

Rigid Poly(Vinyl Chloride) (PVC) Gelation in the Brabender Measuring Mixer. I. Equilibrium State Between Sliding, Breaking, and Gelation of PVC

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ABSTRACT: This article discusses the first part of the Brabender typical torque process curves. Rigid poly(vinyl chloride) (PVC; Polanwil S-61) was processed at various temperatures between 160 and 200°C with blade speeds in the range of 5–40 min⁻¹. The morphological changes of the processed compound was characterized by scanning electron microscopy and optical microscopy, and the degree of gelation was estimated on the basis of DSC thermograms. The values of torque minimum strongly depends on temperature. Shear rate affects mainly the time of reaching the minimum torque. The grains are disintegrated into the non-uniform particles and aggregates of the dimensions between

20 and 4 μm. The significant variation of the gelation degree was found for the sample produced in the same conditions and unloaded from Brabender chamber at minimum of torque. It was found that the value of the minimum of torque described momentary equilibrium state between sliding of breaking grains and increasing degree of PVC gelation. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 966–971, 2004

Key words: poly(vinyl chloride); gelation; morphology; torque; differential scanning calorimetry

INTRODUCTION

Poly(vinyl chloride) (PVC) powder with a complex grain morphology is produced by suspension polymerization. A gelation procedure—which may be described as a disintegration of several morphologic levels, followed by a simultaneous creation of a new secondary structure^{1,2}—has to be realized prior to the molten state processing of this polymer.

It is well known that the properties of products depend on the composition of the PVC compound, as well as on the processing conditions.^{2–5} It has been also repeatedly proved that changes of properties as a function of temperature of processing, often with a local distinct extremum of impact strength or elastic modulus, depend significantly on the degree of gelation of PVC.^{4,6} The nonoptimal gelation level, detected by using diverse techniques,^{7–10} may significantly lower the quality of produced goods. The inhomogeneity of gelation is usually a consequence of extrusion instabilities.^{11,12} We suppose that it may also be related to primary nonhomogeneous PVC gelation level during the first phase of processing (i.e., when the

grains are heated rapidly from the wall of the processing machine). Therefore, we believe that the beginning (first step) of gelation is extremely important for the further course of the processing and therefore should be accurately explained.

The direct and indirect measurement techniques are usually applied by characterization of the PVC gelation, where the electron and optical microscopy, differential scanning calorimetry (DSC), rheology, sorption, and mechanical property measurements are commonly used.^{13,14} Different structural and processing aspects are taken into account, if the above-mentioned experimental techniques are used. The primary grains as well as the samples processed in various conditions are investigated in this case. Although a huge amount of literature describes the PVC processing, any simple universal measurement technique, allowing us to determine the structure changes caused by the gelation process, was found. Only the experiments performed by specially equipped extruders, and by the use of rotary measurement mixers, allow the acquisition of relatively comprehensive, and direct description, of the gelation of PVC.

The melting of the polymer carried out in the torque rheometers allows us to simulate the real charges and flow conditions commonly existing in the processing machines.¹⁵ Two counter-rotating blades with non-symmetric profiles, rotating with various speeds in the heat-mixing chamber, cause a heating of the polymer and its intensive mixing by shearing leading to the

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fulfilling of PVC gelation. The use of a rheometer with a measuring mixer allows us to record the time-dependent changes of the torque, necessary by the characterization of the progress in the gelation process of PVC. The melt temperature is measured simultaneously during this experiment. The run of the typical torque process curve, registered by use of the Brabender and Haake rheometer, was often discussed in the literature.^{15–18} The PVC process ability and the influence of the composition on the gelation process may be determined by the analysis of the measured values, and the time-dependent changes of the PVC compounds may also be characterized in this way.

