Rigid Poly(vinyl chloride) Gelation in a Brabender Measuring Mixer. III. Transformation in the Torque Maximum

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ABSTRACT: The processing and structural effects occurring in a poly(vinyl chloride) (PVC) compound processed in a plastograph, at the time at which the maximum value of the torque (point X on the torque curve) was reached, were studied. The unplasticized PVC compound was processed at various temperatures (150–200°C) with a kneader operating at rotors speeds of 5–40 min^{-1}. The changes in the temperature of the compound due to kneading and its influence on the progress of PVC gelation were analyzed. The gelation progress was studied with differential scanning calorimetry, rheological measurements, and scanning electron microscopy. The maximum value of the torque occurred within the temperature range (170–180°C) of the PVC compound, and it was independent of the adjusted temperature of the mixing chamber. The processing of the PVC compound in the kneader, with high mechanical charges and a comparatively low adjusted temperature (150–170°C), spontaneously generated an effect of self-heating, resulting in an increasing temperature of the compound. Despite the surprisingly high degree of gelation (80–98%) of the PVC compound processed under these conditions (as determined by differential scanning calorimetry), the scanning electron microscopy observations indicated significant nonhomogeneity of the fracture surface. Consequently, the kneaded PVC compound at point X of the torque curve could be treated as a two-phase system composed of a liquid, amorphous phase and elements of a grain structure. The transformation of both phases (particularly the quantitative and qualitative changes), which was significantly dependent on the PVC temperature and the shear rate applied by the rotors, determined the state of the melted compound at this point of the torque curve. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3158–3164, 2007

Key words: differential scanning calorimetry (DSC); gelation; poly(vinyl chloride) (PVC)

INTRODUCTION

The gelation process carried out during the kneading of a poly(vinyl chloride) (PVC) compound in the chambers of Brabender and Haake devices has been widely discussed in the literature.[1–18] The run of the torque recorded by these devices, graphically represented as plastograms, allows researchers to follow time-dependent changes as the gelation progresses. The real temperature of a processed PVC compound is usually measured simultaneously.

In our previous articles,[19,20] we have discussed two other characteristic points of Brabender plastograms: the minimum of the torque curve (point B) and the inflection point of the torque curve (point G). Therefore, the maximum torque (M_X), which occurs at point X on the torque curve, and the time to reach point X (t_X) are emphasized, these values being analyzed most often in the literature. According to several articles,[9,16] the values of M_X and t_X may be defined as the fusion torque and fusion time, respectively. Chen and coworkers[14,16] claimed that at this peak, a material reaches an effectively void-free state and starts to melt at the interface between the compacted material and the hot metal surface.

The fusion percolation threshold is defined as the torque difference between B and X; in this case, M_X was considered.[14] Point X was found to have been caused by compaction and by the onset of fusion, and this provided an idea for a new definition of the PVC fusion mechanism. On the contrary, according to Pedersen,[18] an increase in the torque to its maximum value can be attributed to the gelation of both agglomerates and primary particles progressing. Generally in an analysis of plastograms and especially in a description of characteristic points and in the corresponding interpretation of occurrences taking place in the gelation of a PVC compound, the real temperature of the processed compound is rarely taken into account.

It has to be stressed that the real temperature of a PVC compound during processing generally differs from that determined to be the invariable temperature of the chamber walls. Initially, a slow increase of the real temperature to the value corresponding

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to the chamber-wall temperature may be observed. Beginning at the time at which point G and/or point X is reached on the plastogram, a very rapid rise in the temperature can be noted.[11,21–23] The real temperature of the PVC compound increases during the time in which the torque reaches a state of equilibrium; in the equilibrium state of the torque, the temperature of the polymer reaches a constant value.

Several authors have determined the temperature corresponding to the torque at point X and have described it as the fusion temperature or the temperature of the full fusion of a PVC compound.[12,16] The influence of this temperature on the real state of a gelatinizing compound is not analyzed in any of these articles. Other authors[9] have insisted that the conditions of optimal PVC processing usually should be related to the temperature of the gelatinizing compound at point X; however, they did not analyze the influence of mechanical and thermal charges on the value of this temperature.

