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Fusion study of polyvinyl chloride (PVC): Relation of Processing time and processing temperature to the degree of fusion

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Summary

Several polyvinyl chloride(PVC) compounds were prepared in a Haake Torque Rheometer, equipped with noninterchangeable rotors and an electrically-heated mixing head, at various processing times and processing temperatures, with a constant rotor speed of 60 rpm. A Seiko 220C Automatic Cooling Differential Scanning Calorimeter(DSC) was then used to characterize the degree of fusion of these compounds. Afterwards, a Cambridge 260 Scanning Electron Microscope(SEM) was used to study the morphological characteristics of these compounds. In this paper, a correlation has been established between the processing time and processing temperature and the degree of fusion of these PVC compounds.

Introduction

Ultimately, the goal of this research is to understand the correlation between the fusion characteristics and the mechanical properties of PVC compounds. This knowledge can then be applied to the extrusion process in order to develop formulations that will optimize the mechanical properties of PVC compounds in various demands. This particular study focuses upon the relationship between the processing time and the processing temperature and the degree of fusion of PVC compounds.

The suspension polymerization process is the primary route to preparing PVC in industry today. Batch mixers, such as Brabender and Haake Rheometers, are frequently used in research applications because of their flexibility while experiencing frequent product and formulation changes (1).

Three stages of morphology exists in PVC powder: stage I, stage II and stage III. Stage III particles are known as PVC grain particles and are visible to the naked eye; they are approximately 100-150μm in diameter. Stage II particles, known as microparticles, compose stage III particles, and because they are loosely packed, they give the PVC grain particles a porous nature. The stage II particles are 1-2μm in diameter. Finally, stage I particles, known as submicroparticles, are found in stage II particles and are 100-300Å in diameter. Stage I particles exhibit 5-10% crystallinity. The significance of these stages of morphology lies in their role in determining the mechanical properties of PVC. In order for PVC to have good mechanical properties, the grain boundaries must be eliminated and part of the microparticles must be destroyed so that they can be compacted. During further interfusion of the PVC, the boundaries between the submicroparticles disappear, and the PVC grains from a 3-D network, known as the gelation, or fusion, of PVC (2, 3).

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In this study, DSC thermal analysis was used to characterize the degree of fusion of PVC compounds because of its convenience and the fact that DSC provides a quick, quantitative measurement of the degree of fusion. The main disadvantage of DSC lies in the fact that, due to the small sample weight of 10mg, some poorly dispersed additives may interfere with the final results.
The intent of this study is to understand how processing temperature and processing time affect the degree of fusion of PVC compounds in a Haake Torque Rheometer. Additionally, a relationship will be established between the morphology and the degree of fusion of these compounds, as well as between the processing temperature and fusion time of the PVC compounds.

Experimental

Preparation of the PVC compounds

The PVC was prepared via suspension polymerization and was supplied by the DOW Chemical Company. The PVC masterbatch powder contained 100 parts of PVC grain particles, 1.5 parts of processing aid (K120N), 1.0 parts of wax (XL165), 1.0 parts of calcium stearate, 1.5 parts of heat stabilizer (T-137).

Several PVC compounds were prepared in a Haake Torque Rheometer (Rheocord 90) equipped with an electrically-heated mixing head and noninterchangeable rotors. These PVC compounds were prepared at various processing times and various processing temperatures, specifically, at 160, 170, 180, 190 and 200°C, and blending times of 1, 3, 5, 7 and 8 min. The rotor speed was 60 rpm, and the sample weight was 65g.

Differential Scanning Calorimetry (DSC) thermal analysis

The PVC compounds prepared in the Haake Torque Rheometer were cut randomly, and each sample was prepared to be approximately 10mg. The degree of fusion was characterized by a Seiko 220C Automatic Cooling Differential Scanning Calorimeter (DSC), based on the heat of fusion (mJ/mg). Using DSC, the samples were heated from 25°C to 270°C, at 20°C/min. Three measurements were made for each sample so that an average value for the heat of fusion could be calculated.

