

Studies of Rigid Poly(vinyl chloride) (PVC) Compounds. II. Determination of the Fusion Level

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SYNOPSIS

Rigid poly(vinyl chloride) (PVC) compounds were prepared in a Haake torque rheometer using various blending conditions. The fusion levels of processed compounds were evaluated by a capillary rheometer and differential scanning calorimetry (DSC), based on the entrance pressure drop and the heat of fusion, respectively. S-shaped fusion curves were obtained. Starting temperature of the mixer, rotor speed, and totalized torque are the three major factors that affect the fusion level of PVC compounds blended in the Haake torque rheometer. All three parameters have a significant effect; however, totalized torque has the greatest effect and this can be characterized using a torque rheometer. Both capillary rheological and DSC thermal analysis can be applied to determine the fusion level of a PVC compound. The morphological changes of the various fusion processes were characterized by scanning electron microscopy (SEM). © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Various levels of morphology exist in suspension poly(vinyl chloride) (PVC) powder as illustrated by Butters.¹ Powder particles known as grains are visible to the naked eye. These are irregular in shape and are about 100–150 μm in diameter. Each grain consists of many microparticles which are about 1–2 μm in diameter. These microparticles are loosely packed together, giving the grain its porous nature. Each microparticle is made up of still smaller structures, submicroparticles, which are approximately 100–300 \AA in diameter and contain about 5–10% crystallinity. To achieve good mechanical properties, grain boundaries must be eliminated and the microparticles must be altered and compacted together. After significant interdiffusion, the boundaries of submicroparticles disappear, and a three-dimensional network of polymer chains is formed. This is referred to as the fusion, or gelation, of poly(vinyl chloride) (PVC).^{2,3} Benjamin⁴ reported that a PVC product with the fusion level between 60 and 80% has an optimum value of impact ductility.

Batch mixers have been used to process PVC compounds for a long time due to their superior heat transfer, slightly better dispersion, relatively short mixing cycles, capabilities with large capacities, and flexibility when frequent product and formulation changes are encountered.⁵ Krzewki and Collins^{3,6} reported, in detail, the influence of temperature and additives on the fusion level of PVC compounds in a temperature-programmed Brabender plasticorder. The fusion of PVC compounds is highly dependent upon the additives and the rotor speed, as well as upon its thermal history in a batch mixer. The intention of this study was to understand how temperature, rotor speed, and totalized torque affect the fusion level of PVC compounds in a Haake torque rheometer. Additionally, this study has revealed the relationship between the morphology and the fusion level.

Several different fusion assessment methods have been well developed.² Tensile property measurement,⁷ solvent immersion tests,⁴ optical methods,⁸ capillary rheometry,^{9–11} and thermal analysis^{12–15} are commonly used. In this research, we applied both a capillary rheometer, based on the entrance pressure drop through a zero-length die, and DSC thermal analysis, based on the heat of fusion, to determine the fusion level of PVC compounds.

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EXPERIMENTAL

Preparation of PVC Compounds

The material used in this study is suspension PVC masterbatch powder, containing 100 parts of PVC resin (MW \approx 150,000), 1.5 parts of process aid (K120N), 1.0 part of wax (XL165), 1.0 part of calcium stearate, and 1.5 parts of heat stabilizer (T-137). All samples were supplied by the Dow Chemical Co.

To determine the influence of temperature and totalized torque on the degree of fusion, PVC samples with various fusion levels were prepared in a Haake Rheomix 600 batch mixer with a Haake Rheocord 90 drive, equipped with an electrically heated mixing head. Noninterchangeable roller-type rotors were used. The rotor speed was set at 60 rpm, and the sample weight was always 65 g. Samples were charged into the mixer set at 160, 170, 180, 190, and 200°C and removed at various totalized torques (kg-m-min). Totalized torque is defined as the instantaneous torque integrated over the processing time.

Capillary Rheological Analysis

The viscoelastic property of all processed PVC samples was characterized by the zero-length capillary entrance pressure drop at 180°C. To put samples into the barrel with a diameter of 20 mm, all PVC samples were cracked into small pieces by a hammer. The test conditions are summarized in Table I. The rheological measurements were performed on the advanced capillary extrusion rheometer system (ACER 2000, Polymer Laboratory, now Rheometrics) equipped with a pressure transducer and a measuring range of up to 700 MPa. The entrance pressure drop was read by the pressure transducer every 4 s. An average value was obtained after approximately 150 entrance pressure drop data points were measured. A "zero-length" capillary die was used. To minimize the possibility of slip and maximize the amount of internal deformation, a flat entry was selected for the zero-length capillary.^{3,6} To melt rigid PVC compounds, PVC samples were put in the barrel at an isothermal temperature (180°C) for 25 min before the measurement.