In our previous articles,[21–24] the dependence of the real temperature on the adjusted chamber temperature (T_{ch}) and the speed of rotors is presented and discussed. From an analysis of the relationship between the torque and the real temperature of a PVC compound, we have realized that the most evident gelation effect appears in a narrow temperature range that is significantly dependent on the PVC Fikentscher's number (K) value.[21] An attempt to estimate the influence of a small addition of a plasticizer on the gelation process, with consideration given to the changes in the temperatures of the gelatinizing compound, has also been performed. We have found that the temperature at which the torque corresponding to the intensive gelation of PVC reaches its maximum value is practically independent of the temperature of the chamber wall; the incorporation of about 2 wt % plasticizer into a PVC compound leads to a decrease in the PVC gelation temperature of about 5°C.[24]

Previously, the first part of the torque curves (corresponding to point B) and the transitory stage between the minimum and maximum of the torque (corresponding to point G) have been presented in our articles.[19,20] The value of the minimum of the torque describes the momentary equilibrium state between the sliding of breaking grains and the increasing degree of PVC gelation, allowing us to presume that by reaching point G, a PVC compound may not be treated as a polymeric material in which the gelation process has been completed.

In this article, the effects occurring in a PVC compound, processed in a Brabender plastograph, at t_X are analyzed; the changes in the real temperature of the compound and its influence on the progress of the gelation are particularly studied.

EXPERIMENTAL

The composition and mode of mixing of the dry PVC blend used were similar to those described in refs. 19 and 20.

Material

The material used in this study was a PVC compound containing PVC S-61 (Anwil S.A., Wloclawek, Poland; number-average molecular weight = 47,500, weight-average molecular weight/number-average molecular weight = 2.25; 100 parts), which was mixed with 4 parts of organic tin stabilizer MOK Mark 17M (Acros, Geel, Belgium) and 1 part of paraffin wax Loxiol G22 (Henkel, Düsseldorf, Germany).

Processing

The processing of the PVC compounds was performed under conditions similar to those described before.[20] The dry blend compound, with a weight of 54 g, was processed in the mixing chamber of a Brabender Pl 2200-3 plasticorder at T_{ch} values of 150, 160, 170, 175, 180, 185, and 200°C, and the torque was registered as a function of time. The processing was performed always up to the time at which the equilibrium state of the torque was achieved. The rotation speeds of the blades were 5, 10, 20, 30, and 40 min^{-1} (except at 150°C, at which we also used rotation speeds of 50, 60, and 80 min^{-1}), and the applied friction was 1 : 1.5. These preliminary torque measurements were performed just to determine point X (the characteristic points on the torque curve are described according to refs. 21–23).

Subsequently, in the second run of kneading, which was realized only to point X on the torque–time curve, the material was prepared for further investigation. The samples for observations by microscopy, for differential scanning calorimetry (DSC), and for rheological measurements were taken consequently exactly at t_X.

We analyzed the values of M_X, t_X, and the real temperature of the compound at point X (T_X). For a univocal interpretation, we marked these characteristic points on Figure 1. T_X was determined by means of the resistance temperature device (RTD) situated between the rotors, directly in the kneaded PVC compound, isolated from the walls of the chamber.

The shear rates (2.18, 4.34, 8.69, 13.03, and 17.38 s^{-1}) were evaluated as average values from the highest and lowest shearing according to Schramm[25]; only the radial flow direction was taken into account.

Measurements

The PVC compound processed in the chamber of the Brabender kneader was used for further studies. The fracture surfaces of fused PVC samples were observed
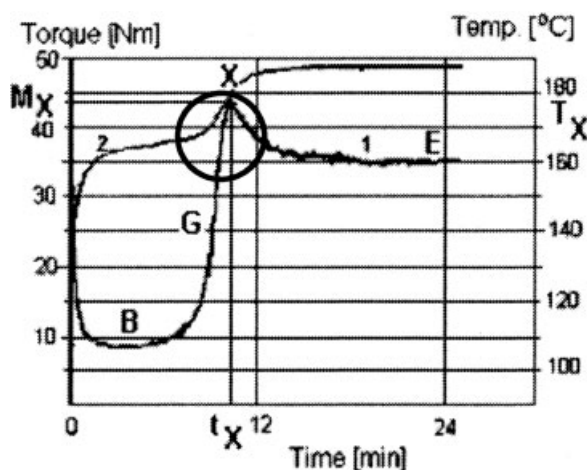
Figure 1 Typical torque rheometry process curve of rigid PVC: (1) torque and (2) temperature.

by scanning electron microscopy (SEM; 14–39 VP, Leo, Carl Zeiss, Jeno, Germany). The thermal transitions related to the melting of the primary and secondary crystallites were determined by means of DSC with a PerkinElmer DSC 7 apparatus (Waltham, MA).