The loading of the PVC compound into the hot rheometer mixing chamber causes a significant increase of the torque, followed by its decrease to the minimum. According to several authors, the minimum point of the torque curve signifies the beginning of the gelation procedure. Its numerical value allows us to determine the fusion percolation thresholds (FPT)¹⁶ as well as the work needed to accomplish the gelation of the PVC.^{15,17,18} C.H. Chen et al.¹⁶ supposed that minimum of torque is caused by the free material flow that fills the chamber. However, such an interpretation brings to mind many doubts because it does not reflect the real state of the compound at this stage. Pedersen¹⁹ suggested that at the minimum of the torque subgrains and agglomerates slide over one another. According to the same hypothesis, all those subgrains and agglomerates have similar dimensions, and the processed polymer is widely homogeneous. Allsopp,²⁰ investigating the gelation of PVC in a classical Brabender measuring mixer (Brabender Plastograph) and Banbury mixer, proposed a separation of the stage of primary grains breakdown—a phase which should be accomplished before the PVC gelation may start. In the description of the mechanism of gelation proposed in this article, any part of the rheometric experimental curve was related to the crumble phase. We suppose that in the Brabender kneader the process of PVC gelation is initiated before the torque reaches the minimal value.

An explanation of the true effects appearing in the processed PVC at the minimum of torque, and the analysis of the influence of the temperature and of the mechanical charges on the first part of the torque rheometer process curve, was the aim of our investigations. In particular, the thermal and mechanical conditions related to the minimum of torque should be investigated and analyzed.

EXPERIMENTAL

Materials

A compound containing the PVC S-61 Polanwil ($M_n = 47,500$, $M_w/M_n = 2.25$; 100 parts) produced by Anwil Wloclawek (Poland), tinorganic stabilizer MOK Mark

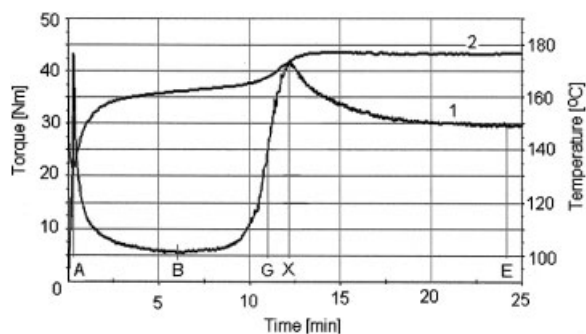


Figure 1 Typical torque rheometer process curve of rigid PVC: 1: torque at (A) the point of loading; (B) the minimum point; (G) the point of inflection; (X) the maximum point; (E) the end of the test (most often at the point of equilibrium); 2: temperature.

17M, produced by Acros (4 parts), and paraffin wax Loxiol G22, produced by Henkel (1 part), was used in our investigations.

Processing

The dry blend compound with a weight of 54 g was loaded into the Brabender mixing chamber (Plasti-Corder PI 2200-3) and was processed in the adjusted temperatures of the chamber at 160, 170, 175, 180, 185 and 200°C, respectively. Following rotation, speeds of the blades were applied at 5, 10, 20, 30, and 40 min^{-1} (Fig. 1, 5, 6). Always a first entire run for all samples was realized with the aim of detecting the local minimum on the torque curve. The samples for the microscopic observation and the DSC measurements were subsequently taken exactly at the point of reaching the minimum value of the torque.

Measurements

The morphology of the compounds (fractures after freezing in a liquid nitrogen) was observed by means of optical microscopy by using the Nikon Eclipse E400, and by a scanning electron microscope (SEM), by using the Canscan MV 2300LV+EPA (Figs. 2–4). Thermal analysis was performed by means of a Perkin-Elmer DSC 7. The skin layer (with a thickness of about 2 mm) was mechanically detached from the lumps taken out from the Brabender chamber. Then, both parts were dipped separately in liquid nitrogen and crumbled. The crumbled samples were in the form of mixture of powder with small lumps. The lumps from the exterior layer and the powder from the internal layer were used in the DSC experiment. The gelation degree was estimated according to the formula proposed by Potente and Schultheis,²¹ based on the melting enthalpies of the primary and secondary crystals:

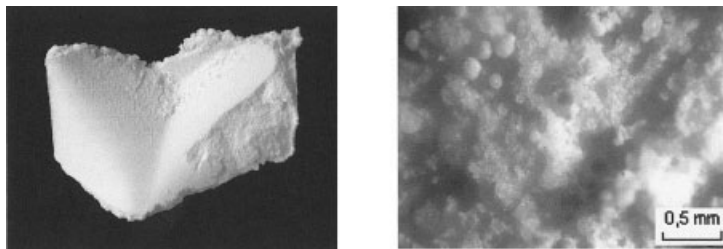


Figure 2 PVC-S61 after processing to minimum of torque (a) and its morphology in reflected light by optical microscope (b).

$$G = \frac{H_A}{H_A + H_B} \times 100\%$$

For the recorded torque curves (Figs. 5 and 6), the relationship between the minimum torque value and the time necessary to reach this value, and between the shear rate ($\dot{\gamma}$) and the chamber temperature (Figs. 7–10), was estimated. The average shear rates ($\dot{\gamma} = 2.18, 4.34, 8.69, 13.03, 17.38 \text{ s}^{-1}$) were calculated for the highest and the lowest shearing, according to Schramm,¹⁵ taking into account only the radial flow direction in the both cases.

RESULTS

A typical torque rheometer process curve, recorded with the Brabender measuring mixer, is presented in Figure 1. After the loading stage, a significant increase of the torque may be observed (point A), with a simultaneous decrease of the temperature measured in the chamber. In the following step, a decrease of the torque with its minimum at point B may be noted. Subsequently, the torque rheometer process curve passes through an inflection point G and reaches the maximum at point X. At this time, the temperature of the processed PVC slightly increases to the nominate value. Usually, at point G and X, an increase in the temperature may be observed. Shortly after point X, a slight decrease and stabilization of the torque may be

seen (point E), whereas the temperature between points X and E remains constant.

The PVC sample discharges from the mixing chamber, at the time corresponding to the minimum of torque, present a form of rigid lumps where their shape is similar to the contour of the chamber [Fig. 2(a)]. In any case, as it may be clearly seen, it is a free-flow material. By use of microscopic observation, an extremely heterogeneous morphology of the polymer may be seen [Fig. 2(b)]. In the lumps, the grain elements as well as the voids with various dimensions may evidently be observed. The shining surface of certain grains is significant for partly melting the face of the PVC grains.

For all compounds taken at the minimum of torque, two clear DSC endotherms, corresponding to the melting of the primary and secondary crystallites, were found. The degree of gelation increases for the rising temperature and shear rate. For the samples processed by the temperature of 150°C, the gelation degree reaches a value from 5% (the inner part of the block) to 14% (the skin part of the lump), and by the temperature of 200°C, 12% (inner part) to 70% (skin of the lump). The gelation degree determined for various pieces of the lumps differs significantly, and in some cases, is surprisingly high. Those differences in the gelation degree are lower for the PVC samples after longer kneading time.

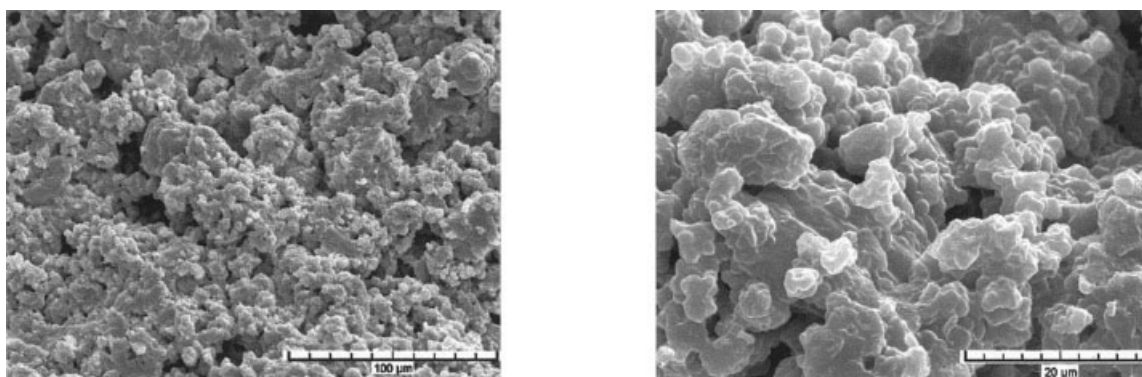


Figure 3 SEM photomicrograph of PVC-S61 after processing to minimum of torque in the Brabender measuring mixer, 160°C, 17.38 s⁻¹.

