

Rigid Poly(vinyl chloride) (PVC) Gelation in the Brabender Measuring Mixer. II. Description of PVC Gelation in the Torque Inflection Point

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ABSTRACT: This article discusses the transitory stage between the minimum and the maximum of the torque, which corresponds to an inflection point on the torque curve (called point G). The unplasticized compound of poly(vinyl chloride) (PVC) (Polanwil S-61) was processed in various temperatures between 150 and 200°C, by rotors speeds in the range from 5 to 40 min⁻¹. The progress of gelation was estimated basing on DSC thermograms and on the rheological measurements, which were realized by means of specially constructed MFR apparatus. The morphological changes of processed compound were characterized by scanning electron microscopy (SEM). It was

found that a general description of gelation progress demand both, the microscopic observation as well DSC and MFR measurements. More significant advancement of gelation, as observed by SEM, was achieved by lower shear rates. However, it may be stated that by reaching an inflection point on the torque curve, the PVC compound may not be treated as a polymer where the gelation process was completed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3688–3693, 2007

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

INTRODUCTION

From numerous investigation techniques used for the estimation of the poly(vinyl chloride) (PVC) gelation,^{1–8} only plastographic measurements allow an immediate observation of the dynamic of changes in the processed material, and their estimation at each step of gelation. Originating on the run of the torque curves, registered by use of Brabender and/or Haake kneader, it is possible to conclude about temporary changes taking place in gelatinating composition of PVC, what is often discussed in the literature.^{9–13}

The effects related to the appearance as well of minimum and maximum value of the torque, as of the state of torque equilibrium, are usually taken into account by the interpretation of torque curves. The most important difference, however, refers to the judgment of effects related to the minimum value of the torque.^{14–16}

In the first part of this article,¹⁶ we have made an effort to estimate the real state of the processed PVC at the minimum of torque, and we have analyzed the influence of the temperature and variable mechanical charges on the first part of the torque

curves.¹⁶ In this article, a huge literature study of the PVC gelation was presented as well. We have suggested that the value of the minimum torque of processed compound of PVC may be related to the momentary equilibrium state between sliding of breaking grains, and increasing degree of PVC gelation.

In results published by now^{12–15,17} of plastographic investigation of PVC, which relate the gelation effect to the run of torque curve, the transitory stage between the minimum and the maximum of torque, visible as an inflection point on the torque curve (called point G), has not been taken into account yet. The increase of the value of torque in this stage may lead to a suggestion that also a significant transformation of the PVC morphology may occur in the processed gelatinating polymeric material.

The aim of this work, as a continuation of our earlier investigation,¹⁶ was to describe the real state of an unplasticized composition of PVC at the inflection point G, on the torque curve. The influence of temperature and of variable mechanical charges, during PVC processing in the chamber of Brabender kneader, was particularly analyzed.

EXPERIMENTAL

Material

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

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Mark 17M, produced by Acros (4 parts), and paraffin wax Loxiol G22, produced by Henkel, (1 part) was used in our experiments. The compound was homogenized using a two-stage hot-cold mixer Kontinomix 40/80, produced by Mixaco, operating at mixing speed of 1500 min^{-1} .

Processing

The processing was performed in the conditions similar as described before,¹⁶ e.g., the dry blend compound with a weight of 54 g was processed in the Brabender mixing chamber (Plasti-Corder PI 2200-3) to the equilibrium state of torque, at temperatures 150, 160, 170, 175, 180, 185, and 200°C , respectively. The rotation speed of the blades was 5, 10, 20, 30, and 40 min^{-1} , and the applied friction was 1 : 1.5. These preliminary measurements were performed just to determine the position of the inflection point, called point G.

Subsequently, in second run of kneading, realized only to the point G, the material for research was prepared. The samples for the microscopic observation, the DSC and rheological measurements were consequently taken exactly at the time point of attainment the value of the torque in inflection point.

Measurements

The thermal analysis was performed by means of Perkin-Elmer DSC 7 with a heating rate of $10^\circ\text{C}/\text{min}$, from 60 to 250°C in nitrogen used as an inert atmosphere. The gelation degree was estimated, according to the formula proposed by Potente,⁸ based on the melting enthalpy of the primary and secondary crystallites.