DSC Thermal Analysis

PVC compounds prepared by the Haake torque rheometer were cut randomly into small pieces, weighted approximately 10 mg, and then characterized by a SEIKO 220C automatic cooling differential

Table I Test Conditions for Capillary Rheological Measurements

Rheometer	ACER 2000
Temperature	180°C
Capillary (flat entry)	Diameter: 1.1 mm Length: 0.33 mm L/D: 0.3
Barrel	Diameter: 20 mm
Shear rate (0.5 mm/min)	23.6 s ⁻¹ , constant
Sample	<ul style="list-style-type: none"> • Small pieces with a diameter less than 20 mm • Always the same amount, 25 g • Preheating 25 min
Measured variable	Entrance pressure drop for extrusion at a constant shear rate, 23.6 s ⁻¹

scanning calorimeter. The samples were heated from room temperature to 270°C at 20°C per min. Three DSC measurements from each Haake preparation were conducted for each PVC compound in order to obtain an average value for the heat of fusion. This average value was used to determine the fusion level of the PVC compound.

SEM Analysis

PVC samples were immersed into liquid nitrogen for 45 s, fractured, and coated with 200 Å gold-palladium film and then examined using a Cambridge S-260 SEM.

RESULTS AND DISCUSSION

Capillary Rheological Analysis

Figure 1 shows the capillary entrance pressure drop for the PVC sample prepared by a Haake torque rheometer at 160°C, 100 rpm, and discharged at a totalized torque of 1 kg-m-min. At the very beginning of the measurement, due to packing of the PVC sample, the extrusion pressure increased slowly. After packing, the steady-state extrusion pressure, with random variation, was achieved. Around 120–150 data points were measured, and an average value was taken. This average value is the elastic response, as measured by the zero-length capillary.

To calculate the degree of fusion for each compound, the extrusion pressure for the unprocessed compound ($P^* = 5.39$ MPa) was taken as the 0% fusion level. The pressure for a processed compound