Scanning Electron Microscopy (SEM) analysis

A Cambridge S-260 Scanning Electron Microscope (SEM) was used. The samples were immersed in liquid nitrogen for 45 seconds, broken and coated with 200Å gold-palladium film. Only the centers of the broken surfaces were examined.

Results and discussion

Haake Torque Rheometer

A typical curve obtained from the Haake Torque Rheometer, such as in the inset of Figure 1, contains five significant locations. The portion of the curve between the loading point (L) and the stopping point (S) is the processing time. The portion of the curve between L and the fusion point (F) is defined as the fusion time (FT), and is the most important portion of the graph. Point O on the graph (not shown) is the point at which the PVC compound begins to degrade, and point D (also not shown) is the actual degradation point. At this point the PVC forms hydrochloric acid

(HCl). PVC that has been processed to this point is black and very porous. Therefore, the stopping point is usually located between points L and O in order to prevent this degradation.

When comparing several curves from the Haake Rheometer, such as in Figure 1, it is noticed that, as the processing temperature increases, for any given time, the fusion time decreases. A graphical representation of this phenomenon is in Figure 2. The PVC compound prepared at 200°C for 7 min had a dramatically lower fusion time than that prepared at 160°C for 7 min. This is probably because, when a higher thermal energy input in encountered, interfusion among the PVC submicroparticles to form a 3-D network occurs at a faster rate.

Differential Scanning Calorimetry (DSC) thermal analysis

Figure 3 contains DSC traces used by Chen (4). The DSC curves obtained in the present study displayed the same trends. Each DSC curve displayed a glass transition temperature (T_g) at approximately 85°C, and an endothermic baseline shift occurred at this temperature. Two significant peaks were noticed: peak A and peak B. Peak A represented the endothermic energy of the PVC crystals melted in the Haake Torque Rheometer and then recrystallized during cooling. Peak B represented the endothermic energy of the PVC crystals not melted in the Haake Torque Rheometer. The endothermic energy contained in peak A was used as a quantitative measure for the degree of fusion (5). In order to determine the relative degree of fusion for each PVC compound, the heat of fusion for the unprocessed PVC compound (0mJ/mg) and the PVC compound processed at 200°C for 8.5 min (13.72mJ/mg) were taken as 0% and 100% degrees of fusion, respectively.

Samples with a low processing time or temperature had no, or a very small, peak A and a very large peak B. When comparing the various DSC curves, it was noticed that with increasing processing times and temperatures, peak A expanded and peak B shrunk. Another observation was that, as the processing temperature increased, peak B shifted to a higher temperature. As seen in Figures 4 and 5, as processing time and temperature increased, the degree of fusion also increased.

Scanning Electron Microscopy (SEM) analysis

SEM analysis provided informative visual aids to study the morphology of the PVC compounds. Figure 6 contains some of the SEM micrographs. A PVC grain particle is seen in Figure 6 I. The grain particle was rounded and had a very porous surface. This PVC grain particle (stage III particle) was approximately 100-150μm in diameter. The PVC compound prepared at 160°C for 7 min had a very poor degree of fusion (refer to Figure 6 II). The texture was very rough and non-continuous, and the interfusion was not strong enough to form a smooth, 3-D network. The PVC compound prepared at 170°C for 7 min had a slightly better degree of fusion. The discontinuity had been reduced in many areas; large crevasses did still occur, but they were confined to smaller areas. The PVC compound prepared at 180°C for 7 min had a much improved degree of fusion (refer to Figure 6 III). Some holes did still appear, but the harsh crevasses were eliminated. A stronger level of

