight;[9] (c) types of clay, especially the types of modifiers of organo-clay;[10] and (d) melt processing conditions,[11,12] including level of shear and residence time. Recent studies have demonstrated that melt processing conditions play a key role in achiev- ing high levels of exfoliation. It was proposed that the layer of clay can be exfoliated under the action of shear during melt processing: the higher shear forces, the smaller stacks of silicate layers.[13] A logical ques-

tion will be raised from this proposal: will layer of silicate be exfoliated in solid state in the presence of high shear force during compounding polymer and layered silicate? The aim of this article is to address this question by employing a new method, solid state shear milling (S³M), using pan-mill equipment, which was invented in our laboratory.[14] Theoretical analy- sis[15] demonstrated that pan-mill equipment can exert fairly strong squeezing force in normal direction and shear force in both radial and tangential directions on milled materials, functioning like pairs of three-di- mensional scissors, and has excellent pulverizing, mixing, and activation effect on polymeric materials. In our previous work,[16] Polypropylene (PP)/Vermic- ulite (VMT) nanocomposites have been successfully prepared by S³M. The nanocomposites exhibited good comprehensive properties as compared to conven- tional composites and neat PP, such as thermal prop- erties, crystallization properties, and mechanical properties. In this communication, we focused on the structure and morphology of VMT suffered from pan- milling, and answered the question whether the lay- ered inorganic filler can be exfoliated under strong shear force even in solid state. By an analysis of mor- phology of VMT in the samples obtained by S³M method, the happening of exfoliation of VMT layer in solid state was easily demonstrated.

EXPERIMENTAL

Materials

Polypropylene (Grade T30s, pellet diameter of 3–4 mm, MFI = 3.2 g/10 min, $M_\eta = 2.92 \times 10^5$, isotacticity ≥ 95%) used in this study was manufactured by Dus-

hanzi Petrolchemical Company, China. The vermiculite, abbreviated as VMT in the study, was purchased from market.

Equipment

The milling of PP and VMT was conducted on a pan-mill equipment that was shown in the previous articles.[15–18]

Preparation of PP/VMT composites

PP/VMT (50/50) mixture was fed into pan-mill through the hopper in the middle of the milling pan at rotating speed 30 rpm between two pans. Repetition operation continued 30 cycles to produce PP/VMT compounding powders, which was abbreviated as PPVMT50p. PPVMT50p as master batch was diluted with neat PP by a twin-screw extrusion. The contrastive sample was a conventional PP/VMT composite prepared by directly compounding PP and VMT, using twin-screw extrusion. The products were granulated by a granulator, and then molded into testing samples by an injector.

Characterization

Powder X-ray analysis was performed using a DX-1000 diffractometer with Cu Kα radiation (40 kV, 25 mA) at a scanning speed 0.03°/s. The VMT powder and PP/VMT compounding powders were mounted on a sample holder with a large cavity, and a smooth surface was obtained by pressing the powders with a glass plate. In the case of PP/VMT composites, measurements were carried out on a sheet. The TEM micrograph was taken with a JEM-100 cx, at an acceleration voltage of 80 kV. TEM specimens were cut from nanocomposite, using a microtome.

RESULTS AND DISCUSSION

Figure 1 shows the XRD profiles of VMT, PPVMT50p, and PP/VMT composites. PPVMT50p is PP/VMT (50 : 50) copowder prepared by pan-milling 30 cycles. PPVMTN10 is a mixture of PP/PPVMT50p, in which the content of VMT is 10 wt %. PPVMTC10 is PP/VMT conventional composite prepared by directly compounding PP and VMT, using twin screw extrusion. The difference of the samples in XRD pattern is obvious. For the VMT [Fig. 1(a)], the interlayer spacing of silicate layer is about 1.4 nm. The PPVMTC10 [Fig. 1(b)] exhibits an apparent peak at $2\theta = 6.3°$ corresponded to 001 diffraction peak of layered structure of VMT. The d-spacing of silicate layer in PPVMTC10 is the same as in the VMT powder, indicating that PP chain does not intercalate into the galleries of VMT silicate layers, and VMT layers are not exfoliated dur-
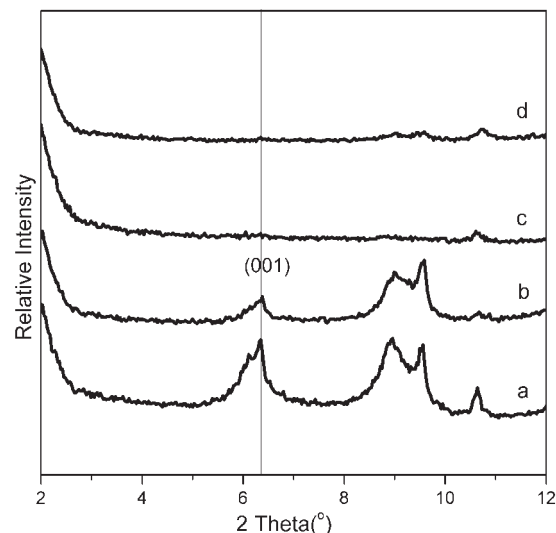