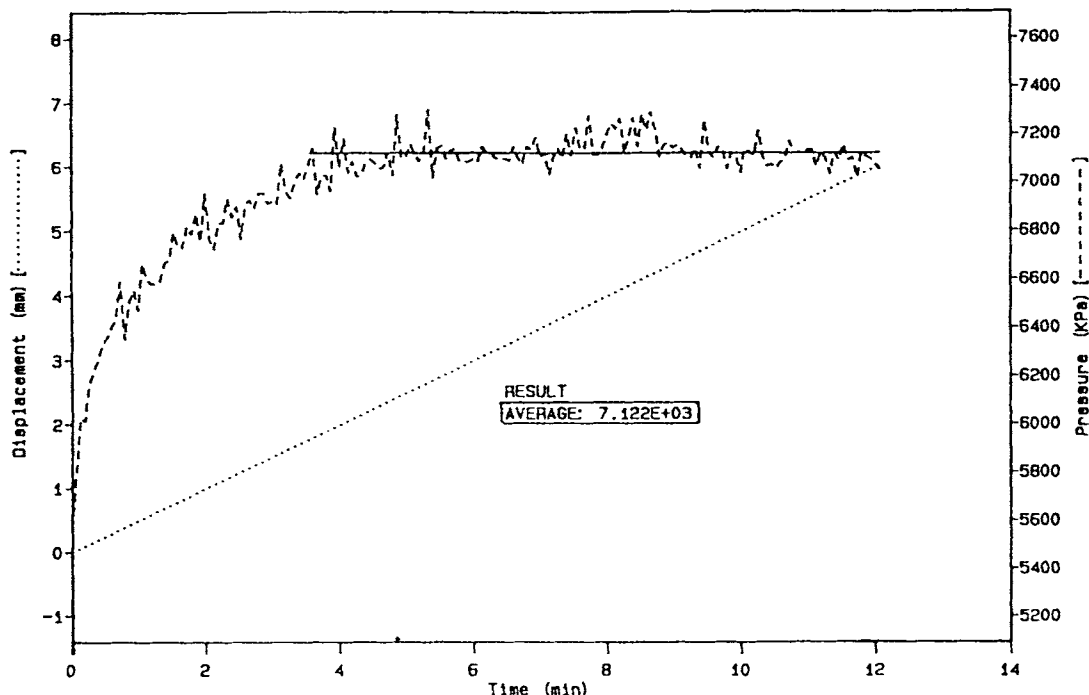


Figure 1 Entrance pressure drop measured by a zero-length capillary die at a constant shear rate of 23.6 s^{-1} and 180°C .

($P_{200,15} = 10.83 \text{ MPa}$), which was processed at a starting temperature of 200°C at a rotor speed of 60 rpm and stopped at a totalized torque of 15 kg-m-min, was taken as the 100% fusion level. The fusion level corresponding to the extrusion pressure (P) was then calculated from the following equation:

Fusion level (%)

$$= (P - 5.39) / (10.83 - 5.39) \times 100\%$$

The degree of fusion of the PVC compound increased with totalized torque, and when plotted against totalized torque, produced an S-shaped curve (see Fig. 2). It can be seen that, as the starting temperature is increased, the slope of the fusion level curve also increases. This is because more thermal energy input occurs at higher starting temperatures.

DSC Thermal Analysis

Figure 3 displays the DSC thermal analysis curves of PVC compounds blended in the Haake torque rheometer at various temperatures. A DSC trace of PVC powder has an endothermic base-line shift at the glass transition temperature (T_g) (approximately 80°C). There are two peaks, A and B, in these DSC traces. Peak B results from the endothermic energy of the original PVC crystals that are not melted in the Haake torque rheometer. When

the processing temperature increases, this peak decreases in size and shifts to a higher temperature. Gilbert and Vyvoda^{2,12} suggested that the size decrease was due to the melting of less perfect, or smaller, crystallites and the temperature shift was caused by annealing of unmelted crystallites. Peak A is related to the endothermic energy of the PVC crystals that are melted in the Haake torque rheometer and recrystallized after cooling at room temperature. The area of peak A was measured in order

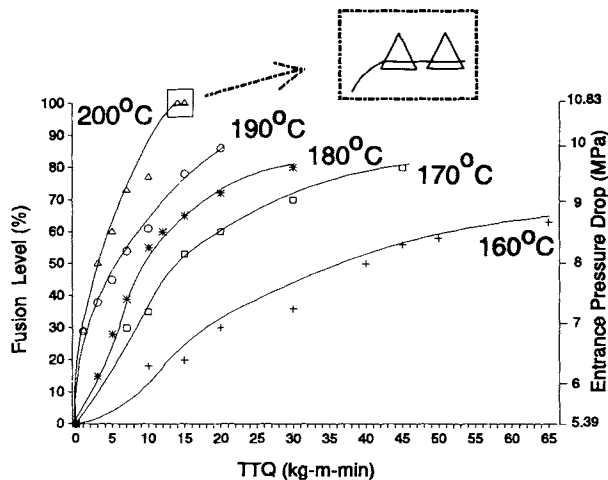


Figure 2 Effect of temperature and totalized torque on the fusion level of PVC compounds measured by capillary rheological analysis.

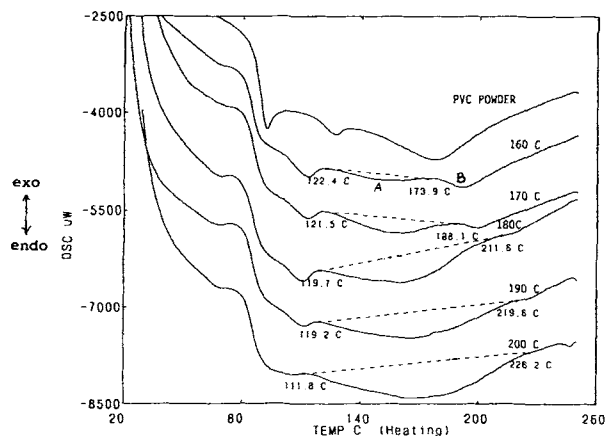


Figure 3 DSC thermal analysis curves of PVC compounds processed in a Haake torque rheometer at rotor speed = 60 rpm, TTQ = 10 kg-m-min, and various temperature.

to determine the heat of fusion of the PVC compound.