The gelation degree, depending on the flow of the PVC compound, was measured with a specially constructed MFR apparatus,[20] which allowed a very high pressure to be applied. These experimental procedures are described in Table I.[19,20]

RESULTS

In Figure 2, the real temperature of the compound versus the shear rate is presented. T_X differs from T_{ch}. For low shear rates of 2.18–4.34 s^{-1}, at T_{ch} values of 160 and 170°C, T_X of the PVC compound increased slightly with the shear rate; on the contrary, at T_{ch} values between 185 and 200°C, T_X slightly decreased (Fig. 2).

It was also ascertained through processing in the chamber of the Brabender kneader at T_{ch} values between 175 and 180°C that the real temperature of the compound did not practically depend on the shear rate; this remark concerns the wide range of shearing conditions applied in this work. Moreover, independent of T_{ch}, for the higher shear rates between 8.69 and 17.38 s^{-1}, influence of shearing on T_X was noted.

The differences between T_{ch} and T_X of the gelatinized PVC compound ($\Delta T = T_X - T_{ch}$), for all shear

TABLE I

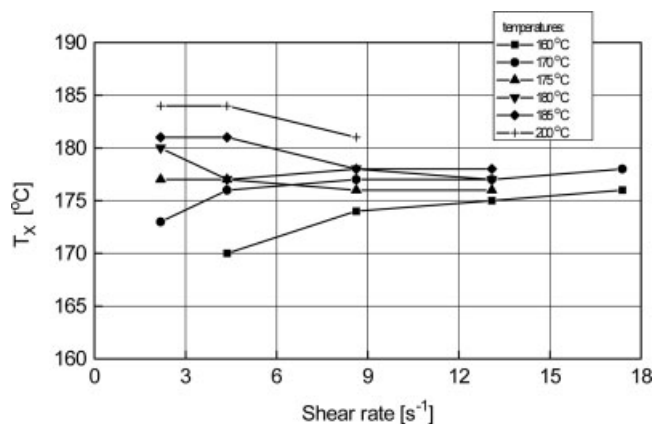|	
Temperature of barrel [°C]	170
Piston load [N]	800
Diameter of piston [mm]	9.5
Length of capillary die [mm]	6
Diameter of capillary die [mm]	2
Time of material heating [min]	10

Figure 2 T_X of PVC compound S61 as a function of the shear rate.

rates and temperatures applied in this work, are presented in Figure 3.

The most significant growth of the PVC temperature with respect to the adjusted temperature (i.e., ΔT values of 22 and 26°C) was observed for the PVC compound processed at shear rates of 17.38 and 34.75 s^{-1} (Fig. 3) at T_{ch} value of 150°C. A much lower increase in the compound temperature was noted when T_{ch} was adjusted between 160 and 175°C. Finally, the temperature of the PVC compound was equal to the T_{ch} value of 180°C for the Brabender chamber when the shear rate ranged from 0.44 to 2.18 s^{-1}. The following growth of T_{ch} did not lead to any rise of T_X; furthermore, under these processing conditions, at M_X, T_X for the PVC compound remained lower than the adjusted temperature. For a T_{ch} value of 200°C, T_X of the processed PVC was lower than the adjusted temperature. ΔT values of about 13–19°C (Fig. 3) for shear rates between 0.44 and 8.69 were observed, respectively.

Therefore, it may be concluded that M_X occurred in a specific range of compound temperatures independently of T_{ch}. When T_{ch} was lower than 175°C, the compound underwent spontaneous heating. However, when T_{ch} was greater than 180°C, gelation took place at 175–185°C; that is, the T_X value of the PVC compound did not reach the adjusted value.

This conclusion is confirmed by the run of T_X of the compound versus T_{ch}, as measured at various shear rates (Fig. 4). Therefore, it follows that the relatively narrow range of the compound temperature of about 170–185°C, in which M_X occurred, was not practically dependent on the shear rate (Fig. 2) or T_{ch} (Fig. 4).

