

Synergistic Toughening Effects of Nucleating Agent and Ethylene–Octene Copolymer on Polypropylene

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ABSTRACT: The synergistic toughening effect of nucleating agent (NA) and ethylene–octene copolymer (POE) on polypropylene was studied in the present work. Two different nucleating agents, such as α -form nucleating agent 1,3 : 2,4-bis (3,4-dimethylbenzylidene) sorbitol (DMDBS, Millad 3988) and β -form nucleating agent aryl amides compounds (TMB-5), were selected to blend with PP or PP/POE blends, respectively. The results show that PP containing 0.5–0.25 wt % DMDBS or 0.5–0.25 wt % TMB-5 has relatively low impact strength. For PP/POE blends, although the impact strength increases gradually with the increasing of POE content, high content of POE is needed to obtain the available PP toughness. However, once nucleating agent and POE are simultaneously added into PP, PP/POE/NA blends show great improvement of tough-

ness even at low POE content. Furthermore, the synergistic toughening effect of POE/TMB-5 is more apparent than that of POE/DMDBS. SEM results show that whether DMDBS or TMB-5 has no apparent effect on the morphologies of POE in the PP/POE/NA blends. Further investigations using DSC and POM indicate that both DMDBS and TMB-5 induce the apparent enhancement of the crystallization temperature of PP and the sharp decrease of spherulites size of PP in the PP/POE/NA blends. The possible synergistic toughening mechanism is discussed in the work. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3270–3280, 2008

Key words: polypropylene; nucleating agent; ethylene–octene copolymer; synergistic toughening effect

INTRODUCTION

Polypropylene (PP) is extensively used in many fields because of its excellent properties, such as outstanding chemical and moisture resistance, low density, easy to process, and relatively low cost. However, its application as an engineering thermoplastic is limited because of the poor impact toughness, especially at low temperature. Therefore, various methods have been developed to overcome this shortcoming. One of the most effective methods is blending PP with various elastomers, such as ethylene–propylene rubber (EPR),^{1–5} ethylene–propylene–diene monomer (EPDM),^{6–10} and ethylene–octene copolymer (POE).^{11–13}

Nevertheless, elastomer-toughening PP is always at the cost of the decrease of tensile strength and modulus because of the poor strength of elastomer and the poor interfacial interaction between matrix and dispersed phase.^{13–15} To further improve the toughness without a dramatic loss in stiffness, many interests have been focused on the PP/elastomer/fil-

ler ternary composites in recent years.^{16–23} There are three different phase morphologies for these ternary composites: i.e., separated structure where the elastomer and filler are dispersed separately, core-shell structure with the encapsulation of the filler by an elastomer shell, and filler-network structure where the majority of elastomer particles surrounded by filler particles. It has been shown that the impact toughness of the ternary composite with core-shell structure is higher than that of composite with separated structure,^{16,17} whereas the latter one exhibits higher modulus than the former one. Particularly, Yang et al.^{18,19} studied the relationship between phase structure and impact strength of PP/EPDM/SiO₂ composites and they found that a filler-network structure could be a key factor for a simultaneous enhancement of toughness and modulus of PP.

Remarkably, the impact toughness of PP/elastomer blends is not only dependent on the properties of elastomer but also those of PP matrix. Nucleating agent (NA) is widely used in semicrystalline polymer processing to control the crystallization behavior of such polymer greatly. Because very small amounts of nucleating agent (typically around 0.2 wt %) can increase the nucleation density and decrease the spherulites size apparently, it is also thought to be one of the toughening agents for PP.²⁴ Moreover, it has been reported that β -form PP crystallites show

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higher toughness.^{25–27} However, the effect of nucleating agent on impact toughness of the PP/elastomer blends has received less attention.^{28–30}

In this work, we attempt to study the effects of nucleating agent, elastomer, and nucleating agent/elastomer on toughness of PP, respectively. Different nucleating agents, such as α -form nucleating agent DMDBS and β -form nucleating agent TMB-5, were used. The elastomer used in the study was POE. The aim is to seek an efficient way in improving PP toughness greatly. Surprisingly, compared with PP/nucleating agent system or PP/elastomer system, the PP/POE/NA blends show the great improvement of the toughness. In other words, the addition of nucleating agent and elastomer into PP simultaneously shows an apparent synergistic toughening effect for PP.

EXPERIMENTAL

Materials

All the materials used in this study are commercially available. PP (F401, Langang Petrochemical Co, Lanzhou, China) with a melt flow rate (MFR) of 2.5 g/10 min (230°C/2.16 kg) was used as the matrix polymer. POE (EXACT 5371, ExxonMobil Chemical Company, USA) with a MFR of 11.0 g/10 min (190°C/2.16 kg, ASTM D-123) and a density of 0.870 g/cm³ was selected as the impact modifier. The α -form nucleating agent 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS, Millad 3988) was produced by Milliken Chemical, Belgium. The β -form nucleating agent aryl amides compound (TMB-5) was supplied by Fine Chemicals Department of Shanxi Provincial Institute of Chemical Industry, China.

Sample preparation

To achieve the best dispersion of the nucleating agent, a two-step process was employed to prepare PP/NA, PP/POE blends, and PP/POE/NA blends, respectively. Namely, a masterbatch of 5 wt % nucleating agent in PP was first prepared through melt blending of nucleating agent and PP; and then the masterbatch was melt blended with different content of PP, POE, or PP/POE to obtain the corresponding blends. The detail sample notation and the corresponding composition of the blends designed in this work are shown in Table I. The melt blending of the blends was carried out on a twin-screw extruder (TSSJ-25). During the extrusion, the screw speed was set as 120 rpm/min and the temperature was 150–215°C from hopper to die. After making droplets, the pellets were injection molded and the standard specimens for impact test were prepared using an injection-molding machine (K-TEC 40). During the injection molding processing, the temperature of the

TABLE I
Sample Notation and the Composition of the Blends

Sample	PP (wt %)	POE (wt %)	DMDBS ^a (wt %)	TMB-5 ^a (wt %)
PP/DMDBS	100	–	0.0–0.25	–
PP/TMB-5	100	–	–	0.0–0.25
PP/POE	100–70	0–30	–	–
PP/15POE/DMDBS	85	15	0.0–0.25	–
PP/15POE/TMB-5	85	15	–	0.0–0.25
PP/POE/0.1DMDBS	100–70	0–30	0.1	–
PP/POE/0.2DMDBS	100–70	0–30	0.2	–
PP/POE/0.1TMB-5	100–70	0–30	–	0.1
PP/POE/0.2TMB-5	100–70	0–30	–	0.2

^a The content of nucleating agent is related to the actual content of PP in the blends.

melt from hopper to nozzle was set as 190–215°C, and the mold temperature was 25°C.