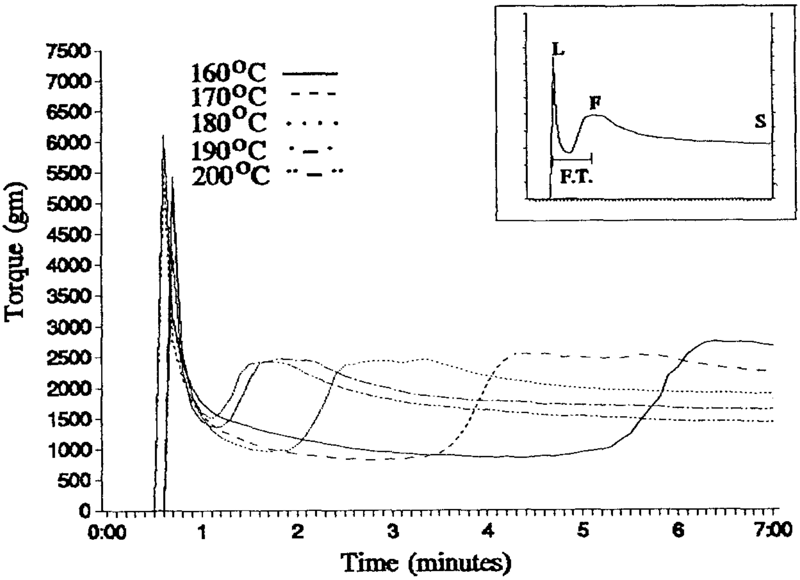

Figure 1 An overlapp of several curves obtained from the Haake Torque Rheometer, displaying a decrease in the fusion time.

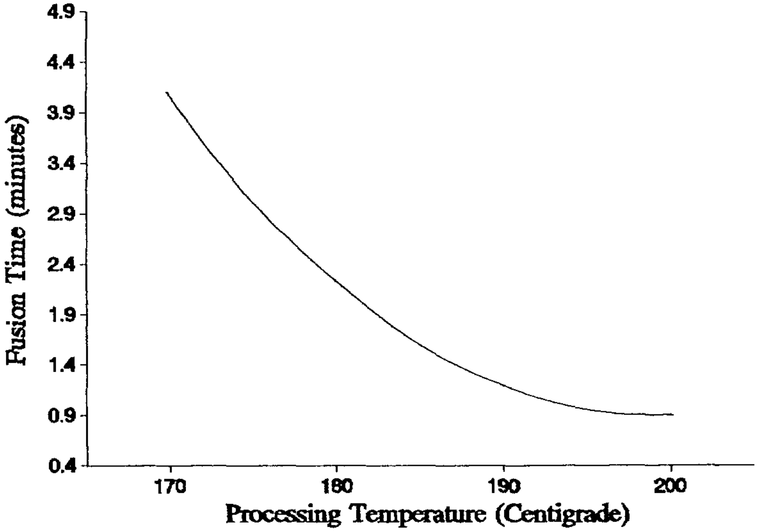

Figure 2 The relationship between the processing temperature and the fusion time of PVC compounds.

interfusion was noticed. The PVC compound prepared at 190°C for 7 min had a still higher degree of fusion than that of previous samples. The texture is still not smooth, but is much more continuous. There were no drastic changes when moving on to the PVC compound prepared at 200°C for 7 min, but a slightly higher fusion level was noticed. The PVC compound prepared at 200°C for 8 min was used as the standard for a degree of fusion of 100% (refer to Figure 6 IV). A much higher degree of fusion was noticed with a much smoother continuity. The stronger interfusion between the PVC particles caused a much smoother 3-D network of the polymer chains to be formed in this sample. Because the distribution of energy in the Haake Torque Rheometer was not very uniform, some PVC primary particles were observed in all samples.

Conclusions

At a constant rotor speed of 60 rpm, as the processing temperature and processing time of the PVC compounds increased, the degree of fusion of the PVC compounds also increased. Furthermore, as the processing temperature increased, for a given processing time, the fusion time decreased. Due to a higher thermal energy