The fracture surfaces of PVC samples processed at T_{ch} values of 150–170°C and at shear rates of 2.18–17.38 s^{-1}, discharged from the mixing chamber at t_X, are presented in Figure 5. For all samples kneaded to point X, a significant increase in the homogeneity, with respect to samples taken at points B[19] and G,[20]
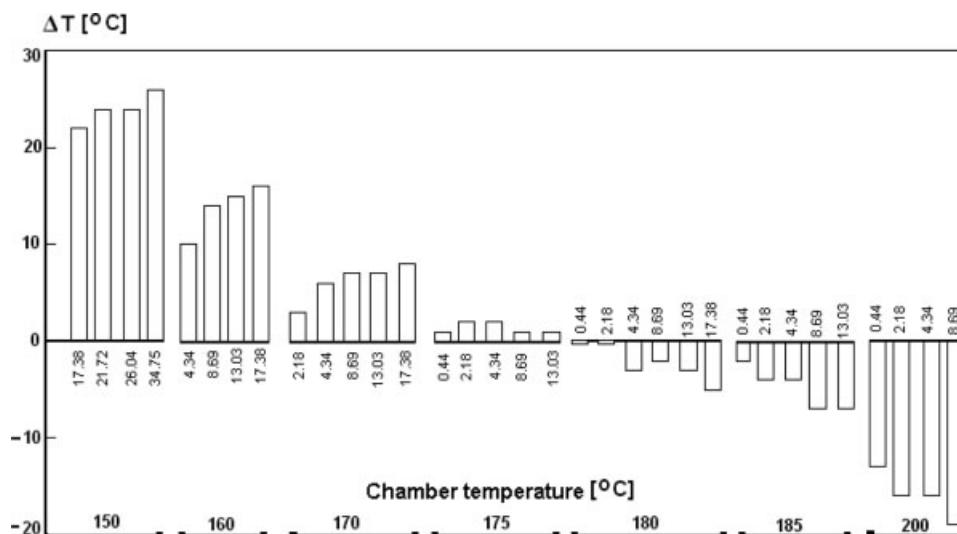
Figure 3 Difference between T_X of PVC compound S61 and T_{ch} as a function of the shear rate.

can be observed. The lamellar structure, characteristic of gelatinized PVC, can be seen on the fracture surfaces of these samples.[1,26] The sample processed at $T_{ch} = 150°C$ and at a shear rate of 17.38 s^{-1} [Fig. 5(a,b)] was characterized by lower homogeneity, and a certain number of grain elements with average dimensions of 10 μm [Fig. 5(b)], as single primary particles, are visible.

A certain number of grains that did not undergo any changes during processing at $T_{ch} = 150°C$ [Fig. 5(b)] probably formed especially durable parts of the impacted ball type.[26] It may be supposed that the durability of the observed grain elements was due to an impetuous increase in T_X of the compound as a result of its spontaneous heating at point X, which was related to the intensive PVC gelation. The sample was characterized by a surprisingly high degree of gelation of about 98%, despite the inhomogeneity and the content of preserved elements of the grain structures.

The fractures of the samples processed at a higher T_{ch}, that is, 170°C [Fig. 5(c–f)], were characterized by greater homogeneity. There were no agglomerates of small primary particles found, but small elements of about 1 μm were quite visible. However, the decreasing MFR value (Fig. 6, curve 2), corresponding to the increase in the value of the degree of gelation, as estimated from DSC thermograms (Fig. 6, curve 1), may prove the increasing durability of the PVC structure, which was achieved by the growth of the shear rate.

M_X reached values between 22 and 47 Nm (Figs. 7 and 8) at all shear rates and temperatures used in these experiments. For a constant T_{ch} value, the augmentation of the value of M_X was due to the shear rate (Fig. 7). This increase was relatively slow in the case of PVC samples processed at $T_{ch} = 160°C$ (an

increase from ca. 40 to 47 Nm). On the contrary, the higher T_{ch} was, the more impetuous the increase in M_X was as a function of the shear rate.

The most significant differences of the M_X values as a function of T_{ch} were noted for the PVC compound processed at low shear rates, that is, 2.18 and 4.34 s^{-1} (Fig. 8). The compound processed at $T_{ch} = 160°C$ reached the highest value of M_X, whereas at 200°C, the lowest value of M_X for the investigated range of T_{ch} was observed.

As for the run of M_X measured at shear rates between 2.18 and 8.69 s^{-1}, a slight decrease in its value as a function of increasing T_{ch} could be noted; on the contrary, at shear rates above 13.03 s^{-1}, the M_X value was practically constant, being independent of T_{ch}.

