

EFFECT OF PLASTICIZER ON THE MICROSTRUCTURE OF PS/PVC BLENDS

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ABSTRACT

In this work, controlling of the particle size of PVC in PS/PVC blends was studied. It is shown that viscosity ratio and particle size can be changed by adding a third composition, such as plasticizers, and the distribution of the third composition in two phases plays a very important role in controlling viscosity ratio and particle size. When DOP was used as the plasticizer of PVC in PS/PVC blends, the particle size of PVC could not be reduced due to the transference of DOP into PS phase. When polycaprolactone (PCL) was used as the plasticizer of PVC in the same blends, the particle size of PVC could be decreased obviously because PCL does not migrate to PS phase.

INTRODUCTION

Many researchers have worked on the controlling of particle size in polymer blending for a long time^[1,5], because particle size of dispersed phase affects the properties of polymer blends very much. It has been demonstrated^[4] that the key factors of controlling of particle size are stress and stress transferring for a fixed polymer blend system, that is, if a smaller particle size is expected in a polymer blend, a larger stress on the blend system is demanded and the stress must be easily transferred to the particle of dispersed phase. Stress can be expressed by the complex factor $SV/F^{[4]}$ (where S is the shear rate, V is the viscosity of the blend system and F is the volume fraction of dispersed phase). The stress transferring is controlled by the viscosity ratio between dispersed phase and continuous phase. Normally changes of shear rate, viscosity and volume fraction are limited by the equipment

used, materials used and properties needed, therefore, the particle size can not be changed significantly through changing of shear rate, viscosity and volume fraction. It has been proved^[1,5] that viscosity ratio is easier to control and the particle size is the least whenever viscosity ratio is equal to one in a polymer blend. In this work, it was found that adding a third composition, such as plasticizer, can affect the viscosity ratio and the particle size in the polymer blends. It was also found that the distribution of third composition in two phases plays a very important role in the controlling of particle size. For example, some additives can reduce the particle size and some others can not.

EXPERIMENTAL

Blending experiments were conducted under the same conditions in a special blender that is a conventional rubber mixer with a capacity of 30 ml and was improved by the authors. The particle size was measured by using phase contrast microscope, STEM and image analysis system Quantimet 520, etc. The viscosity was measured by Rosand Precision Capillary Rheometer. Commercial polystyrene (PS) and polyvinyl chloride (PVC) were used as blending materials and dioctyl phthalate (DOP) and polycaprolactone (PCL) were used as plasticizers for PVC.

Table 1 Relationship between shear rate and viscosity ratio of PS vs. PVC with different amounts (phr) of DOP at 180°C

Shear rate (s^{-1})	Viscosity ratio of PS/PVC				
	60phr	50phr	40phr	30phr	20phr
270	1.96	1.08	0.91	0.59	0.45
450	2.17	1.20	0.91	0.67	0.45
600	2.22	1.20	1.0	0.67	0.45
750	2.08	1.18	0.91	0.67	0.48
Average	2.08	1.16	0.91	0.63	0.45

RESULTS AND DISCUSSIONS

1. *Measuring of viscosity ratio*

Torque ratio stands for viscosity ratio in the research of polymer blends^[1], which is not very suitable because torque is not only an unstable factor in polymer systems at high temperature, but also it can not be obtained in many mixers. Furthermore,

viscosity ratio does not change largely during a certain range of shear rate as shown in Table 1.

It is obvious that the viscosity ratio is almost a constant for a certain pair of materials in normal range of shear rate for normal mixers; therefore, the average viscosity ratio measured by the rheometer in the range of shear rate 270 to 750 s^{-1} was used in this work.

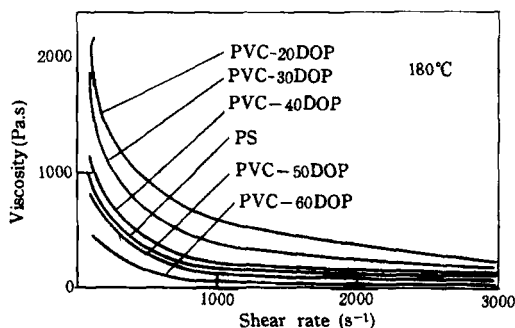


Fig. 1 Relationship between viscosity and shear rate for PS and PVC with different amounts of DOP

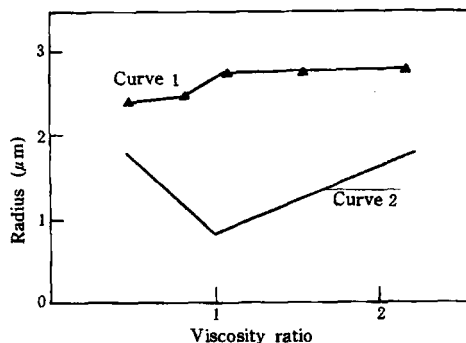


Fig. 2 Relationship between particle size and viscosity ratio in PS/PVC with DOP blends