**Figure 1** The XRD patterns of (a) VMT, (b) PPVMTC10, (c) PPVMT50p, and (d)PPVMTN10.

ing conventional melt mixing. On the other hand, there is no characteristic peak in XRD pattern of PPVMTN10 [Fig. 1(d)] above 2°, which is the limit of XRD equipment. The result of XRD indicates that the silicate layers of VMT in the PPVMTN10 are not stacked regularly. An exfoliated type PP/VMT nanocomposite may be prepared by milling PP with PPVMT50p. We further examined the morphology of VMT in PP matrix using TEM

Figure 2 is the TEM micrographs of PPVMTN10. It can be seen that the VMT is dispersed well as nanolayers in PP matrix. Some tactoids are observed together with exfoliated platelets. In the tactoids of VMT, intercalation of PP into VMT nanolayers is clearly evident. The interlayer spacing reaches about 10 nm, which cannot be seen in XRD pattern above 2°. In this case, XRD and TEM confirm that partly delaminated VMT and partly intercalated VMT/PP nanocomposites have been obtained.

In XRD pattern, the (001) characteristic peak of VMT in PPVMTC10 is the same as in VMT sample, while the one of VMT in PPVMTN10 cannot be seen. The difference between PPVMTC10 and PPVMTN10 is that the VMT in PPVMTN is suffered from solid state shear milling. PPVMTN10 was prepared by compounding PP/PPVMT50p, using twin screw extrusion. The question is logically raised: at which stage the partly exfoliated VMT happens? Does it happen in the process of solid state shear milling or in the process of extrusion? Further investigation of process of exfoliation was undertaken by characterization of PPVMT50p using XRD and TEM. Figure 1(c) is the XRD pattern of PPVMT50p. The characteristic peak of VMT layer cannot be seen. The result of XRD indicates that the exfoliation of VMT layer happens in solid state by comilling PP and VMT powder. Figure 3 is the TEM micrographs of PPVMT50p
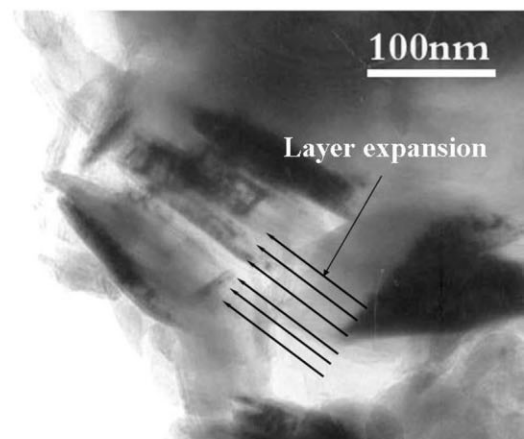
(a)
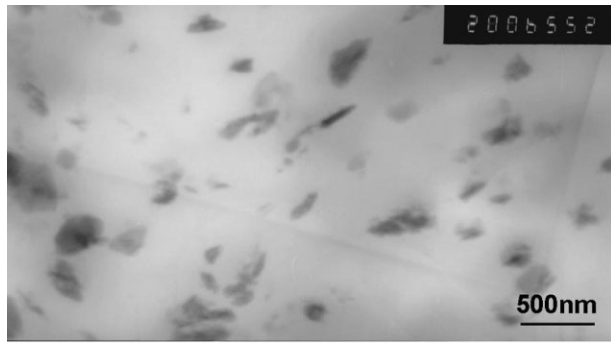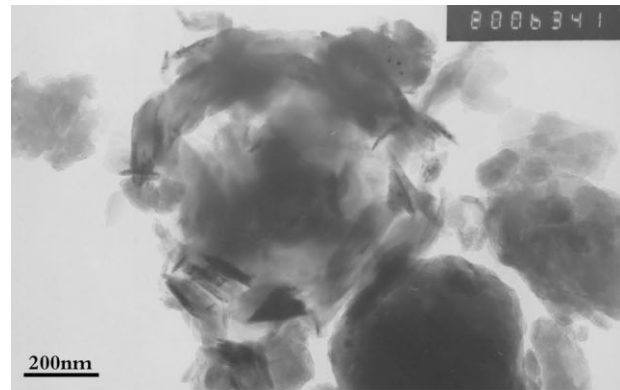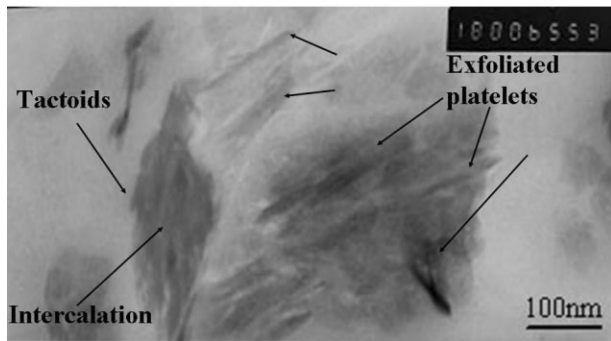
(b)