The endothermic peak A appears and increases in size when the totalized torque is increased at the same starting temperature and a rotor speed of 60 rpm. The energy of this endothermic reaction, ΔH_A , increases with totalized torque and, when plotted against totalized torque, produces an S-shaped curve (see Fig. 4). It can be seen that as the starting temperature increased the slope of the fusion level curve also increased. Again, this is because more thermal energy input occurs at higher starting temperatures. To calculate the relative fusion level for each PVC compound, the heat of fusion for the unprocessed compound (0 mJ/mg) was taken as 0% fusion level, and the processed compound (13.72 mJ/mg) (processed at a starting temperature of 200°C, a rotor speed of 60 rpm, and stopped at a totalized torque of 15 kg-m-min) was taken as 100% fusion level. DSC thermal analysis has experimental advantages because it provides a convenient, quantitative measure of the fusion level and uses a very small sample (approximately 10 mg).

Rheological Analysis vs. Thermal Analysis

Although similar fusion curves are obtained comparing Figure 2 (rheological analysis) with Figure 4 (thermal analysis), one important difference exists. The degree of fusion of PVC, processed at a low processing temperature or low totalized torque and determined by the rheological analysis, is much higher than is the result indicated by thermal analysis. This may be because the preheating process, 25 min at 180°C, provides enough thermal energy to improve the fusion of non-well-fused PVC par-

ticles which were preprocessed in a Haake torque rheometer. Figure 5 shows the morphological changes of PVC powder, low fusion level, medium fusion level, and high fusion level PVC samples before and after the rheological analysis. It illustrates that the preheating process does improve the fusion of nonfused PVC particles. Therefore, a significant fusion level is increased for non-well-fused particles due to the preheating process. For well-fused PVC compounds, this preheating process causes very little effect on the degree of fusion.

The capillary rheological analysis has a main advantage in that this method uses a sample large enough to eliminate local inhomogeneity in the degree of fusion. The two main disadvantages of this method are that the preheating process may interfere with the degree of fusion of PVC and the necessity of obtaining a standard fusion curve for each compound processed in specific processing equipment. Also, the elastic response as measured by the rheological analysis is strongly composition-dependent.⁶

DSC thermal analysis has attracted attention recently because it provides a convenient, quantitative measure of the fusion level and uses a very small sample (approximately 10 mg). The main disadvantage of thermal analysis is that some additives may interfere with the final results because the sample size is very small.

SEM Analysis

The surface morphology of a suspension PVC grain particle, approximately 100–150 μm in diameter, is shown in Figure 6. Figure 7 shows the surface mor-

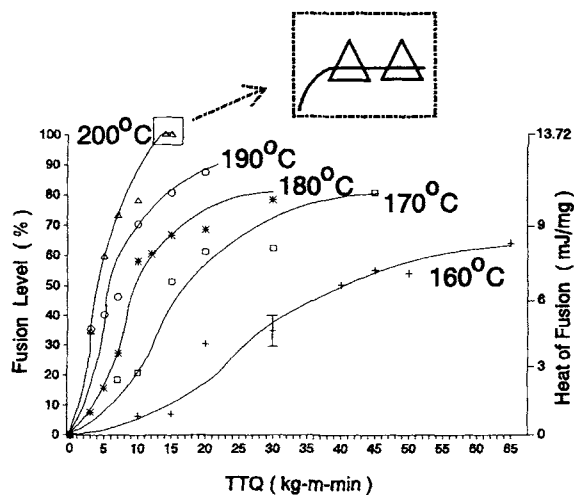


Figure 4 Effect of temperature and totalized torque on the degree of fusion of PVC compounds measured by DSC thermal analysis.

