

EFFECT OF MOLECULAR WEIGHT OF PDMS ON MORPHOLOGY AND MECHANICAL PROPERTIES OF PP/PDMS BLENDS*

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Abstract A series of polydimethylsiloxane (PDMS) with varied molecular weights ($M_w = 3 \times 10^6$, 1×10^6 and 0.5×10^6) were melt blended with PP to investigate the effect of PDMS molecular weight (MW) on the morphology and mechanical properties of PP/PDMS blends. Scanning electron microscopic (SEM) examination showed that the size of PDMS domains was dependent on the MW of PDMS. It was found that the lower the value of PDMS MW, the better dispersion of the PDMS domains in the PP matrix. Tensile and Izod impact tests revealed that the addition of PDMS with lower MW would lead to a more significant increase in impact strength of the blends compared with the blends with higher MW ones, while the influence of the molecular weight on tensile strengths of the blends was relatively small in the MW range studied. Differential scanning calorimetry (DSC) results also showed that the crystallization temperature of PP was increased with decreasing PDMS MW, indicating a better nucleation capability of lower MW of PDMS. Melting flow rate (MFR) measurements indicated that the processibility of PP could be enhanced by adding PDMS, and again the lower MW PDMS resulted in better data. Our work demonstrates that not only the processibility but also the mechanical properties of PP could be enhanced to a more significant degree by using low MW PDMS than the higher ones.

Keywords: Polypropylene; Polydimethylsiloxane; Molecular weight.

INTRODUCTION

Recently, the study of polyolefin/polydimethylsiloxane (PDMS) blends has elicited considerable interest due to the fact that PDMS may modify polyolefin in several positive aspects^[1–12]. In particular, PDMS can improve the processibility, surface properties and wear resistance of polymer blends. Furthermore it appears that these properties could be enhanced without significant reducing mechanical properties. Mauler *et al.*^[1] studied both binary high-density polyethylene (HDPE)/PDMS and ternary HDPE/PDMS/HDPE-vinyltriethoxysilane (VTES) blends and found that the addition of HDPE-VTES could significantly reduce the size of silicone particles. Data of final torque and melting flow rate (MFR) showed that PDMS improved the processibility of pure HDPE. In the range of PDMS composition studied, the mechanical properties of blends lowered slightly compared to those of pure HDPE. Yilgor *et al.*^[2] studied the effect of the addition of (PDMS)-containing block copolymers to HDPE and PP, and improvements in the processibility and surface and tribological properties of PP and HDPE were achieved without any change in their thermal behavior or mechanical performance. Jana *et al.*^[3] investigated the chemo-rheological characteristics of 50/50 low-density polyethylene (LDPE)/PDMS blends with varying proportions (0–8 wt%) of ethylene-co-methyl acrylate (EMA) at four different shear rates. It was found that EMA reacted with vinyl groups of PDMS rubber at a temperature of 190°C during extrusion through

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the capillary of Monsanto Processability Tester (MPT), forming EMA-grafted-PDMS rubber (EMA-*g*-PDMS), which acts as the compatibilizer for the blend systems. Jana *et al.*^[4] also studied the difference of four kinds of ethylene copolymers in use as compatibilizer and showed that EMA was the best compatibilizer for the LDPE/PDMS blend system. Falender *et al.*^[5] reported lowered moduli and mixing energies of ethylene-vinyl acetate (EVA)/PDMS blends when compared to pure polyethylene. The effect of compatibilizer on micromechanical deformations and morphology of dispersion in PP/PDMS blends was investigated by Gupta *et al.*^[6]. They found that addition of PP-*g*-MAH could reduce the size of dispersed PDMS domains and narrow the domain size distribution. It was also reported that the tensile properties were significantly altered. Similar PP/PDMS and ternary PP/PDMS/PP-VTES blends were studied by Mauler *et al.*^[7], they found that the PDMS domains could serve as nucleating agent, leading to increase of the degree of PP crystallinity.

Despite these encouraging academic studies, work on the effects of PDMS molecular weight (MW) on the phase morphology and mechanical properties of these blends is quite limited. Most articles have focused on polyolefin systems blended with ultrahigh MW PDMS^[1–7] or certain MW PDMS^[2–6, 8–12]. Previous reports have shown that the addition of a third component as compatibilizer can significantly reduce the size of the dispersed domains^[1–12], while adjusting the intrinsic properties affecting the processing of the blends can also reach a fine dispersion^[8, 13–15]. Such properties include the molecular weights and the viscosity of the pure constituents, interfacial tension and shear rate. Only a few reports^[9–12] exist which describe the effect of block copolymer MW on the phase morphology of the blend system. For example, Macosko *et al.*^[10] found that an optimal block copolymer molecular weight was needed. They argued that the block copolymer needed to be short enough to diffuse quickly to the interface but also had to be long enough to entangle sufficiently with the homopolymers to prevent coalescence during static annealing. However, few studies related to the MW effects of PDMS on the morphologies and properties of these blends have been reported.