Notched Izod impact strength measurement

Notched Izod impact strength was measured using an XC-22Z impact tester (Made in Chengde, China) according to ISO179-1982. For each blend, the average value reported was derived from at least five specimens. The measurement was carried out at room temperature (23°C).

Scanning electronic microscope (SEM)

The impact-fractured surfaces of samples were characterized by using a Fei Quanta 200 environmental scanning electronic microscope (ESEM, America) with an accelerating voltage of 20 kV. For the phase morphologies of the blends, the samples were cryogenically fractured perpendicular to flow direction after being immersed in liquid nitrogen about half an hour and etched in *n*-heptane at 50°C for 3.5 h to remove the POE phase from the PP matrix. The etched surfaces were carefully washed with fresh *n*-heptane and ethanol successively. The samples were dried and then coated with a thin layer of gold prior to SEM characterization.

Wide angle X-ray diffraction (WAXD)

Wide angle X-ray diffraction (WAXD) was employed to study the crystalline structure of PP matrix. WAXD patterns of the blends were obtained on a Panalytical X'pert PRO diffractometer with Ni-filtered Cu-K α radiation. The continuous scanning angle range used in this study is from 10° to 35° at 40 kV and 40 mA.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC, Netzsch STA 449C Jupiter, Germany) was used to study the crys-

tallization behaviors of the blends. The weight of each sample was about 8 mg. DSC scanning program was set as follows: first, the sample was heated to 200°C at the heating rate of 10°C/min and maintained at this temperature for 10 min to erase the thermal history; second, the sample was cooled down to 30°C at the cooling rate of 10°C/min. All the DSC measurements were carried out in helium atmosphere.

Polarization optical microscope (POM)

Polarization optical microscope (POM, XPN-203, China) with a hot-stage was used to characterize the crystallization morphologies of the blends. First, a sample of about 5 mg was placed between two glass slices and heated to melt completely, and then the sample was pressed to obtain a slice with the thickness of about 20 μm ; Second, the sample was transferred to the hot-stage with the setting temperature of 125°C and maintained at this temperature until the crystallization of the blends was finished completely. The crystallization morphologies of the blends were taken images via a digital camera.

RESULTS AND DISCUSSION

It is well known that normally PP has three basic crystal forms: monoclinic (α), hexagonal (β), and orthorhombic (γ). Among all these crystallites, β -form of PP shows higher impact strength because of a special tied-molecule structure among the intra- and inter-spherulites and the stronger boundary strength between spherulites^{25,26} Undoubtedly, α -form nucleating agent DMDBS and β -form nucleating agent TMB-5 used in this work should induce PP crystallization in α -form and β -form, respectively. However for the blends of PP with elastomer and nucleating agent simultaneously, what will happen for the crystal structures? Figure 1 shows the WAXD patterns of PP, PP/POE (85/15), PP/15POE/0.2DMDBS, and PP/15POE/0.2TMB-5 blends. Compared with the pure PP, in which the characteristic diffraction peaks for α -form of PP at $2\theta = 14.1^\circ$, 16.8° , 18.5° , 21.1° , and 21.7° are clearly visible in the diffraction patterns shown, corresponding to the following crystalline planes (110), (040), (130), (111), and (130), respectively, PP/POE (85/15) blend shows an additional characteristic diffraction peak around 16.1° , the main characteristic of the β -form associated with (300) plane.^{31,32} This means that in the blend of PP/POE, the addition of POE is in favor of the formation of β -form PP crystallites, although the main PP crystallites are still α -form. In the blend of PP/15POE/0.2DMDBS, only the characteristic peaks of α -form are observed. Obviously, the addition of DMDBS induces PP crystallization in α -form and

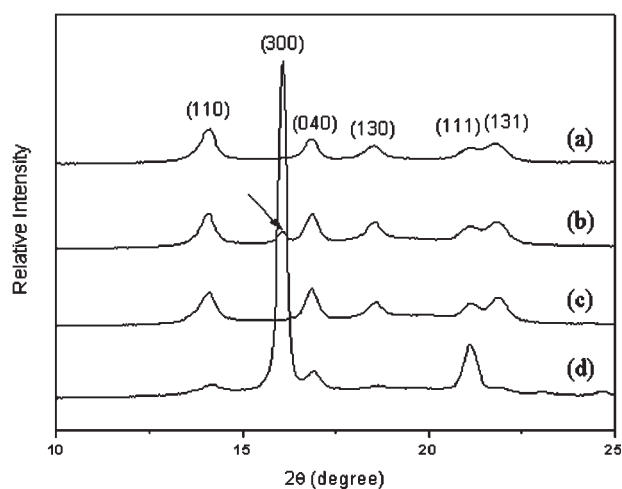


Figure 1 WAXD patterns of PP/POE blends with different nucleating agents. (a) PP, (b) PP/POE (85/15), (c) PP/15POE/0.2DMDBS, and (d) PP/15POE/0.2TMB-5.

prevents the nucleation of POE in PP crystallization. Namely, the nucleation role of DMDBS is more efficient than POE, which will be further discussed in the latter part of the work. For PP/15POE/0.2TMB-5 blend, the strong characteristic peaks of β -form and very weak characteristics peaks of α -form are observed, which means that in this blend, almost PP crystallizes in the β -form.

Now, since PP crystallizes in α -form with the existence of DMDBS and in β -form with TMB-5, the effects of nucleating agent, POE, and POE/nucleating agent on impact toughness of PP are discussed based on the type of nucleating agent. An advantage of the processing way is that one can see which composition of the blends is the best one in improving PP toughness.