Figure 2 TEM photos of PPVMTN10.

showing the formation of partly exfoliated VMT sheets in the presence of PP powder. Figure 3(a) reveals that exfoliated VMT layers exist in PP/VMT copowder. Moreover, the exfoliated layer presents ring-shaped structure, which can be caused by the strong shear force of pan-mill. PP and VMT are comilled with the pan-type mill; they will be pulverized, well mixed, and embed into each other. And VMT may slide and dislocate between layers. Because of the existence of PP powder, the contrast between VMT layer decreases. However, the fine structure of VMT can be observed in the higher magnification of TEM images. The number of stacked platelets of VMT decreased. And the distance of some VMT sheets can be enlarged to 5–20 nm after pan-milling [Fig. 3(b, c)]. The results of XRD and TEM of PPVMT50p indicate that the partly exfoliated VMT and layer expansion of VMT are realized in solid state. The layer expansion would be caused by appearance of intercalation between VMT and PP in solid state. The TEM micrograph of PPVMTN10 in Figure 2(b) confirms the result. The fine dispersion of layered clay in PP is rather difficult to achieve by conventional mixing because of the nonpolar molecular structure of PP. That is why organoclay and compatibilizer are necessary for preparation of PP/clay nanocomposite via melt blending. In this study, the intercalation between VMT and PP does occur [Fig. 2(b)] by milling PP and PPVMT50p, which only results from the effect of solid state shear milling. So it is evident

(a)

(b)
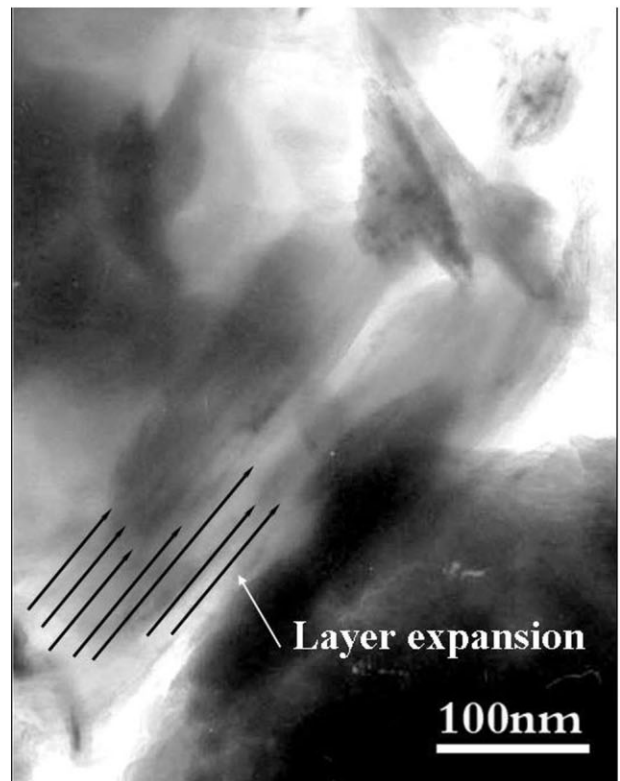
(c)