Polypropylene (PP) is one of the most widely used commodity polymers due to its low price and balanced mechanical properties. However, its brittleness, especially at low temperatures, is a significant drawback for many applications. In order to improve the impact resistance of PP and extend its application range, it is often blended with elastomeric polymer materials. In this way, blends of polypropylene (PP) with PDMS are of particular interest. In this paper, we have investigated the effect of PDMS molecular weight (MW) on the morphology and mechanical properties of PP/PDMS blends. PDMS with a MW range of 0.5×10^6 to 3×10^6 was used to prepare various PP/PDMS blends with different PDMS concentrations (0.5 wt%–5 wt%). Essentially, crystallization and the morphology of the blends are dependent upon the MW as well as the composition used. As mentioned above, the change of the PDMS MW could lead to differences in rheology properties of the blends, which may result in noticeable effect on the phase morphology and mechanical properties.

The objective of the present study was to complete a comprehensive assessment of PP/PDMS blend properties over a low range of PDMS concentrations. In order to make these blends commercially viable, only commercially available PP and PDMS and standard processing equipment were used. With regard to this, it was hoped to show that not only the processability but also the mechanical properties of PP could be enhanced to a significant degree for little extra expense, especially when compared with PP/PDMS blends in presence of a compatibilizer.

EXPERIMENTAL

Materials

Three commercial PDMS samples (from Chengdu Guibao Co.) with different molecular weights were used for the preparation of the blends. The PP was supplied by Du Shan Zi Petroleum Chemical, China. Characteristics of the materials are given in Table 1.

Table 1. Characteristics of materials used in this study

Sample code	Brand	M_w	MFR
PP	T30s	—	1.00 g/10 min (190°C, 2.16 kg)
	PDMS-1	3×10^6	—
PDMS	PDMS-2	1×10^6	—
	PDMS-3	0.5×10^6	—

Specimen Preparation

PP and PDMS were melt blended in a TSSJ-2S co-rotating twin-screw extruder. The temperature of the extruder was maintained at 165°C, 180°C, 190°C, 190°C and 185°C from hopper to die, and the screw speed was about 110 r/min. After a conventional extrusion step, the PP/PDMS blends were compounded by a PS40E5ASE (Japan) injection molding machine at 180–200°C to obtain standard specimens for mechanical properties tests.

Scanning Electron Microscopy (SEM)

The morphology of the blends was studied by preferential etching of PDMS phase in tetrahydrofuran (THF) for 24 h. The samples were cryogenically fractured in the direction perpendicular to flow direction in liquid nitrogen before etching. The etched samples were carefully washed for several times by using fresh THF, then alcohol washed for three times. The samples were dried under vacuum at room temperature for 24 h. Then the fractured samples were observed in a JEOL JSM-5900LV SEM instrument, using an acceleration voltage of 20 kV, which could show the dispersion of PDMS in PP matrix.

Mechanical Property Tests*Izod impact test*

The notched Izod impact strength was used to evaluate the toughness of samples. The notched specimens were tested with a VJ-40 impact test machine at room temperature, according to GB/T 1834-1996 standard. Each impact test was repeated at least five times, and the results were averaged.

Tensile yield strength test

Standard tensile strength tests were conducted on dumbbell shaped specimens using an AG-10TA tensile testing machine at room temperature. Test speed was kept at 50 mm/min, according to GB/T 1040-92 standard. The test was carried out in five folds.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry spectra were recorded on a Perkin-Elmer DSC Pyris-I differential scanning calorimeter calibrated with indium, and then the crystallization behavior of specimens can be obtained. All DSC measurements were performed under nitrogen atmosphere.

In these experiments, about five milligrams of dried samples was first hold in 50°C for 0.5 min, then heated quickly from 50°C to 200°C at a rate of 100 K/min and hold for 5 min at 200°C in order to eliminate the influence of thermal history. After that, the samples were cooled from 200°C to 50°C (at –10 K/min) to designate the crystallization temperatures (T_c), kept for 1 min at 50°C. At last, the temperature increased from 50°C to 200°C (at 10 K/min) to designated the melting temperature (T_m).