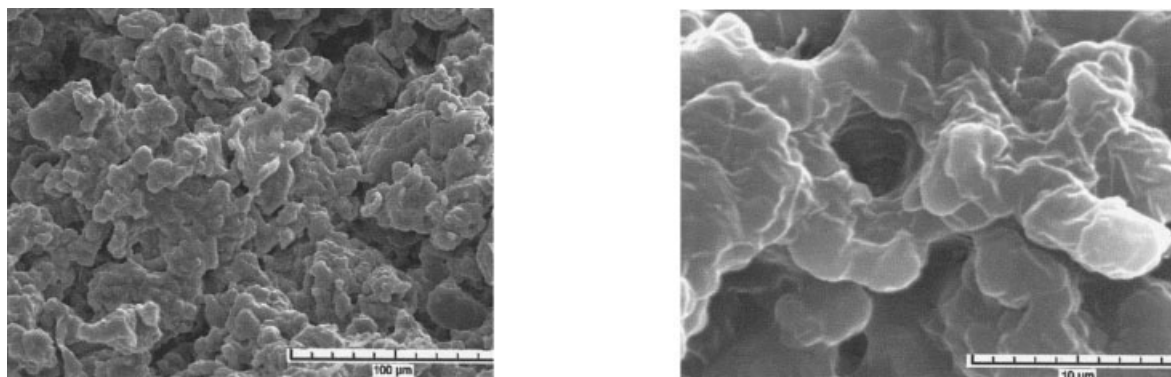


Figure 4 SEM photomicrograph of PVC-S61 after processing to minimum torque in the Brabender measuring mixer, 180°C, 4.34 s⁻¹.

The SEM observation confirmed that the primary grains are mostly disintegrated into the particles with average dimensions between 4 and 20 μm (Figs. 3 and 4). The dimensions of the particles created in this way correspond generally to the dimensions of agglomerated primary particles.²² It was also found that those aggregates are not uniform, as was suggested by Pedersen,¹⁹ and are connected one to another to various coverage. Free volumes may be seen between the particles, signifying the differences in packing of the aggregates as well in their homogeneity.

From the comparison of Figures 3 and 4, it may be concluded that the dimensions of the agglomerates, created short before the minimum of torque was achieved, are significantly temperature and rotation speed dependent.

This observation is also confirmed by the analysis of the torque rheometry chart produced during kneading of the compound in various temperatures, and by various rotation speeds (Figs. 5 and 6). Figure 5 presents the dependence of the torque on the kneading time for the PVC compound processed by various chamber temperatures (160, 175, and 185°C), and by a constant rotation speed of the blades 20 min⁻¹ ($\dot{\gamma} = 8.69$ s⁻¹). The torque values are higher for elevated nominal temperature, whereas the time necessary to

reach point B is significantly shorter. During this time, the PVC compound does not attain the final nor the nominal temperature.

A similar time shortening necessary to attain point B was observed on the torque process curve presented in Figure 6, for the compounds processed in a constant temperature of 170°C, and by various rotation speeds of the blades at 5, 10, and 20 min⁻¹ ($\dot{\gamma} = 2.18, 4.34, 8.69$ s⁻¹). In this case, the value of minimum of torque depends to some extent only on the rotation speed of the blades.

The relationship between minimum of torque, temperature, and rotational speed are presented in Figures 7–10. The value of the minimum of torque increases with growing temperature. For the temperatures between 170 and 175°C, the increase is relatively slow, and for the lowest rotation speed of 2.18 s⁻¹, it remains constant. Above 175°C, the torque value increases, and the changes are only slightly shear rate dependent. A small rise of the minimum of torque may be observed if the rotation speed increases from 2.18 to 4.34 s⁻¹. For the elevated rotation speed, the minimum of torque remains constant, and this value is characteristic for a given temperature (Fig. 8).