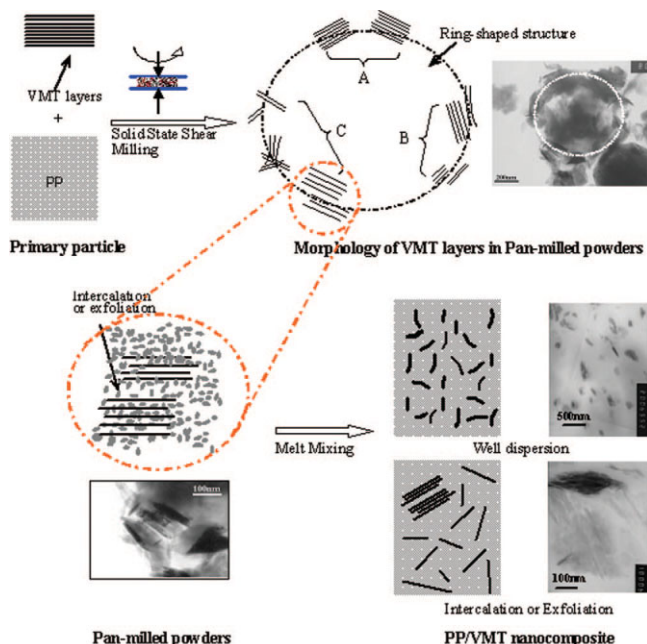**Figure 3** TEM photos of PPVMT50p pan-milled for 30 times.

Figure 4 Dispersion and exfoliation mechanism of VMT in PP matrix by solid state shear milling (S³M) using pan-mill. Pulverization of VMT (stage A), sliding of VMT platelets (stage B), and exfoliation of VMT layers (stage C) are occurring simultaneously during pan milling. The copowder shows ring-shaped structure caused by strong shear force of pan mill equipment. When the PP/VMT copowder prepared by S³M is diluted by melt mixing with PP, PP/VMT nanocomposite could be prepared, in which VMT is well dispersed in PP matrix and has exfoliated and intercalated structure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

that the exfoliation and intercalation of VMT layers in solid state have been successfully achieved by employing an innovative S³M technique without any compatibilizer.

The mechanism of exfoliation of VMT by S³M technique, based mostly on the results of this work, is suggested. Because of the viscoelastical properties of PP, which conduce that PP will easily adhere to the surface of VMT, weak layered structure of VMT, and function of pan-mill equipment, PP and VMT will be pulverized, well mixed, and embed into each other when they are comilled with pan-type mill. The morphology of VMT in pan-milled powders can be described in three stages (Fig. 4). Stage A shows the pulverization of VMT. VMT layer and PP are pulverized into small particles because of pulverization function of pan-type mill. In stage B, stacks of platelets are decreased in height by sliding platelets apart from each other under the action of shear force. The fresh surfaces of VMT layer will be conglutinated by PP powder. Stage C shows exfoliation of VMT and layer expansion does occur. As stronger shear force is exerting, the platelets appear to peel apart from the edge of the clay galleries. The exfoliated nanoscale sheets of

VMT were separated by PP powder, i.e., nanocompositing of VMT with PP is realized. It is important to note that the platelet may be able to curl away during comilling with PP, since the platelets are able to bend. The three stages are occurring simultaneously during pan milling. The morphology of VMT in copowders includes all morphology shown in three stages [Fig. 3(a)]. Figure 3(a) also shows that the copowder may present ring-shaped structure. When the PP/VMT copowder prepared by S³M is diluted by melt mixing with PP, PP/VMT nanocomposite with different VMT content could be prepared, in which VMT has exfoliated and intercalated structure, as observed in Figure 2. Obviously, S³M is a new approach to realize exfoliation of layered filler and to make intercalated polymer/layered filler.

CONCLUSIONS

The PP/VMT nanocomposites were successfully prepared by S³M, using pan-mill equipment. The results of XRD and TEM show that the VMT sheets were partly exfoliated, and the distance of VMT sheets was enlarged, forming intercalated structure in solid state. It can be seen from the TEM micrograph of PP/VMT composite (PPVMTN10) that the partly exfoliated VMT is dispersed well as nanolayers in PP matrix. At the large magnification of TEM, the full exfoliated VMT and intercalated VMT stacked layers can be observed in the micrograph.

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