The shear-rate-dependent relationship of t_X was similar to the corresponding relationship of the times of reaching points B and G, as described earlier.[19,20]
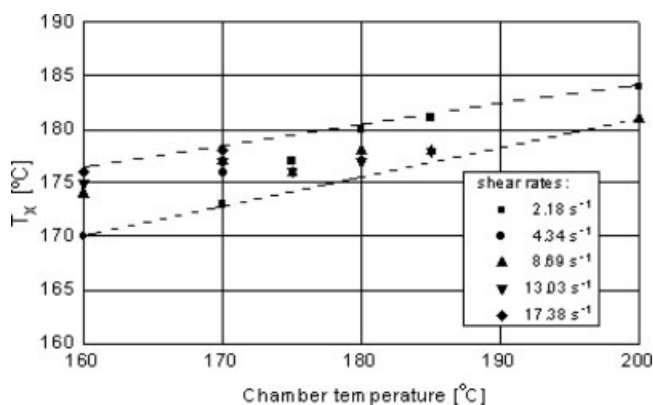

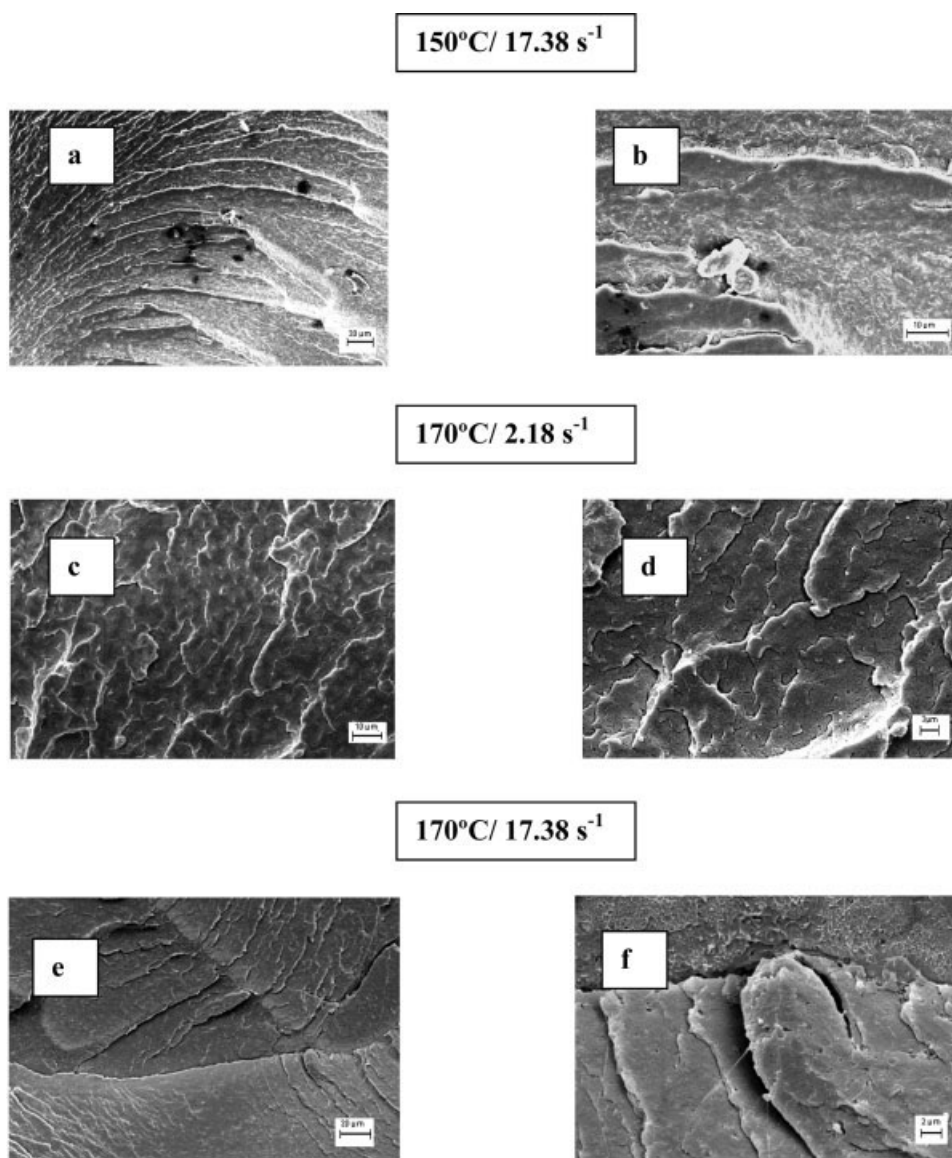**Figure 4** T_X of PVC compound S61 as a function of T_{ch}.