It should be stressed that every sample was taken from similar place in the kneader chamber, e.g., at the position where the thickness of the material layer was lowest. This procedure is a consequence of a statement that a large variation in fusion level was observed for pieces of the lumps taken out from various positions the Brabender chamber.¹⁶ Hence, the samples for the microscopic observation, prepared by cryogenic fracture, were taken out as well from the same position.

The investigations by scanning electron microscopy (SEM), using the LEO 14-39 VP apparatus, (Figs. 1 and 3) were performed just on surfaces of fracture of well-fused PVC samples.

The rheological measurements were realized by means of specially constructed MFR apparatus,¹⁸ giving the possibility to apply very high pressure. The experimental conditions of the MFR investigations are listed in Table I.

RESULTS

A significant nonhomogeneity of structure of the PVC composition, processed to attain the point G on

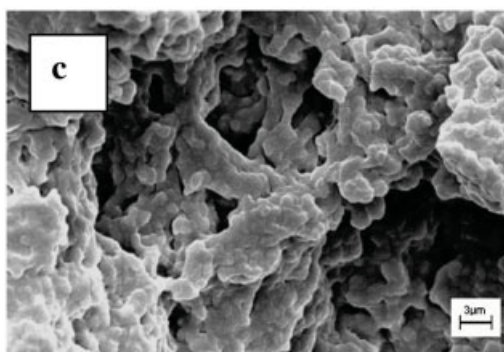
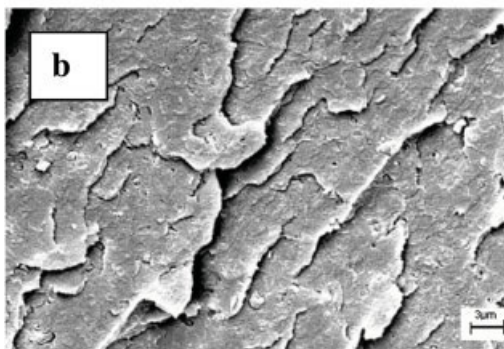
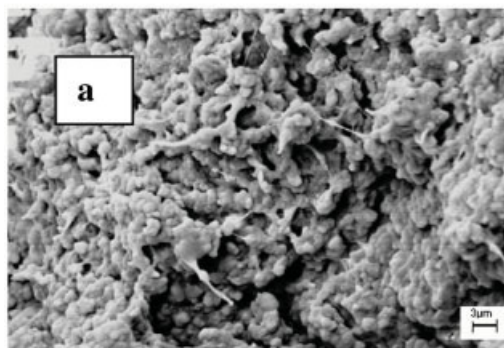
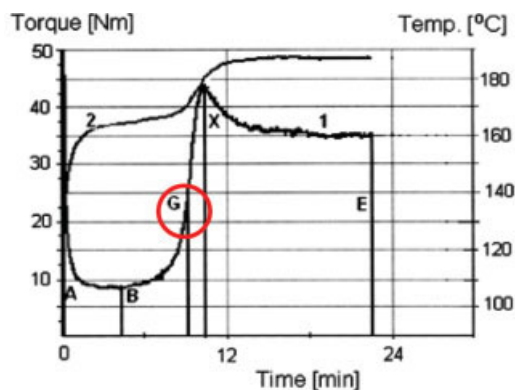


Figure 1 SEM photomicrograph of PVC-S61 after processing to inflection point of torque curve in the Brabender measuring mixer: (a) 150°C , 17.38 s^{-1} , (b) 170°C , 2.18 s^{-1} , (c) 170°C , 17.38 s^{-1} . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the plastograms, may be seen on the SEM observation (Fig. 1). Similarly, as in the case of the composition processed to the minimum of the torque,¹⁶ the

TABLE I
The Measurement Conditions of the MFR Investigations

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

structure of the composition, corresponding to the G point, is nonhomogeneous, especially for the PVC samples processed at the chamber temperature of 170°C, by the shear rate 17.38 s⁻¹, [Fig. 1(c)]. The occurrence of primary small particles and of their agglomerates on the fracture may be observed in this case.