2. Effect of the third composition on viscosity ratio and particle size

There are several methods to control the viscosity ratio in polymer blending researches, such as, by using polymers with different molecular weight^[1] or by mixing at different temperature^[5], etc. Addition of third composition, such as, some plasticizers, can change viscosity ratio as well and the distribution of the third composition in two phases plays a very important role in viscosity ratio controlling; therefore, the latter factor should be considered carefully before addition a plasticizer to a polymer blend in order to change the viscosity ratio. Sometimes the addition of the third composition can cause the particle size even larger since the distribution of third composition does not act like what we expected.

(1) The effect of adding DOP on viscosity ratio and particle size

The relationship between viscosity of PS and PVC and shear rate after adding DOP to PVC is shown in Fig.1. It is obvious that viscosity of PVC with 40 phr DOP and PVC with 50 phr DOP are the closest to that of PS; therefore, it seems that the particle size should vary similarly to the Curve 2 in Fig. 2 according to the "Viscosity Ratio Theory"^[1,5]. But the practical curve is the Curve 1 in Fig. 2.

This situation is due to the distribution of DOP in PS/PVC blends. During blending some DOP in PVC can transfer to PS, which was proved by the following

facts: (1) When a sheet of PS film was covered with another sheet of PVC with 60 phr DOP and then heated at 180°C for 5 min., a certain amount of DOP did transfer to PS as evidenced from the $\nu_{C=O}$ bands (1723 and 1730 cm^{-1}) of DOP in the FT-IR spectrum of PS film (see Fig. 3); (2) When a PS bar was immersed in DOP at 140°C for 10 min, the weight of the bar increased from 0.432g to 0.568g.

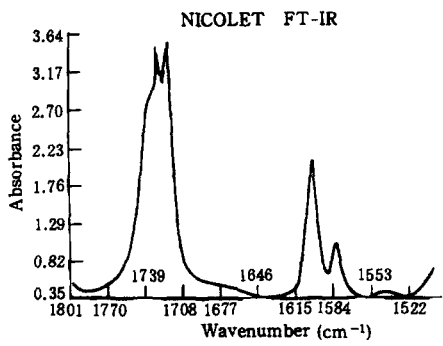


Fig. 3 FT-IR spectrum of PS with sucking DOP

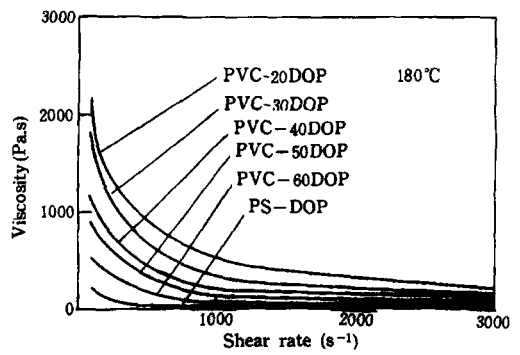


Fig. 4 Relationship between viscosity and shear rate of PS with sucking DOP

As a result of the transference of DOP from PVC to PS, the viscosity of PS was reduced and the viscosity of PVC with DOP was increased, which was shown in Fig. 4.

It is obvious that the viscosity ratio of PS/PVC blends with DOP were not as expected.

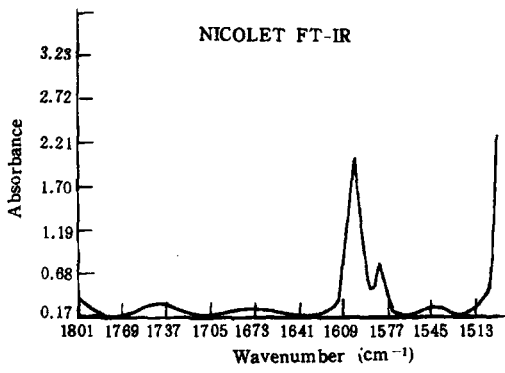


Fig. 5 FT-IR spectrum of PS without sucking PCL

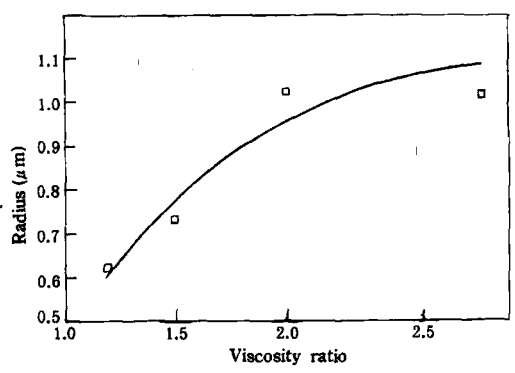


Fig. 6 Relationship between particle size and viscosity ratio in PS/PVC with PCL blends