Synergistic toughening effect of DMDBS and POE on PP

The effects of DMDBS, POE, and POE/DMDBS on impact strength of PP are shown in Figure 2. Figure 2(a) shows the variation of impact strength of PP and PP/15POE/DMDBS blends as the function of DMDBS content. It can be seen that, for PP/DMDBS binary blends, the impact strength of the blends has no apparent change compared with the pure PP, but remains almost constant as the content of DMDBS increase from 0.5 to 0.25 wt %. However, for PP/15POE/DMDBS blends, addition of 15 wt % POE induces an apparent variation of impact strength with the change of DMDBS content. At lower DMDBS content, less than 0.1 wt %, the blends show lower impact strength than binary blend of PP/POE. At higher DMDBS content, the blends exhibit remarkable increase of impact strength in the DMDBS concentration range between 0.1 and 0.20 wt %. As

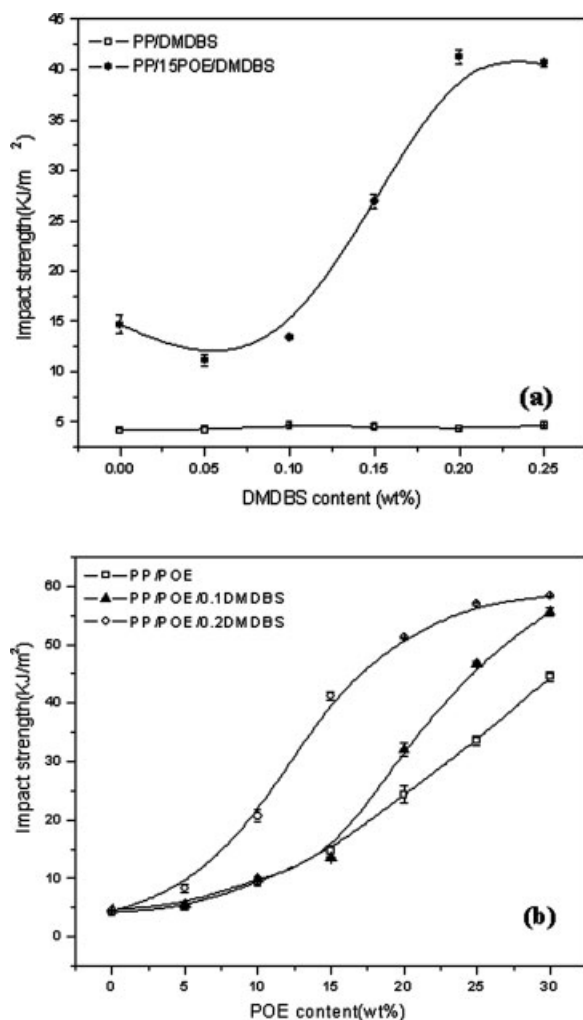


Figure 2 (a) Impact strength of PP/DMDBS and PP/15POE/DMDBS blends as the function of DMDBS content and (b) impact strength of PP/POE, PP/POE/0.1DMDBS, and PP/POE/0.2DMDBS blends as the function of POE content.

expected, the impact strength of the ternary blends reaches a maximum value of about 41 KJ/m² and remains invariable at DMDBS concentration exceeding 0.2 wt %. It should be pointed out that, PP/15POE/0.2DMDBS shows more than 10 times increase of impact strength compared with pure PP, and even two times increase of impact strength compared with PP/POE (85/15) binary blend.

Figure 2(b) shows the variation of PP/POE/0.1DMDBS and PP/POE/0.2DMDBS blends as the function of POE content. For the binary blends of PP/POE without DMDBS, the impact strength increases gradually with the increasing of POE content. The same results are widely reported in the literatures.³³ But for PP/POE/DMDBS blends, the impact strength shows different variation trend. The blends with 0.1 wt % DMDBS show no apparent change of impact strength at lower POE content.

Only when the content of POE exceeds 15 wt %, the impact strength of the blends has an apparent increase with the increasing of POE content. But for the blends with 0.2 wt % DMDBS, even the POE content is as low as 5 wt %, the blends show an apparent increase of impact strength compared with the binary blends without DMDBS, and even a brittle-ductile transition in the POE concentration of 10–15 wt % is observed.

As discussed earlier, PP with either POE or DMDBS cannot exhibit the expected impact toughness, whereas the PP/POE/DMDBS blends show a dramatically enhancement of impact strength. In other words, DMDBS and POE have a synergistic toughening effect on PP when they are simultaneously in the blends.

Synergistic toughening effect of TMB-5 and POE on PP

As described earlier, β -form PP shows good toughness than that of α -form PP. The existence of β -form nucleating agent TMB-5 in PP/POE blends results in almost PP crystallization in β -form. One question is that, what will happen for the toughness of PP when the elastomer and β -form nucleating agent are simultaneously in the blends. The effects of TMB-5 and POE on toughness of PP are shown in Figure 3, respectively. Figure 3(a) shows the variation of blends toughness of PP/TMB-5 and PP/15POE/TMB-5 as the function of TMB-5 content. For PP/TMB-5, the toughness of PP is slightly improved as expected before. But for the PP/15POE/TMB-5 blends, similar to the blends of PP/15POE/DMDBS, the impact strength is increased dramatically. Only a few amounts of 0.05 wt % TMB-5 in the blends, the impact strength increases from 14.7 kJ/m² of PP/15POE binary blend to 52.7 kJ/m² of PP/POE/TMB-5 blend, about four times enhancement. The impact strength continues to increase with the increasing content of TMB-5 in the blends, but at a slower rate. This means that for the impact toughness of the PP/15POE/TMB-5, there is a saturation of the toughening effect of TMB-5 in the blends.