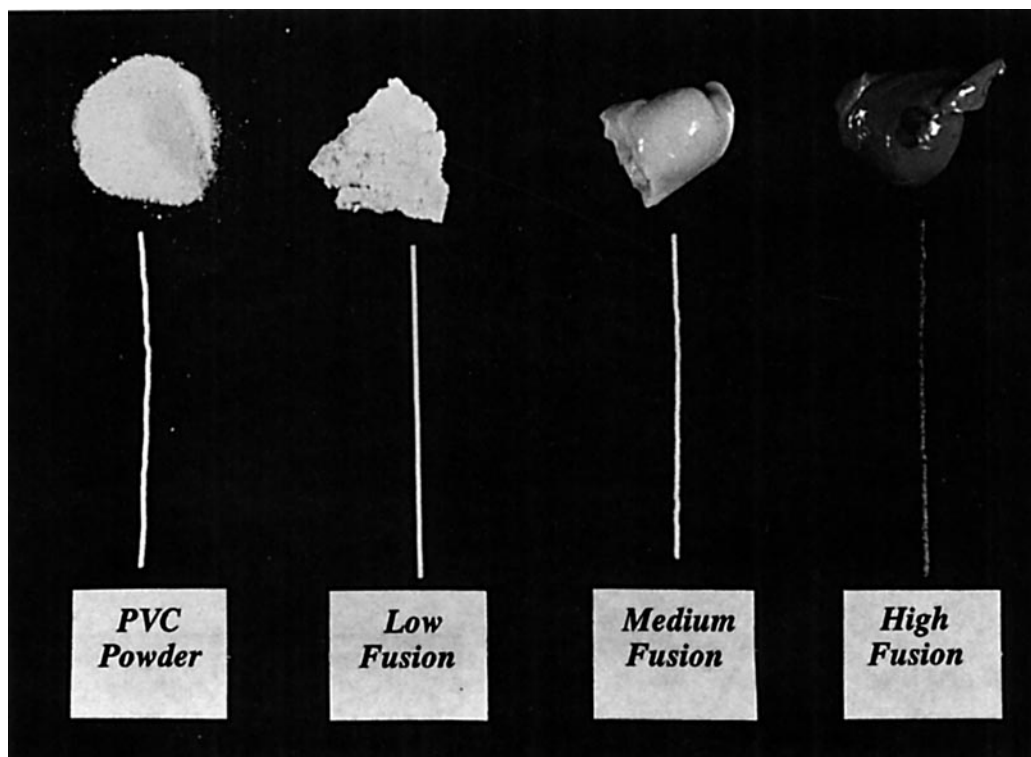


Figure 5 Morphological changes of PVC compounds: (a) PVC powder and (b) low, (c) medium, (d) high fusion levels, extruded from the capillary rheometer.

phology of the very beginning of fusion of PVC particles. It illustrates that some PVC grain particles were broken down to PVC microparticles and a few PVC grain particles still remained intact. Both the

PVC grain particles and the microparticles were compacted together. After this stage, if more energy was put into the PVC compound, the boundaries of

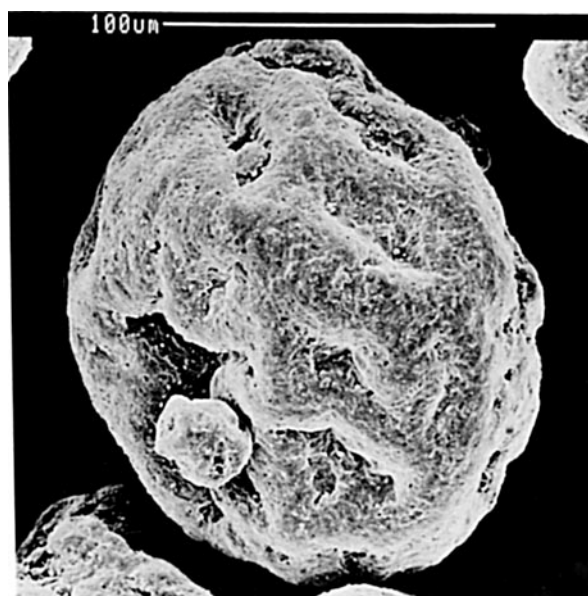


Figure 6 Surface morphology of a suspension PVC powder.