However, the primary small particles are connected one to another, forming the bridge-like connections of a considerable size, with dimensions in the range from 3 to 5 μm. The bridges between small primary particles are visible also on the fracture of the sample processed at the temperature of 150°C [Fig. 1(a)]. The size of the bridges is in this case considerably smaller; however, the disintegration of grains occurs significantly more homogeneous than for the sample processed in a higher temperature. A similar effect of bridges formation in the first stage of the transformation may be observed for the composition of unplasticized PVC, processed using the method of rolling.¹⁹

On the contrary, the PVC samples prepared in the chamber temperature of 170°C, by shear rate of 2.18 s⁻¹ show unpredictably a homogeneous structure [Fig. 1(b)]. The fracture surface of these samples presents lamellar structure, characteristic for gelatinated PVC,^{10,20} which may be an evidence of a high degree of gelation of the PVC composition. However, this conclusion was not confirmed by the measurement of the MFR, showing the biggest value particularly for this sample (Fig. 2, the curve 2). The above described observation may indicate the appearance of gelation instability, produced at this stage of PVC compound processing, the effect which occurs during measurements of MFR. The degree of gelation of the composition kneaded in the presented conditions of temperature and shear rate, as evaluated from the DSC thermograms, is not very high and reaches value of about 27% (Fig. 2, the curve 1).

To explain the influence of shear rate on the transformation of morphology of the PVC composition, obtained from the kneader chamber at the point G, the SEM observations of the fractures of samples kneaded at the temperature of 170°C, in the wider range of the shear rates, were realized and are presented in Figure 3.

For the samples processed in the chamber at the temperature of 170°C, with the increase of the shear

rate, significantly bigger inhomogeneity of the structure of the composition, discharged from the mixing chamber at the time corresponding to the inflection point G, were noted by SEM observation. On the contrary, the fracture of the samples processed at lower shear rates, i.e., between 2.18 and 8.69 s⁻¹ [Figs. 3(a)–3(c)] indicate the occurrence of the lamellar structure. However, high values of MFR and low degree of gelation evaluated from DSC thermograms (27%) (Fig. 2) may be a proof of a low stability, related probably to the insufficiently formed structure of a physical network.

The SEM observation of samples processed by higher shear rates i.e., by 13.03 s⁻¹ and 17.38 s⁻¹ are different from the ones discussed above. The structure is very heterogeneous, especially the one of the sample processed by the shear rate of 13.03 s⁻¹ [Fig. 3(d)]. Apart from some remaining grain elements, the structure in the fibrous form may be observed on the surface of its fracture. This may be comprehended as an evidence of a progressive connection of primary particles. The formation of such structures may indicate a considerable influence of shear rate on the gelation of PVC.

The occurrence of grain elements on the surface of fractures of samples, processed by the highest shear rate, is related to a significant shortening of the time necessary to reach the point G. In Figures 4 and 5, the time to reach the point G as a function of the shear rate and of temperature of the chamber are presented.

The correlation between the time of reaching the point G (t_G), the temperature and the shear rate is practically identical as in the case of time of reaching the minimum of the torque, as it was shown before.¹⁶ The longest time of reaching M_G was observed for the composition kneaded at the temperature of 160°C, and by shear rate 4.34 s⁻¹ (28 min).

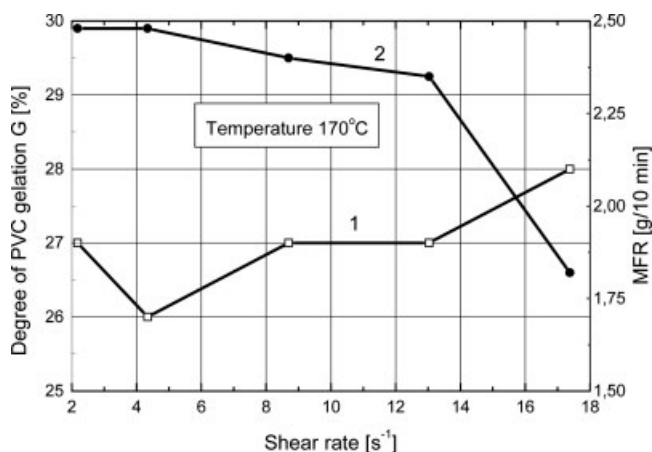


Figure 2 The degree of gelation (1) and MFR (2) of PVC S-61 after processing to inflection point of torque curve, at temperature 170°C as a function of the shear rate.