Melting Flow Rate Tests

The melt flow rates (MFR) of pure PP and PP/PDMS blends were measured by using a plastometer, under the condition of loading force (P) = 21.2 N and temperature (T) = 230°C (GB/T 3682-2000).

RESULTS AND DISCUSSIONS

The results of the addition of PDMS into the PP matrix will be discussed below. Emphasis is given to the effects of PDMS molecular weight and blend composition.

SEM Observation

SEM experiments were carried out to understand the phase morphology of binary blends. Figure 1 shows the

SEM micrographs obtained for the six blends after etching in tetrahydrofuran (THF) for 24 h. Resulting from the removal of the PDMS phase during etching, the presence of dark holes is clearly observed on these micrographs. These micrographs show that as the PDMS MW falls down from 3×10^6 to 0.5×10^6 , the domain size of PDMS obviously decreased. Furthermore, the blend containing lower PDMS MW showed a narrower domain size distribution in comparison with that containing higher PDMS MW. Therefore, the MW of PDMS does have a significant impact on the phase morphology of dispersion. The reduction in domain size with reducing the PDMS MW may probably result from the easier breakage of the dispersed phase droplets. That is to say, PDMS molecules with higher MW are more likely to entangle with each other, which tend to form larger domains than the lower MW ones. Furthermore, the reduction of PDMS MW increases the concentration of chain ends and decreases the viscosity of the blends. The viscosity ratio of the pure constituents at the melt mixing temperature is of great importance: it has been shown^[8, 9] that the particle size of the dispersed phase can be significantly decreased when the viscosity ratio is close to unity. These factors may also partly affect the phase morphology of the blends, and the domain size of the dispersed phase is increased with the increasing of PDMS content (from 1 wt% to 5 wt%). This may be due to the coalescence of the dispersed particles, or the insufficient breakage of the dispersed phase droplets.

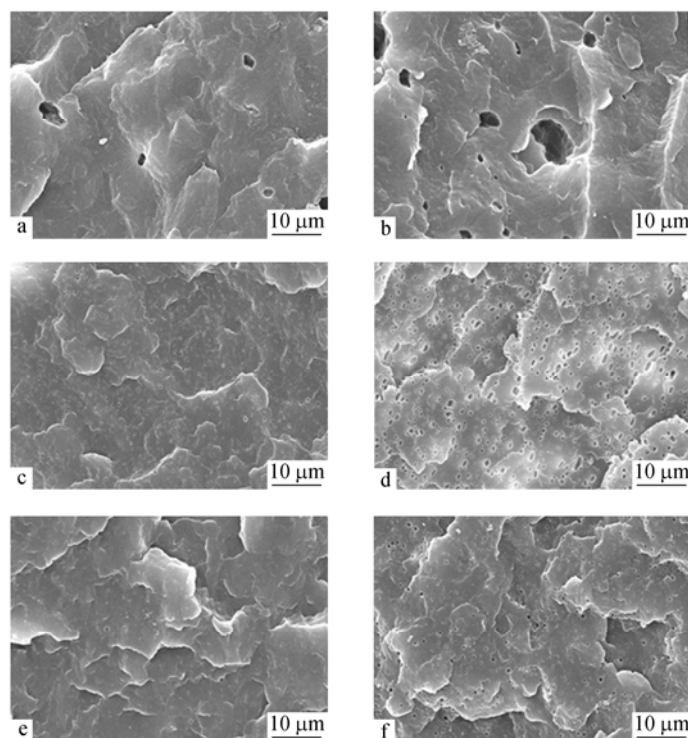


Fig. 1 SEM micrographs of PP/PDMS blends with different content and molecular weight of PDMS
a) 1 wt% PDMS of 3×10^6 MW; b) 5 wt% PDMS of 3×10^6 MW; c) 1 wt% PDMS of 1×10^6 MW;
d) 5 wt% PDMS of 1×10^6 MW; e) 1 wt% PDMS of 0.5×10^6 MW; f) 5 wt% PDMS of 0.5×10^6 MW

Izod Impact Strength

Impact strength is of prime importance because the poor low-temperature fracture is a significant drawback of PP for several applications. Many researchers have studied the mechanical properties of polyolefin /PDMS systems. However, few of them have reported the effect of the addition of PDMS on the impact strength of these blends. In this study, we found that the impact strength of PP was remarkably enhanced after being blended with PDMS. The results were at first unexpected, because in most previous work, mechanical properties have been found to be decreased after blended with PDMS, especially when no compatibilizer was added. As shown in

Fig. 2, the impact strength of PP/PDMS blends is increased with the increasing of PDMS content no matter what kinds of PDMS is used. When the lowest MW PDMS in the range studied is applied, the impact strength of the blends at 5 wt% contents of PDMS is enhanced up to 500% of that of the pure PP. What different is that the lower the MW of PDMS, the higher the value of impact strength of the blends. This difference in impact response for the three different systems is in accordance with SEM observations shown in Fig. 1.