Figure 5 SEM photomicrographs of PVC-S61 after processing to point X in a Brabender measuring mixer: (a,b) 150°C and 17.38 s^{-1}, (c,d) 170°C and 2.18 s^{-1}, and (e,f) 170°C and 17.38 s^{-1}.
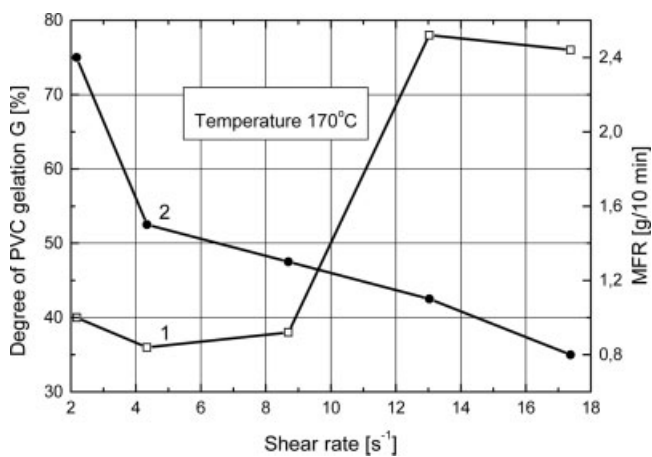

Figure 6 (1) Degree of gelation and (2) MFR of PVC S-61 after processing to point X at 170°C as a function of the shear rate.
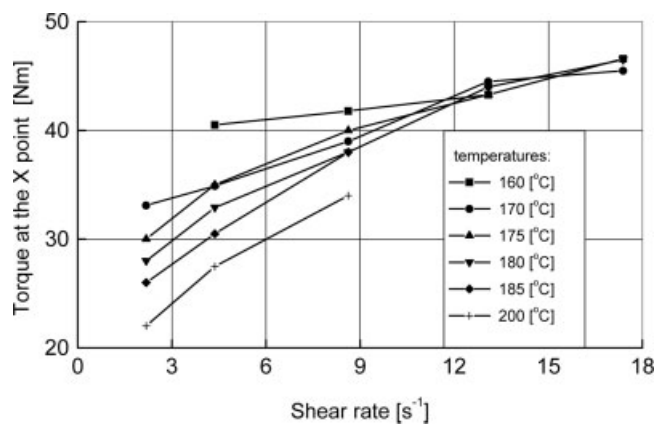

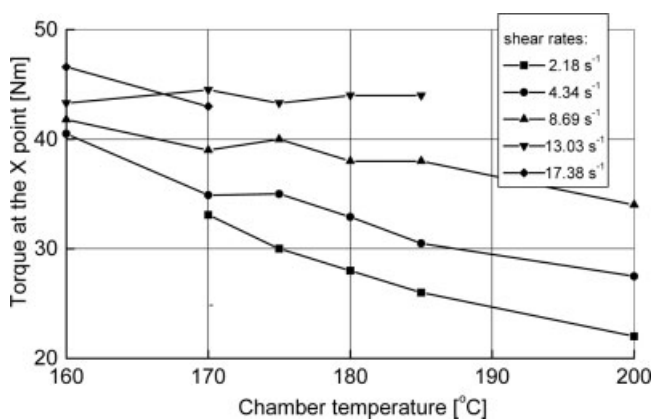**Figure 7** M_X as a function of the shear rate at various values of T_{ch}.

Figure 8 M_X as a function of T_{ch} at various shear rates.

As for t_X (Fig. 9), in a range of low shear rates (from 2.18 to 8.69 s^{-1}), it decreased suddenly with increasing T_{ch}, and for the sample kneaded at a shear rate of 4.34 s^{-1} at T_{ch} = 160°C, this time reached its greatest value, that is, about 34 min. For higher applied shear rates, with T_{ch} in the range of 160–170°C, a slight shortening of t_X was observed. Above this temperature, t_X practically did not change, and at shear rates between 13.03 and 17.38 s^{-1}, the observed t_X values were in the range of 0.7–5 min.

DISCUSSION

The PVC compound processed at 150°C at a shear rate of 13.03 s^{-1} did not gel; the run of the time-dependent torque was characteristic for the mixing of a PVC powder.[27] An increase in the shear rate to 17.38 s^{-1} led to the gelation of the compound, an effect visible on the plastogram in the form of M_X. The temperature of the PVC compound at this point was considerably higher than the adjusted temperature (150°C), and the difference between T_{ch} and T_X became higher with an increasing shear rate. Despite the surprisingly high degree of gelation (ca. 98%) of the compound processed in the chamber at 150°C at shear rates above 17.38 s^{-1}, SEM observations indicated significant nonhomogeneity of the fracture surface (Fig. 5). The significant changes in the run of the DSC thermograms connected to the self-heating of the gelatinizing PVC compound were described by Fillot et al.[28]

The effect of nonhomogeneity was probably due to insufficient disintegration of the grains in the earlier stage of the processing, as already confirmed by our supplementary investigations, which will be presented in a future article.