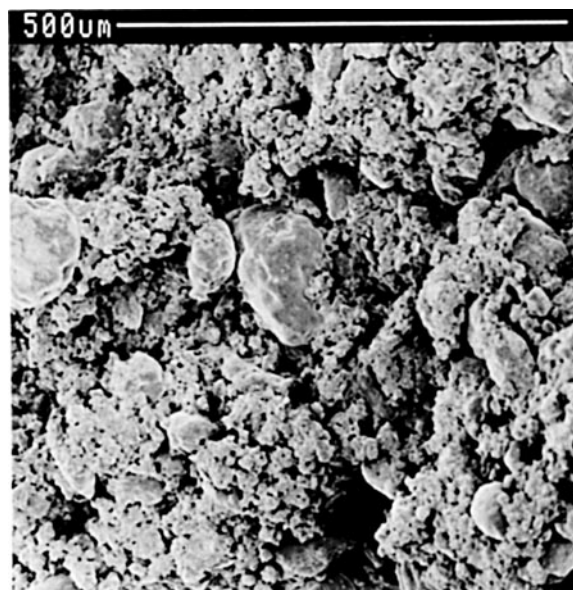


Figure 7 Surface morphology of PVC blended in a Haake torque rheometer at temperature = 190°C, rotor speed = 100 rpm, and TTQ = 1 kg-m-min.

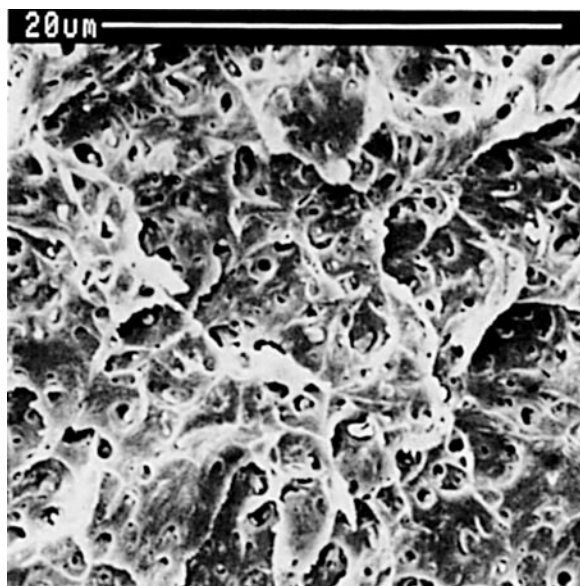


Figure 8 Surface morphology of PVC blended in a Haake torque rheometer at temperature = 160°C, rotor speed = 60 rpm, and TTQ = 10 kg-m-min.

the PVC microparticles could be broken down into submicroparticles and the submicroparticles could begin to fuse together in order to form a 3-D network.

Figures 8–10 show the 3-D network surface morphological changes of PVC compounds which were blended in the Haake torque rheometer at a rotor speed of 60 rpm, 10 kg-m-min totalized torque, and starting temperatures of 160, 180, and 200°C, respectively. At the lowest starting temperature, 160°C, the surface morphology of the PVC compound is not very smooth because the interfusion between the PVC particles was not good enough to form a smooth, 3-D network. At the medium starting temperature, 180°C, the surface morphology of the PVC compound is much smoother than that for 160°C, because of the better interfusion between the PVC particles. At the highest starting temperature, 200°C, the surface morphology of the PVC compound is smoother and less porous than that for 180°C, because of the much better interfusion between the PVC particles. Figure 11 shows the surface morphology of the well-fused PVC compound with embedded small particles of additives. The blending condition for this sample was set at a starting temperature of 200°C, rotor speed of 60 rpm, and stopped at a totalized torque of 15 kg-m-min in the Haake torque rheometer. The color of this PVC sample was black because some PVC particles were overfused and burned when processed in the Haake torque rheometer. Because the distribution of energy in the Haake torque rheometer is not very uniform,

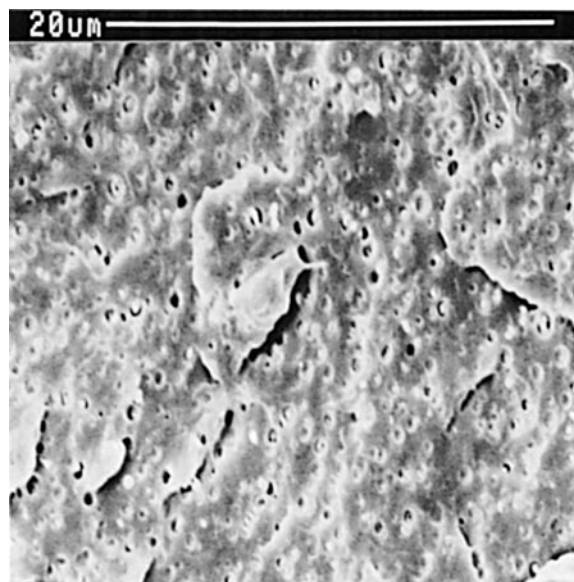


Figure 9 Surface morphology of PVC blended in a Haake torque rheometer at temperature = 180°C, rotor speed = 60 rpm, and TTQ = 10 kg-m-min.

few PVC submicroparticles are still observed in Figure 11.