(2) The effect of adding PCL on the particle size of PS/PVC blends

According to the result mentioned above, if smaller particle size is expected, the

distribution of the third composition should be carefully considered before it is used. It has been proved that PCL is soluble in PVC and is not compatible with PS by the following facts: When PCL is blended with PVC, transparent material can be obtained and when PCL/PS blend is reheated, separation of two phases (PS and PCL) occurs. Furthermore when a sheet of PVC with 40 phr PCL was placed on another sheet of PS and then heated at 180°C for 5 min., no PCL was found by FT-IR in the sheet of PS, as shown in Fig. 5. The relationship between particle size and viscosity ratio in PS/PVC blends with PCL is quite reasonable as the curve shown in Fig. 6.

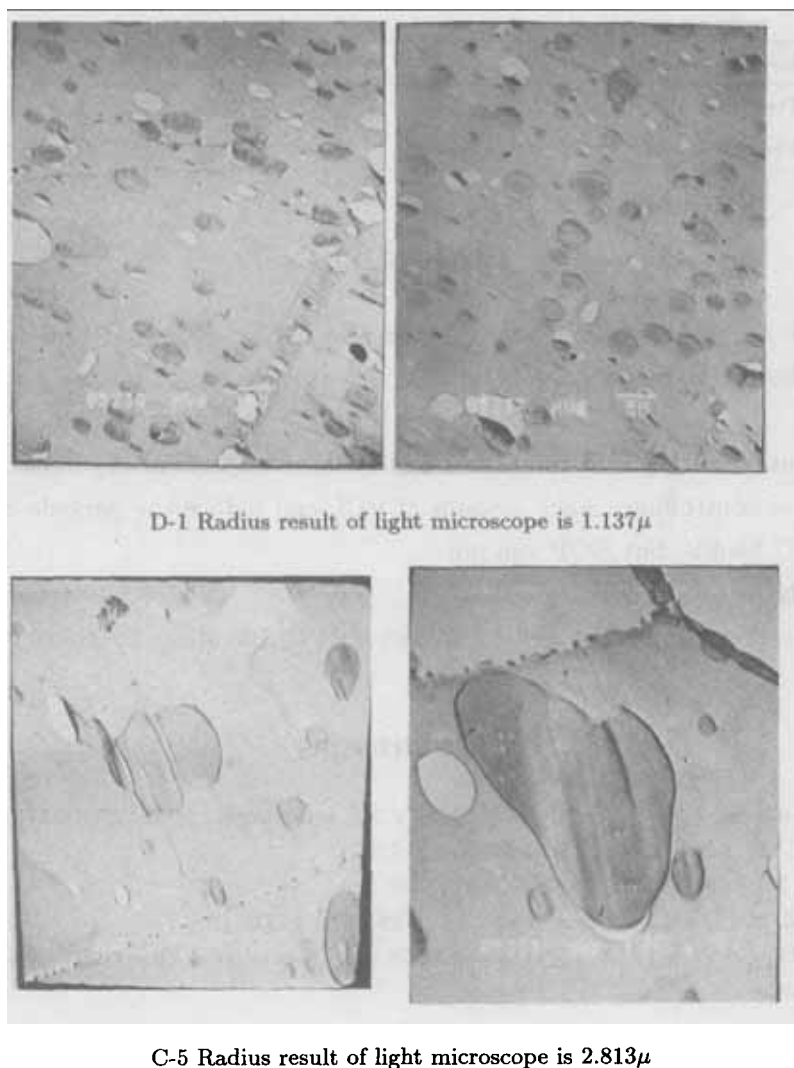


Fig. 7 Comparison of particle size results of PVC in PS/PVC blends of light microscope with photos of STEM (STEM 2000)

3. Reliability of the results

In order to guarantee the particle size results of light microscope, they were checked by STEM. The result was found to be quite reliable as shown in Fig. 7.

4. The relationship between particle size and starting materials

The particle size was found independent on starting materials, which is shown in Table 2. It shows that the particles have been already in their equilibrium state of combining and breaking, that is, the blender improved by the authors is efficient enough for polymer blending study.

Table 2 The relationship between particle size and starting materials

Starting materials	Particle size (μ)		
Powdered PVC	2.635	2.708	2.651
Processed PVC	2.436	2.813	2.793

CONCLUSION

1. Particle size of dispersed phase may be affected by adding a third composition, such as plasticizer in polymer blends due to the change of viscosity ratio of two materials.
2. Distribution of the third composition in two phases plays a very important role in particle size controlling. Some amount of PCL can reduce the particle size of PVC in PS/PVC blends, but DOP can not.

Keywords:

Viscosity ratio; Microstructure; Polystyrene; PVC; Blending; Plasticizer

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