The very high mechanical charges existing during kneading in the chamber at a comparatively low adjusted temperature (150–170°C) led to a consider-

able augmentation of T_X of the compound. This effect was followed by an increase in the degree of gelation, as observed by the DSC measurement (for T_{ch} = 170°C and at a shear rate of 2.18 s^{-1}, the degree of gelation was ca. 40%, whereas at a shear rate of 17.38 s^{-1}, a degree of gelation equal to 80% was noted). An increase in the structural homogeneity was observed in this case, but the higher durability of the structure was proven by a decrease in the MFR value (Fig. 6).

The increase in T_X of the compound was due to an effect of spontaneous self-heating. The intensive self-heating of the PVC compound, taking place especially at a low T_{ch} value and a high applied shear rate (> 17.38 s^{-1}), may be explained by significant friction forces between grains, between grains and the chamber wall, and between grains and the surfaces of rotors. The self-heating was the origin of the high values of the degree of gelation, despite the relatively low value of T_{ch}.

The observed influence of spontaneous self-heating on the transformations of the crystal structure of PVC and indirectly on the degree of gelation corresponds to the suggestions of Bottrill and Stephenson.[29] As an explanation of this effect, they proposed that the effect of the pressure drop in a capillary rheometer for samples processed in a Banbury mixer is probably due to the progressive destruction of primary crystallites under conditions of a high temperature concurrent with intensive shearing. They also suggested that the efficiency of shearing increases as the processing temperature decreases.

On the one hand, an increase in the real temperature of the compound is an advantageous occurrence because the PVC compound gels despite a low value of T_{ch}. On the other hand, gelation under such conditions leads to the formation of a heterogeneous structure for the gelatinized material. If the sample remains heterogeneous to the end of the processing,
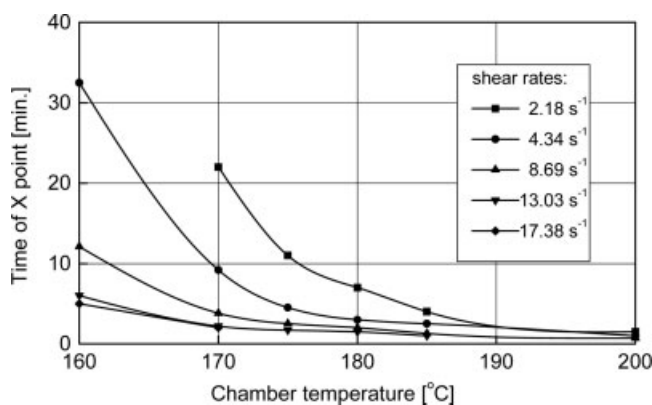

Figure 9 t_X as a function of T_{ch} at various shear rates.

that is, during the kneading to the equilibrium state, then the remaining inhomogeneity may lead to a certain degradation of specific properties.

The higher T_{ch} is, the lower the rise is of the real temperature of the PVC compound; it was even noted that above 180°C, the compound did not reheat to the adjusted temperature (Fig. 3). This effect may be explained by a rash shortening of t_X (Fig. 9); that is, the residence time of the PVC compound in the chamber, for the applied temperatures and shear rates, is much shorter. In this short time, the gelation of PVC is achieved; M_X is always observed at T_X between 175 and 180°C, that is, at the temperature defined as T_{EG},[22] and is suggested to be a universal parameter characterizing the gelation of PVC compounds.

The kneaded PVC compound at point X of the torque run may be treated as a two-phase system, the first being a liquid, amorphous phase and the second being elements of the grain structure. The transformations of both phases (regarding the quantitative and qualitative changes) are significantly dependent on the temperature and shear rate. Such a description of a melted PVC compound corresponds to the idea proposed by Berard,[13] who found that a melted compound can be treated as a fluid with primary particles as fillers; however, he did not analyze the influence of the shear rate on the transformation of such fillers.