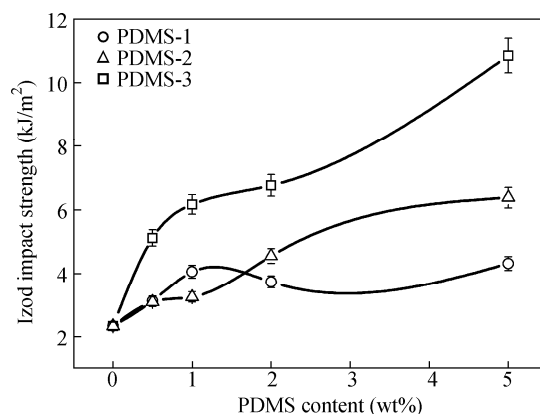


Fig. 2 Izod impact strength versus PDMS content of different PP/PDMS blends

PDMS-1: PDMS of 3×10^6 MW; PDMS-2: PDMS of 1×10^6 MW; PDMS-3: PDMS of 0.5×10^6 MW

Due to the large difference in solubility parameters between PDMS and PP^[7], the PDMS dispersed phases are likely rejected from the matrix when PDMS is used in blends. So, the mechanical properties of such blends were most likely decreased after blending with PDMS. In this article, we used a twin screw extruder to melt blend the PDMS with the PP at a maximized shear rate (110 r/min) which gave rise to the best dispersion of the PDMS phase in the PP matrix. Except for the difference of PDMS MW, the shear rates is considered as the most probable reason for the better mechanical properties shown in this study.

Tensile Strengths

The tensile properties of the different samples are illustrated in Fig. 3 as functions of PDMS content. It is very interesting to see that the tensile strengths of all the PP/PDMS blends are enhanced at lower PDMS contents and reach to a maximum at PDMS contents of about 0.5 wt% disregarding the molecular weight used. However, no regular trend was observed in the tensile strength with PDMS MW. Therefore, the simultaneous enhancement of

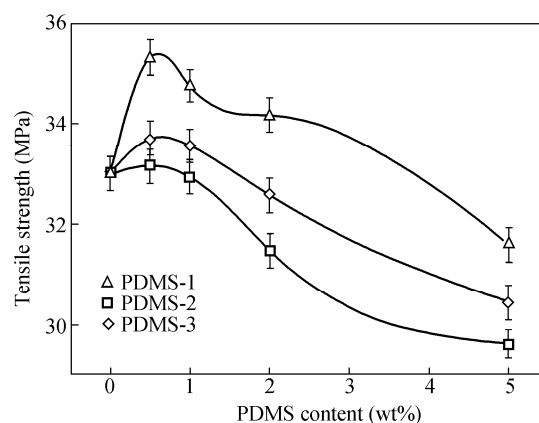


Fig. 3 Tensile strength versus PDMS content for different PP/PDMS blends

PDMS-1: PDMS of 3×10^6 MW; PDMS-2: PDMS of 1×10^6 MW; PDMS-3: PDMS of 0.5×10^6 MW

impact strength and tensile strength of PP can be achieved by adding small amount of PDMS. At higher PDMS concentrations above 1 wt%, the tensile strength slightly decreased with increasing PDMS content in PP. Nevertheless, the maximum decrease in tensile strengths was no more than 10%. Similar trend was found by Hill *et al.*^[16] that the tensile strength of TPU/PDMS blends showed optimum properties at a PDMS blend concentration of 1.5%–2%, and properties diminished rapidly at PDMS concentrations above the optimal level. It can be proposed that the addition of PDMS facilitates an improved packing efficiency (analogous to antiplasticization) in matrix polymer, leading to improved material performance. Beyond the optimum PDMS concentration, phase separation of PDMS becomes significant, plasticization sets in, and mechanical properties then begin to diminish rapidly.