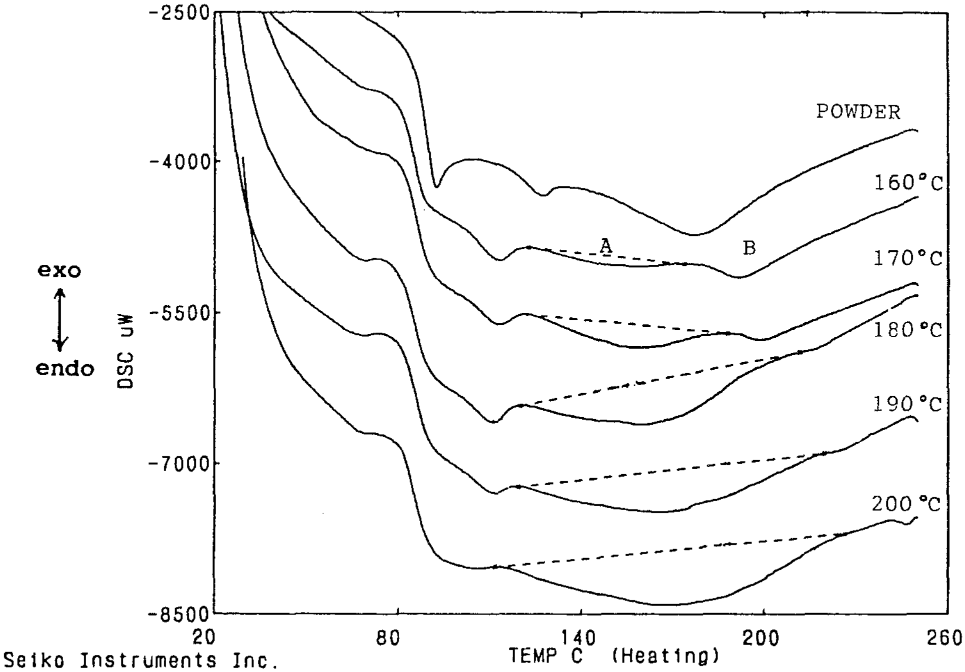

Figure 3 DSC traces obtained for the PVC compounds. (4)

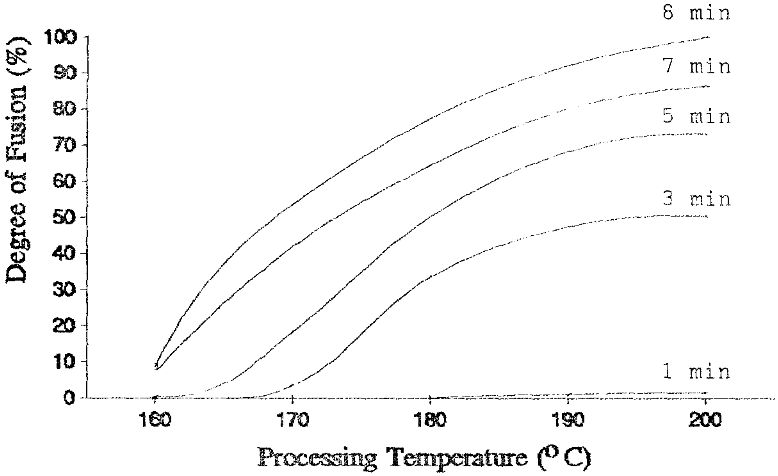

Figure 4 The relationship between the processing temperature and the degree of fusion of PVC compounds.

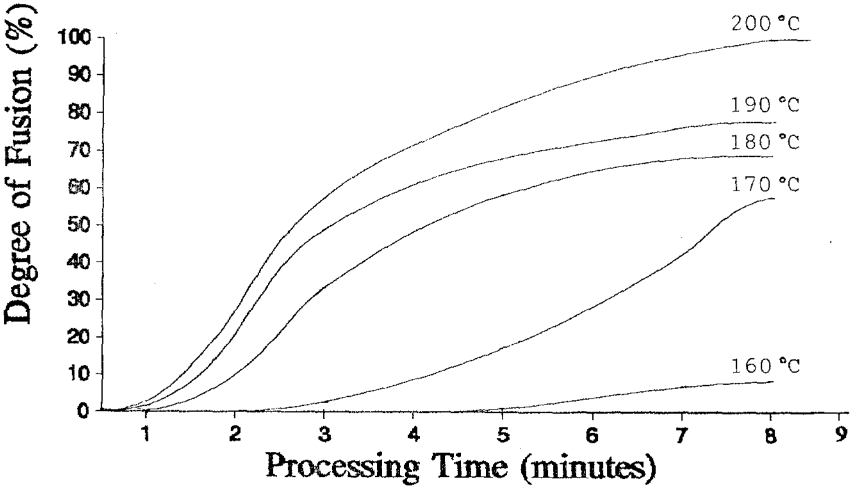

Figure 5 The relationship between the processing time and the degree of fusion of PVC compounds.