From our observations, it follows that the higher shear rate is, the larger the quantity is of the remaining grain elements (Fig. 5). The structural effects related to the presence of the remaining primary particles dominate in the lower range of processing temperatures (up to 180°C). The increase in the viscosity of this system depends on the content of the surviving particles; this observation is in agreement with the Berens and Folt model, which shows that particle slippage is favored at a low temperature.[30]

The rise of the processing temperature leads to a reduction of the viscosity of the liquid, amorphous phase, and therefore the remaining grains may effortlessly translocate. As a result, a decrease in the friction may be observed, and M_X decreases with the temperature. This effect is confirmed by the lower resistance of the processed PVC compound against rotating blades. The lowering of the viscosity should be accompanied by an increase in the MFR value (greater flow). However, for samples processed to point X, we observed a decrease in the MFR value, which was due to the progressive occurrence of PVC gelation. The intensive formation of a physical network of secondary crystallites probably dominates in this stage of the kneading.[3,13,29]

CONCLUSIONS

The real temperature of gelation of a PVC compound (T_X) may be treated as a limit temperature, below which the transformation taking place in the phase containing the remainder of the grain elements determines the state of the melted compound. The effects related to the thermal changes in the amorphous phase dominate above this temperature. The aforementioned conclusions are in an agreement with the propositions included in the article of Collins and Krier,[31] who found that the evidence of two distinct flow activation energies may be an indication of different rheological flow units, as observed in regions of low and high processing temperatures.

References

1. Faulkner, P. G. J Macromol Sci Phys 1975, 11, 251.
2. Schramm, G. Int Plast Eng 1965, 12, 2.
3. Krzewki, R. J.; Collins, E. A. J Vinyl Technol 1981, 3, 116.
4. Shah, P. L. J Vinyl Add Technol 1996, 2, 5.
5. Bambrick, C. R.; Hoegy, L. R.; Ferrari, L. P. J Vinyl Technol 1994, 16, 62.
6. Hawkins, T. J Vinyl Technol 1982, 4, 110.
7. Yu, A.; Boulier, P.; Sandhu, A. J Vinyl Technol 1984, 6, 110.
8. Cogswell, F. N. Pure Appl Chem 1983, 55, 178.
9. Bortel, K.; Szewczyk, P. Polimery 1993, 38, 578.
10. Shah, P. L. Soc Plast Eng J 1973, 29, 65.
11. Menges, G.; Klenk, P. Kunststoffe 1969, 59, 753.
12. Małyshew, L. N.; Shtarkman, B. P. Plast Massy 1971, 12, 19.
13. Berard, M. J Vinyl Add Technol 2000, 6, 140.
14. Chen, C.-H.; Mao, C.-F.; Lo, Y.-W. J Appl Polym Sci 2001, 81, 3022.
15. Berard, M. T. J Vinyl Add Technol 2002, 8, 246.
16. Chen, C. H.; Wesson, R. D.; Collier, J. R.; Lo, Y. W. J Appl Polym Sci 1995, 58, 1107.
17. Chen, C. H.; Wesson, R. D.; Collier, J. R.; Lo, Y. W. J Appl Polym Sci 1995, 58, 1101.
18. Pedersen, T. J Vinyl Technol 1992, 14, 54.
19. Tomaszewska, J.; Sterzyński, T.; Piszczek, K. J Appl Polym Sci 2004, 93, 966.
20. Tomaszewska, J.; Sterzyński, T.; Piszczek, K. J Appl Polym Sci 2007, 103, 3688.
21. Piszczek, K.; Tomaszewska, J.; Sterzyński, T. Polimery 2004, 49, 646.
22. Tomaszewska, J. Polimery 2006, 51, 42.
23. Piszczek, K.; Tomaszewska, J.; Sterzyński, T. Conference of the Polymer Processing Society: Proceedings, Athens, Greece, 2003; p 104.
24. Piszczek, K.; Tomaszewska, J. Chemik 2003, 56, 12.
25. Schramm, G. A Practical Approach to Rheology and Rheometry (in Polish); Poznań, Poland, 1998.
26. Piszczek, K.; Skraga, J.; Zajchowski, S. Polimery (Warsaw) 1981, 26, 170.
27. Skraga, J.; Zajchowski, S.; Piszczek, K. Polimery 1981, 26, 91.
28. Fillot, L.-A.; Hajji, P.; Gauthier, C.; Masenelli-Varlot, K. J Vinyl Add Technol 2006, 12, 98.
29. Bottrill, M.; Stephenson, R. C. Plast Rubber Process Appl 1984, 4, 27.
30. Berens, A. R.; Folt, V. L. Polym Eng Sci 1969, 9, 27.
31. Collins, E. A.; Krier, C. A. Trans Soc Rheol 1967, 11, 225.