Figure 3(b) shows the variation of impact strength of PP/POE/0.1TMB-5 and PP/POE/0.2TMB-5 blends as the function of POE content. To make a clear comparison, the impact strength of PP/POE without TMB-5 is also shown in the same figure. From this figure one can see that, compared with the PP/POE binary blends, only addition of 0.1 wt % TMB-5 into the blends can increase the impact strength dramatically in the whole range of POE content from 5 to 30 wt %. The impact strength of the PP/POE/TMB-5 blends increases with the increasing of POE content at lower POE content until the POE content is up to a critical value, 20 wt %.

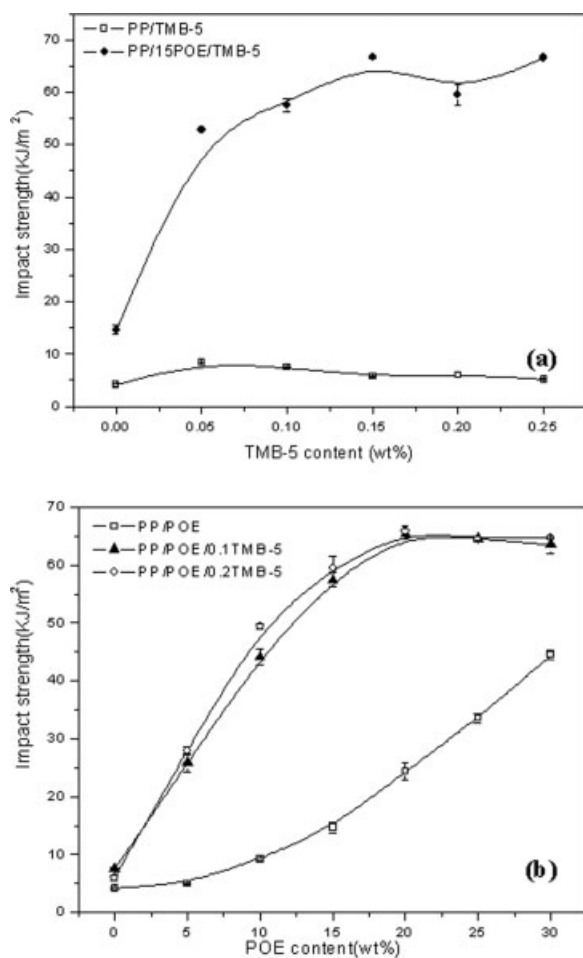


Figure 3 (a) Impact strength of PP/TMB-5 and PP/15POE/TMB-5 blends as the function of TMB-5 content and (b) impact strength of PP/POE, PP/POE/0.1 TMB-5, and PP/POE/0.2 TMB-5 blends as the function of POE content.

Further increasing the POE content in the blends, the impact strength has no apparent variation. This also means that, for impact strength of PP/POE/0.1TMB-5, there is also a saturation toughening effect of POE in the blends. Furthermore, one also can see that the addition of more TMB-5 has no apparent effect in improving the impact strength of the blends, which is different from the results of PP/POE/DMDBS blends described earlier.

Obviously, compared with the binary blends of PP/TMB-5 and PP/POE without TMB-5, the blends of PP/POE/TMB-5 show a great improvement of impact toughness. In other words, TMB-5 and POE also have a synergistic toughening effect on PP. So, it can be deduced that nucleating agent and elastomer have a synergistic toughening effect on PP when they are in the blends simultaneously whether the nucleating agent is α -form nucleating agent or β -form nucleating agent. To reveal the synergistic toughening effect of the two different nucleating agents and POE on PP more clearly, some represen-

tative blends are further studied. As shown in Figure 4, the impact strength of binary systems, whether PP/0.2 nucleating agent or PP/15POE blend, does not show expected improvement. However, the addition of only 0.2 wt % nucleating agent to PP/15POE blend induces great improvement of impact toughness. It is evident that nucleating agent, i.e., DMDBS or TMB-5, and POE are synergistic in improving the toughness of PP. Furthermore, one also can see that PP/15POE/0.2TMB-5 blend has better impact strength than that of PP/15POE/0.2DMDBS blend. The same phenomenon is observed for other compositions of these blends from Figures 2 and 3. That is, the synergistic toughening effect of POE/TMB-5 is better than that of POE/DMDBS, possibly due to the formation of large number of β -form crystallites of PP.

Phase morphologies of POE in the ternary blends

Now, since one knows that nucleating agent and elastomer have a synergistic toughening effect on PP when they are in the blends simultaneously, it is easy to ask what the synergistic toughening mechanism of them is. It is well known that the toughening effect of elastomer on PP is dependent on both the polymer matrix characteristics but also the elastomer dispersed phase. Nucleating agent has a characteristic to shorten injection-molding cycles by increasing the crystallization temperature and accelerating crystallization rate of semicrystalline, apparently. So, it is possible that the higher crystallization temperature and faster crystallization rate could influence the dispersed phase morphology of POE through delaying the evolution of POE phase up to equilibrium state during the injection molding, and then affect the impact strength of PP/POE/DMDBS and PP/POE/TMB-5 blends. Therefore, the morphologies of POE in PP/POE blends with or without

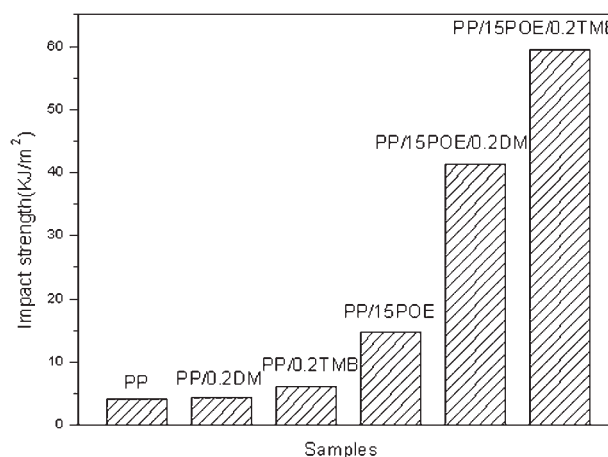


Figure 4 Synergistic toughening effect of nucleating agent and POE on PP.