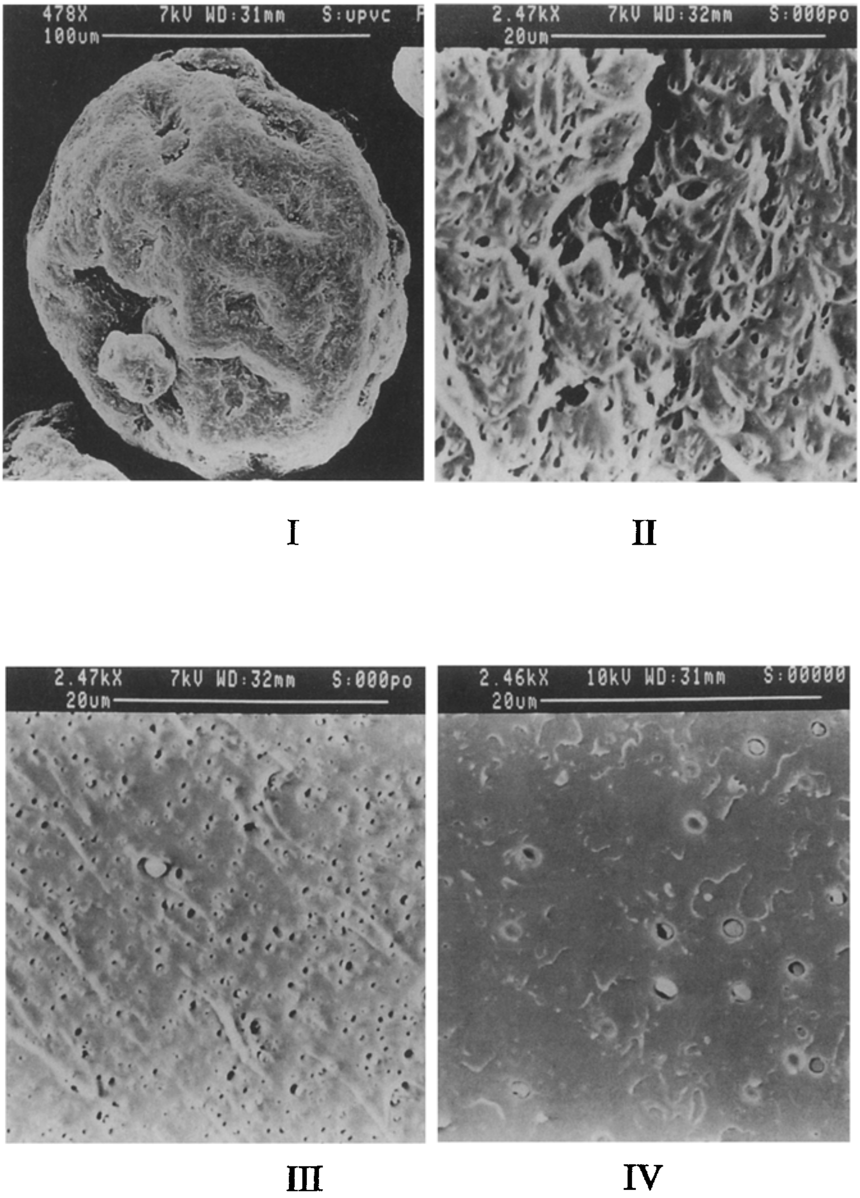

Figure 6 SEM Micrographs: I-unprocessed compound;II-160 °C; III-180 °C;IV-200 °C.

input, at higher processing temperatures, interfusion between PVC microparticles caused the formation of a 3-D network among polymer chains at a much faster rate. At lower temperatures, such as 160°C, this 3-D network is very poor and discontinuous. Conversely, at higher temperatures, such as 200°C, this 3-D network is very strong and smooth.

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