CONCLUSIONS

S-shaped fusion curves were obtained. Starting temperature of the mixer, rotor speed, and totalized

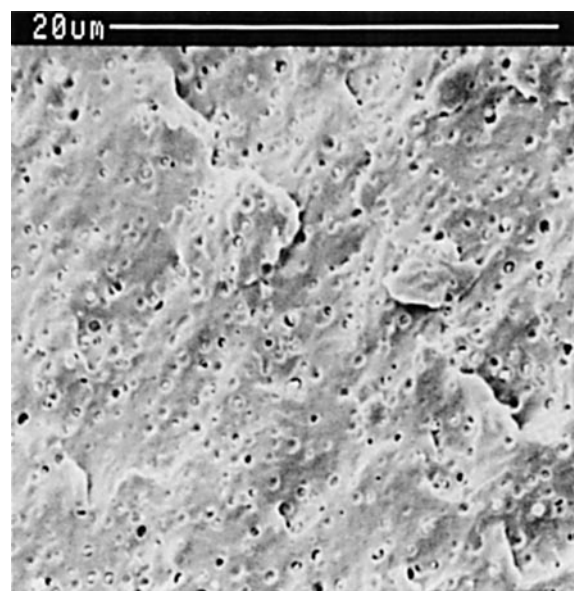


Figure 10 Surface morphology of PVC blended in a Haake torque rheometer at temperature = 200°C, rotor speed = 60 rpm, and TTQ = 10 kg-m-min.

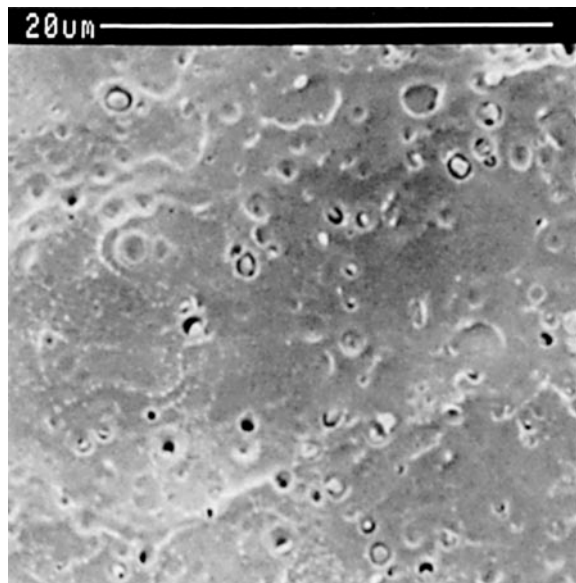


Figure 11 Surface morphology of PVC blended in a Haake torque rheometer at temperature = 200°C, rotor speed = 60 rpm, and TTQ = 15 kg-m-min.

torque are the three major factors that affect the degree of fusion of PVC compounds blended in the Haake torque rheometer. To obtain high-impact strength PVC compounds which were used in this study, optimal mixing conditions may be to set the starting temperature of the mixer at 180 or 190°C, the rotor speed at 60 or 70 rpm, and the totalized torque at 10 kg-m-min. Optimal mixing conditions may be varied based upon compound formulation. Both capillary rheological and DSC thermal analysis can be applied to determine the degree of fusion of a PVC compound.

The main advantage of capillary rheological analysis is that it uses a sample large enough to eliminate local inhomogeneity in the degree of fusion. The two main disadvantages of this method are that the preheating process may interfere with the degree of fusion of PVC and the necessity of getting a standard fusion curve for each compound processed in certain processing equipment. Also, the

elastic response, as measured by the rheological analysis, is strongly composition-dependent.⁶

DSC thermal analysis has attracted attention recently because it provides a convenient, quantitative measure of the fusion level and uses a very small sample (approximately 10 mg). The main disadvantage of thermal analysis is that some additives may interfere with the final results because the sample size is very small.

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