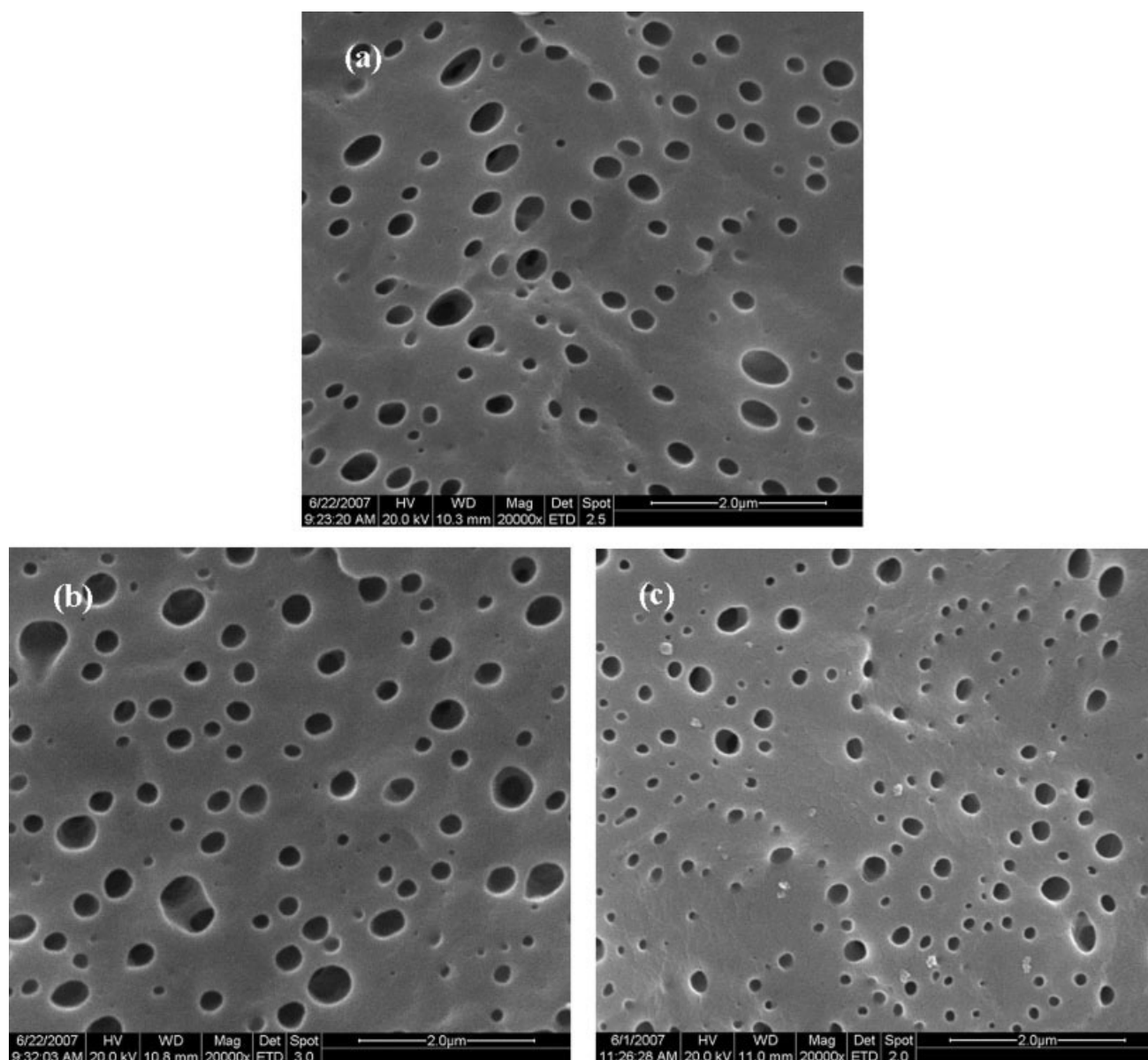


Figure 5 SEM micrographs of cryogenic fractured and etched surfaces of PP/POE blends with different nucleating agents. (a) PP/POE (85/15), (b) PP/15POE/0.2DMDBS, and (c) PP/15POE/0.2TMB-5.

nucleating agent were characterized by SEM and the results are shown in Figure 5. In these photographs, the dark holes represent the POE particles, which were etched out from PP matrix by *n*-heptane. Interestingly, compared with PP/15POE binary blend, the blends of PP/15POE/0.2DMDBS and PP/15POE/0.2TMB-5 show no apparent change in POE phase morphology. In other words, controlling the dispersed phase morphology during the injection molding through increasing the solidifying rate of PP matrix is not available in this condition. It is obvious that the great improvement of the toughness of PP/POE/DMDBS and PP/POE/TMB-5 ternary blends should be attributed to other reasons.

Effect of nucleating agents on crystallization behavior of PP matrix

The nonisothermal crystallization behaviors of PP/NA, PP/POE, and PP/POE/NA blends were investigated by DSC. The cooling curves are not shown in the article because of the large number of data. The crystallization temperature (T_c) of the blends is shown in Figures 6 and 7, respectively. From Figure 6(a) one can see that, for PP/DMDBS binary blends, T_c increases with the increasing of DMDBS content until a critical value (0.2 wt %) is achieved. Once the DMDBS content exceeds 0.2 wt %, T_c keeps invariant with further increasing DMDBS content. Obviously, there is a saturation of the nucleation effect