The time necessary to attain the minimum of torque is shorter for higher temperatures (Fig. 9). For the

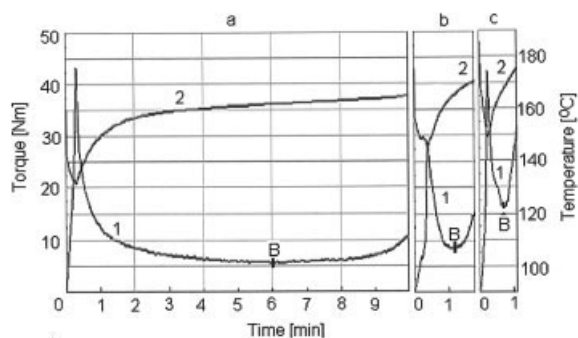


Figure 5 Torque rheometer process curves of PVC-S Polanvil compound processed at shear rate 8.69 s⁻¹ and temperatures: (a) 160; (b) 175; (c) 185°C.

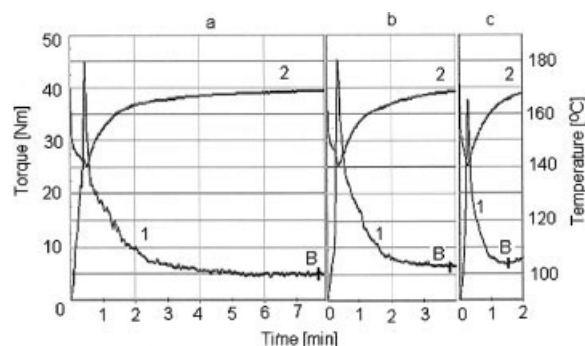


Figure 6 Torque rheometer process curves of PVC-S Polanvil compound processed at a temperature of 170°C and shear rates: (a) 2.18; (b) 4.34; (c) 8.69 s⁻¹.

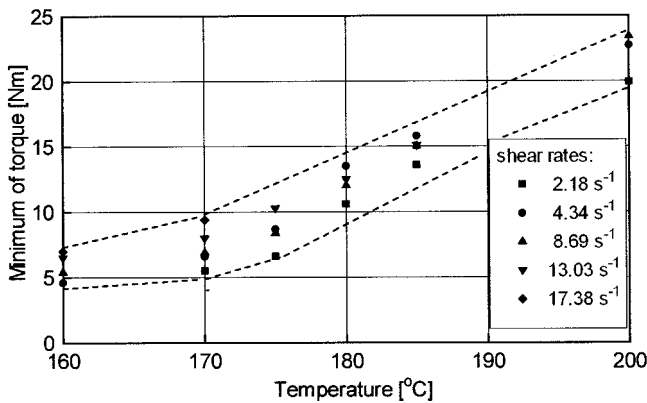


Figure 7 The minimum torque as a function of the processing temperature at various shear rates.

kneading temperature above 180°C, the time when the minimum is reached is practically independent from both the shearing rate and the chamber temperature. This effect is especially clear for the shearing rate lower than 13.03 s⁻¹, although for higher shearing rates, the time of torque minimum is very short.

Our investigations have confirmed that the processing of the compound in a Brabender measuring mixer, during time when the torque minimum is attained, is sufficient to accomplish just a part gelation of the PVC. The gelation degree, for established PVC composition, is temperature and shearing rate dependent. Therefore, it should not be concluded that the gelation starts first after reaching the minimum of torque.

In our research, we did not find proof indicating that in the point of torque minimum there is a free flow of material, as was suggested by Chen et al.¹⁶

It may be concluded that various simultaneous effects appear in the processed PVC compound. After the loading stage into the Brabender mixing chamber, the grains that are in touch with the chamber wall are very rapidly heated. As a consequence of shearing, a total of the grains is gradually, but nonhomo-

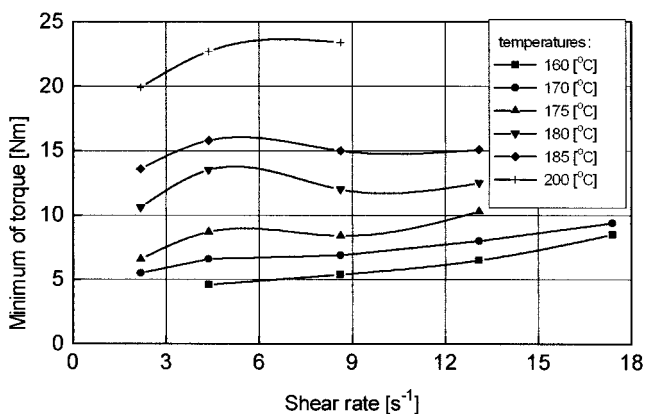


Figure 8 The minimum torque as a function of the shear rates at various processing temperatures.