Differential Scanning Calorimetry

Figure 4 shows the differential scanning calorimetry (DSC) results for unmodified PP and its binary blends with 5 wt% of PDMS of different molecular weight. An unmodified PP shows T_c at 115.1°C. Addition of PDMS to PP led to an increase in this value. Furthermore, it seems that MW of PDMS shows a significant effect on the crystallization temperature of PP. The lower the MW of PDMS, the higher the value of T_c of the blends. This implied that the lower MW PDMS had a better nucleation capability on the crystallization of PP than the higher ones. When the PDMS of 0.5×10^6 MW was applied, the PP/PDMS blends showed the highest values of T_c , indicating a more pronounced nucleating effect. From these results, it can be said that the PDMS phase domains may act as nucleating agents promoting crystallization of PP at their surface and hence lead to a blends with higher T_c values. Besides, the increase in the nucleating efficiency of PDMS of lower MW in the PP system is attributed to the increase of interfacial area between PP and PDMS, which is resulted from the reduction of the PDMS domain size. These results agree well with the SEM observations. The enhanced mobility of PP chains accompanied with the decreasing viscosity of the blends, which is caused by the reduction in the PDMS MW, is another possible reason for the increase of the nucleating effect in the blends. Further studies will be performed to clarify this point.

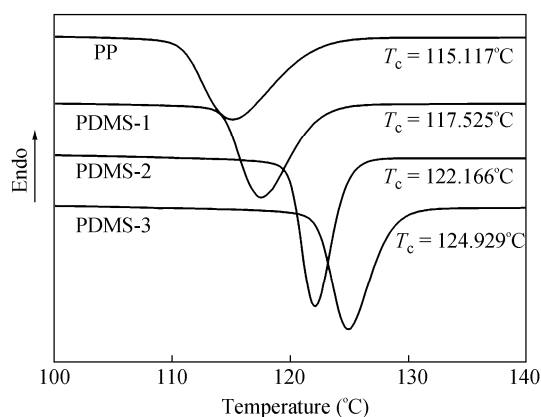


Fig. 4 DSC thermograms of pure PP and PP blends with 5% PDMS

Melting Flow Rate

Because the improvement in processing is a very important advantage of PDMS, the melting flow rates (MFR) of the pure PP and its blends with PDMS have also been investigated. The dependence of the MFR for the PP/PDMS blends on the weight per cent and MW of PDMS is shown in Fig. 5. For PP/PDMS-3 blend, MFR is significantly increased with the increase in the PDMS content. The maximum MFR value of the blend is 1.6 times larger than that of pure PP. As higher MW PDMS was applied, the MFR also increased with increasing of PDMS content, but in this case, not much increase of MFR was observed. It is expected that the flow properties of PP can be improved obviously by blending with PDMS, since the melt viscosity (the inverse of the MFR) of PDMS is much lower than that of PP.

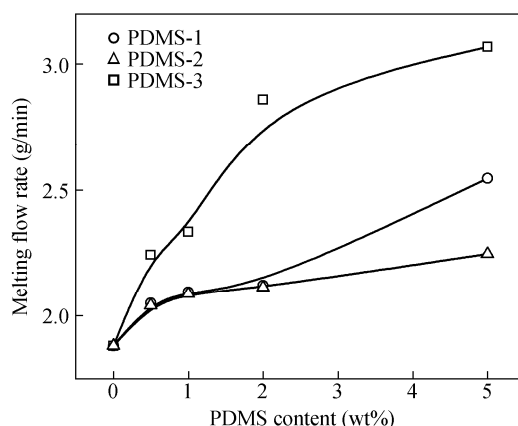


Fig. 5 MFR versus PDMS concentration of different PP/PDMS blends

PDMS-1: PDMS of 3×10^6 MW; PDMS-2: PDMS of 1×10^6 MW; PDMS-3: PDMS of 0.5×10^6 MW

CONCLUSIONS

A series of PP/PDMS blends with different molecular weight and concentrations of PDMS were prepared. Phase morphology of dispersion, mechanical properties, and differential scanning calorimetry of these blends were investigated. Interestingly, these properties were essentially dependent on the PDMS molecular weight being used. It was found that the lower the value of PDMS MW, the better the impact strength of the PP/PDMS blends with 5 wt% of PDMS. This result is in contrast to the general notion that using higher MW of elastomers may lead to better mechanical properties of blends. This is consistent with the fact that the lower molecular weight PDMS has better dispersion than that of the higher ones, which is confirmed by the SEM observations. On the other hand, the influence of the PDMS MW on tensile strengths of the PP/PDMS blends was relatively small in the range studied. A simultaneous enhancement of processibility, impact strength and tensile strength of PP can be achieved by adding low content of PDMS around 0.5 wt%.

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