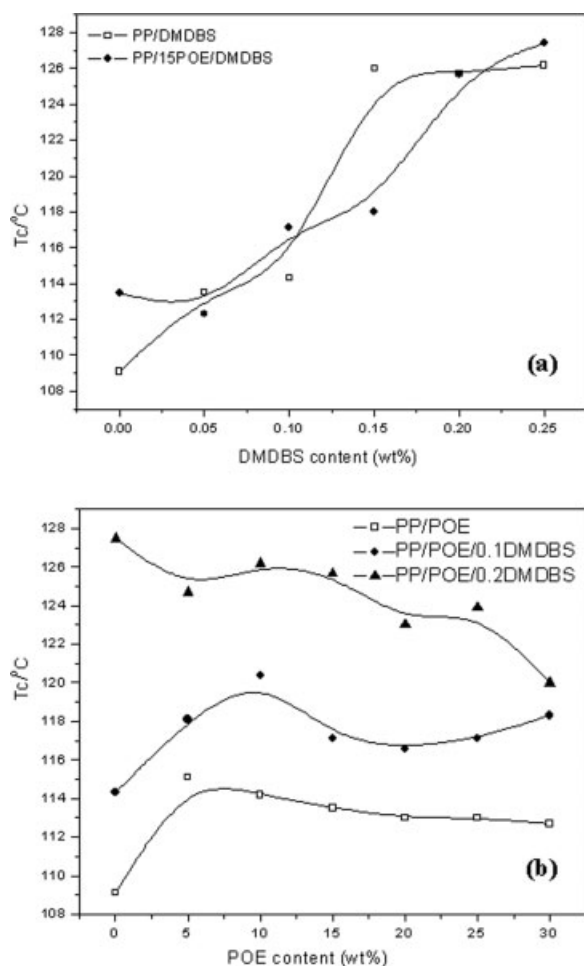


Figure 6 (a) Variation of T_c of PP/DMDBS and PP/15POE/DMDBS blends as the function of DMDBS content and (b) variation of T_c of PP/POE, PP/POE/0.1DMDBS, and PP/POE/0.2DMDBS as the function of POE content.

of DMDBS in PP.^{34–36} For PP/15POE/DMDBS, although at lower DMDBS content the T_c shows smaller value, it increases gradually with further increasing of DMDBS content in the blends. This means that the nucleation effect of DMDBS in the PP/15POE/DMDBS blends is still very apparent. From Figure 6(a,b), one also can see that for PP/POE binary blends, POE also has a nucleation effect in PP crystallization, although the nucleation effect becomes weak with the increasing of POE content in the blends. The T_c of the binary blends is higher than that of pure PP in the whole range of POE content from 5 to 30 wt %. The nucleation effect of POE for PP crystallization has been proved in previous work.³³ The crystallization of PP in PP/POE blends maybe take place in the presence of the octene microdomain structure.³⁷ On the other hand, the good compatibility between PP and POE maybe decrease the nucleation activity energy of PP, which results more PP nuclei formation during the crystal-

lization process. Further work should be done to understand the nucleation effect of POE on PP.

Furthermore, compared with the binary blends of PP/POE, the T_c of PP/POE/0.1DMDBS and PP/POE/0.2DMDBS is much higher. For example, the T_c of PP/15POE/0.2DMDBS is 125.7°C, much higher than that of pure PP (109.1°C) and PP/15POE blend (113.5°C). Similar to the PP/POE binary blends, in which the T_c depends on the POE content, the T_c of PP/POE/DMDBS also depends on the POE content. For PP/POE/0.1DMDBS, T_c initially increases with the increasing of POE content, and then decreases with further increasing POE. But for PP/POE/0.2DMDBS, T_c decreases gradually with the increasing of POE content.

Figure 7 shows the variation of T_c of PP/TMB-5 and PP/POE/TMB-5. One also can see that T_c increases with the increasing content of TMB-5 in PP/TMB-5 and PP/15POE/TMB-5 blends until a critical value (0.1 wt %) of TMB-5 is achieved. Further increasing the TMB-5 content, the T_c keeps

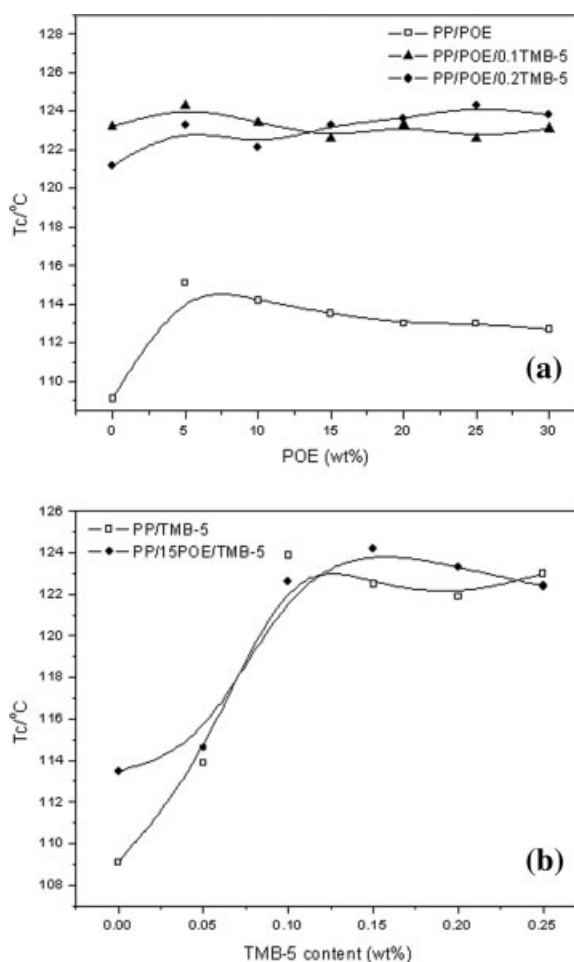


Figure 7 (a) variation of T_c of PP/POE, PP/POE/0.1TMB-5, and PP/POE/0.2TMB-5 as the function of POE content and (b) Variation of T_c of PP/TMB-5 and PP/15POE/TMB-5 blends as the function of TMB-5 content.