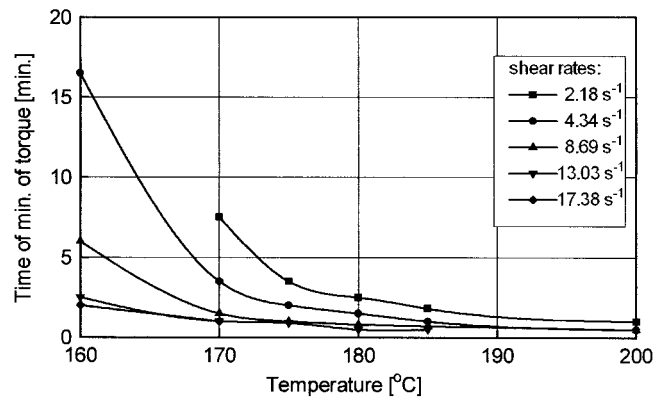


Figure 9 The time of reaching the minimum torque as a function of the processing temperature at various shear rates.

neously, disintegrated, although the degree of breaking is significantly shear rate dependent. For a similar time of torque minimum, the grains sheared in a lower temperature of 160°C, with a higher rate ($\dot{\gamma} = 17.38 \text{ s}^{-1}$), are disintegrated to a higher extent, compared to grains sheared in the temperature of 180°C by $\dot{\gamma} = 8.61 \text{ s}^{-1}$ (Figs. 3, 4, and 9). The smallest disintegrated particles are melted at first; a part of polymer undergoes a viscoelastic state, an effect which increases the flow ability of the remaining polymer grains (a lubrication effect). The other grains are not melted, whereas they may be easily dislocated in the chamber. All those effects result in a lowering of the torque. On the other hand, the dimensional inhomogeneity of the disintegrated particles results in a better packing, giving higher efficiency of shearing. A very intensive mixing of progressively disintegrated and melted particles leads to an improvement of the diffusion of the PVC macromolecular chains, an effect starting the gelation procedure. After a certain relatively short time, the intensity of torque lowering becomes smaller, and a minimum value of torque rheometer process curve appears.

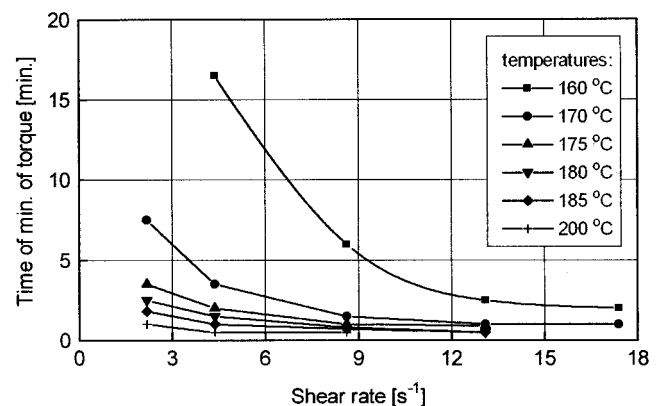


Figure 10 The time of reaching the minimum torque as a function of the shear rate at various processing temperatures.

Therefore, the value of minimum of torque of the PVC processing may be treated as representative for a transitory equilibrium state between sliding of broken grains and increasing degree of gelation of the compound.

It is evident that the value of minimum of torque, and the time necessary to reach this characteristic point on the Brabender processing curve, depends both on the temperature and on the shearing rate. The gelation mechanism proposed above is in good agreement with the relationship between minimum torque and the filling grade of the chamber, as suggested by Pedersen.¹⁹

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