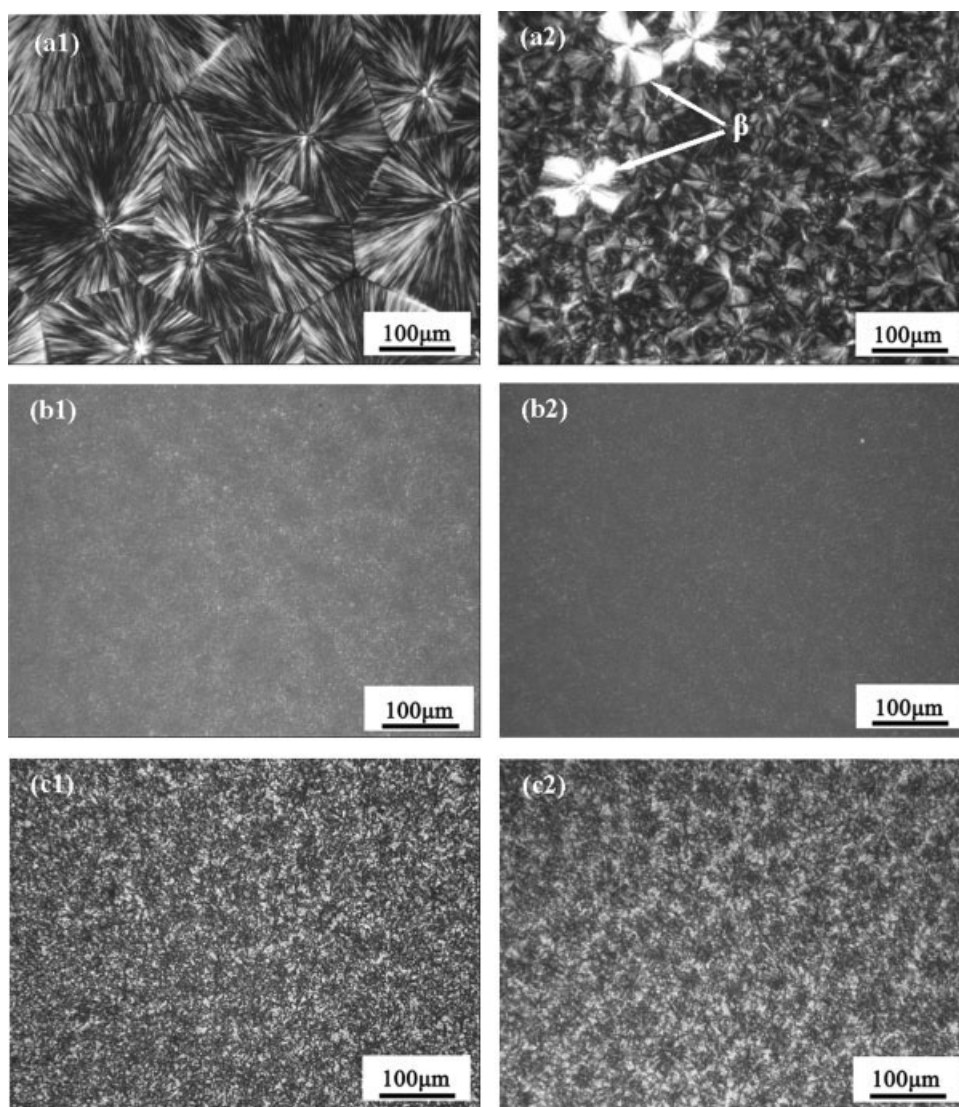


Figure 8 Isothermal crystallization morphologies of PP and PP/POE blend with different nucleating agents. (a1) Pure PP, (a2) PP/POE (85/15), (b1) PP/DMDBS (100/0.2), (b2) PP/15POE/0.2DMDBS, (c1) PP/TMB-5 (100/0.2), and (c2) PP/15POE/0.2TMB-5.

invariant. Obviously, there is also a saturation of the nucleation effect of TMB-5 whether in PP/TMB-5 or in PP/POE/TMB-5. Furthermore, for the blends of PP/POE/0.1TMB-5 and PP/POE/0.2TMB-5, although the T_c is much higher than that of PP/POE binary blends with the same POE content, it has no apparent change in the whole range of POE content from 5 to 30 wt %. The different variation trend of T_c is observed for PP/POE/DMDBS blends, in which the T_c depends on the content of POE. Here, the T_c of PP/POE/TMB-5 is independent on the POE content. In other words, in the PP/POE/DMDBS blends, the increase of POE content prevents the nucleation effect of DMDBS in PP crystallization. However in the PP/POE/TMB-5 blends, the existence of POE has no effect on the crystallization of PP because of the strong nucleation effect of TMB-5.

The apparent nucleation effect of DMDBS or TMB-5 in the PP/POE/NA blends means the increase of the nucleation density in PP crystallization and the decrease of the spherulites size.²⁴ Based on the above description, the isothermal crystallization morphologies of some blends were investigated by POM and the results are shown in Figure 8. The perfect and big spherulites are observed for pure PP and the average diameter of spherulites is larger than 200 μm . As aforementioned, the PP/15POE blend has smaller spherulites and the average spherulites diameter is about 40 μm , which also proves the nucleation effect of POE in PP crystallization. However, very small, homogeneous, and better dispersion of PP spherulites are observed for the blends with 0.2 wt % nucleating agent. An apparent nucleation effect of DMDBS or TMB-5 in PP crystallization is proved.

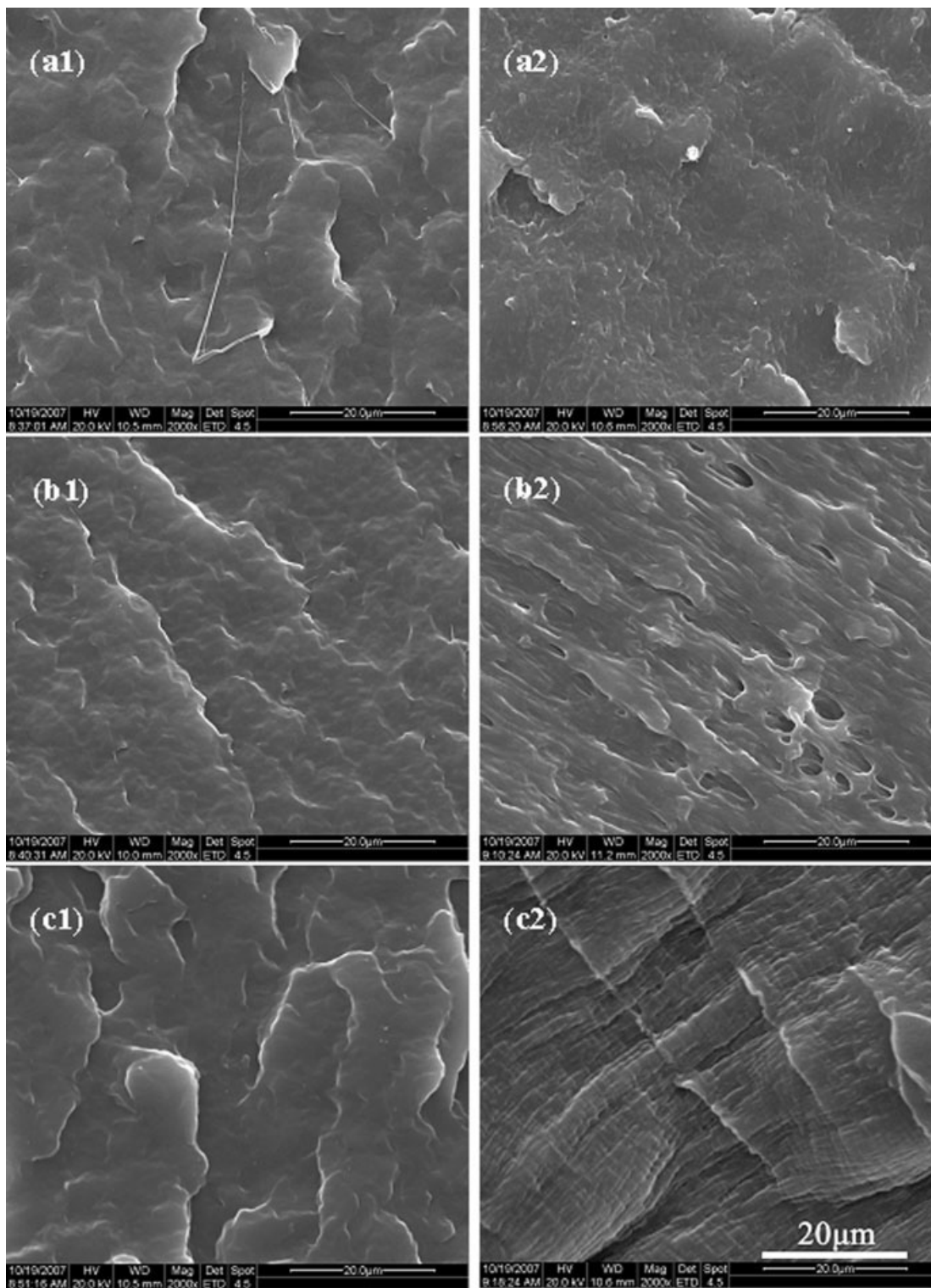


Figure 9 SEM images of impact-fractured surface of PP and PP/POE blends with different nucleating agents: (a1) Pure PP, (a2) PP/POE (85/15), (b1) PP/DMDBS (100/0.2), (b2) PP/15POE/0.2DMDBS, (c1) PP/TMB-5 (100/0.2), and (c2) PP/15POE/0.2TMB-5.

These results are in good agreement with the results of DSC. Considering the variation of toughness of PP/POE/NA blends when 0.2–0.25 wt % DMDBS or 0.1–0.25 wt % TMB-5 is added into the blends, it is

believed that the existence of POE phase and the sharp decrease of PP spherulites size are the main reasons for the great improvement of impact toughness.

Synergistic toughening effect and mechanisms

Based on the above-mentioned results, the great improvement of toughness in the blends of PP/POE/DMDBS or PP/POE/TMB-5 is a result of synergistic toughening effect of POE and nucleating agent. It is well known that the main mode of energy absorption during the impact process of elastomer toughened PP is shear yielding of matrix. The easier the shear yielding of the matrix, the better impact toughness of the blends has.^{38,39} The shear yielding of the matrix is dependent on the matrix properties, for example, the spherulites size of the matrix. The shear yielding of matrix becomes more difficult with the increase of the spherulites size possibly due to the stress propagation becomes more difficult. In this work, POE particles as a stress concentration in PP/POE/NA blends induce the shear yielding of PP matrix during the impact process. Nucleating agent induces the formation of homogeneous small spherulites of PP matrix, which leads to the formation of stress field around POE particles and the stress propagation in matrix become easier during the impact process and finally results in the great improvement of impact toughness of PP/POE/NA blends. In this condition, POE and nucleating agent have a synergistic toughening effect on PP impact toughness.

To prove that the shear yielding of matrix in PP/POE/NA blends is easier than that in PP/NA and PP/POE blends during the impact process, the impact-fractured surfaces were characterized via SEM and the results are shown in Figure 9. From Figure 9, one can see that for pure PP sample and PP/NA samples, the impact-fractured surfaces are very smooth and without any shear yielding or plastic deformation of matrix, indicating the typical brittle fracture behavior. For PP/POE samples, although the impact toughness is higher than that of pure PP and PP/NA samples, the impact-fractured surface is still very smooth. However for PP/POE/NA samples, apparent shear yielding or plastic deformation of matrix can be observed in the fractured surface. In PP/POE/DMDBS sample, large striations or fibrils are clearly visible, indicating the severe plastic deformation processes. Furthermore, some toughening cavities are observed, also implying considerable degree of plastic deformation of material. For PP/POE/TMB-5 sample, besides the shear yielding of matrix in large region, the second plastic deformation zones are widely observed in this sample, indicating the great impact toughness.

It is necessary to point out that, for PP/POE/TMB-5 blends, the presence of β -form is another important mechanism for the significant improvement of toughness of such blends.

CONCLUSIONS

In summary, the impact toughness of PP/NA, PP/POE, and PP/POE/NA blends has been studied in this work. Blending PP with either DMDBS or TMB-5 achieves only low impact strength. Regarding PP/POE blends, the impact strength increases gradually with the increasing content of POE. However, PP/POE/NA blends show a great improvement of impact strength. POE and nucleating agent have a synergistic toughening effect on PP. Further results show that the great improvement of PP/POE/NA blends toughness is mainly attributed to the sharp decrease of PP spherulites size and the homogeneous dispersion of such spherulites. Because of the formation of large number of β -form crystallites, POE and TMB-5 have better synergistic toughening effect than that of POE and DMDBS.

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