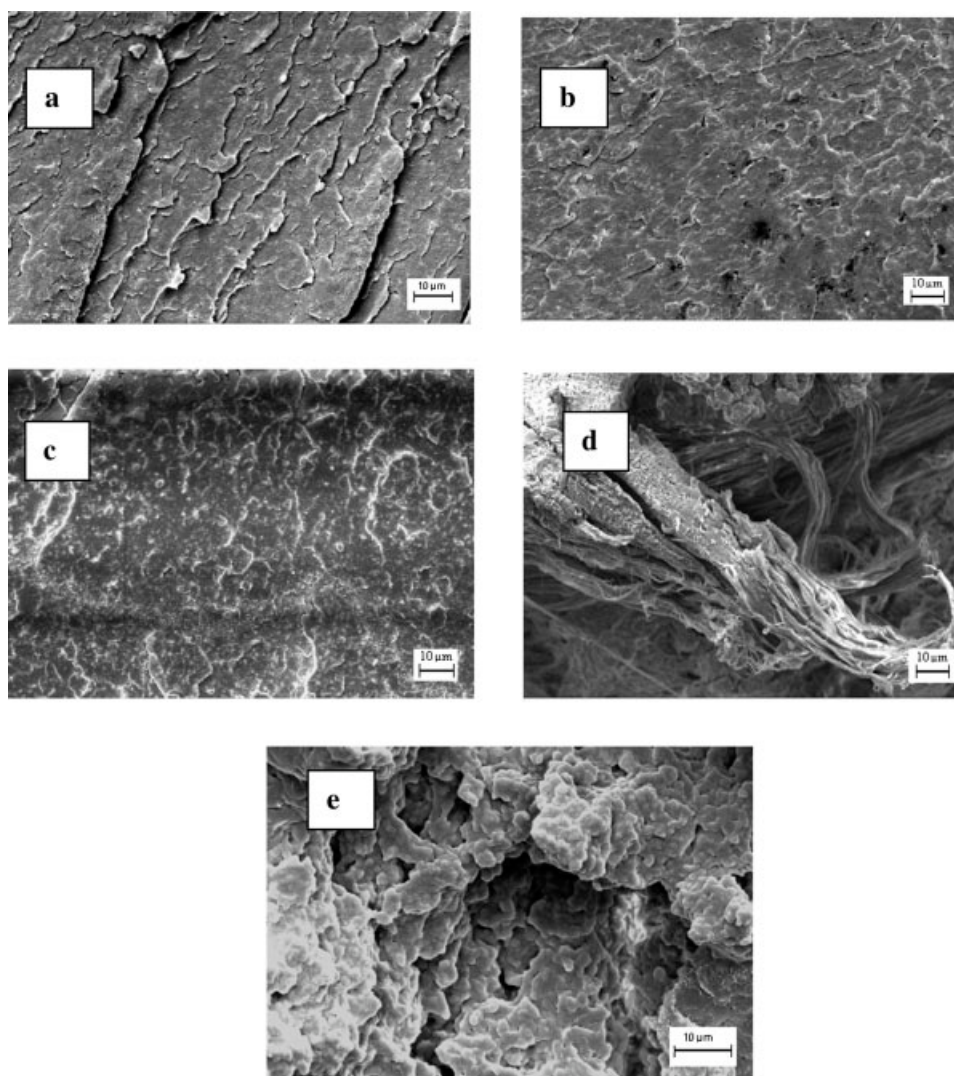


Figure 3 SEM photomicrograph of PVC-S61 after processing to inflection point of torque curve in the Brabender measuring mixer by the temperature 170°C: (a) 2.18 s⁻¹, (b) 4.34 s⁻¹, (c) 8.69 s⁻¹, (d) 13.03 s⁻¹, (e) 17.38 s⁻¹.

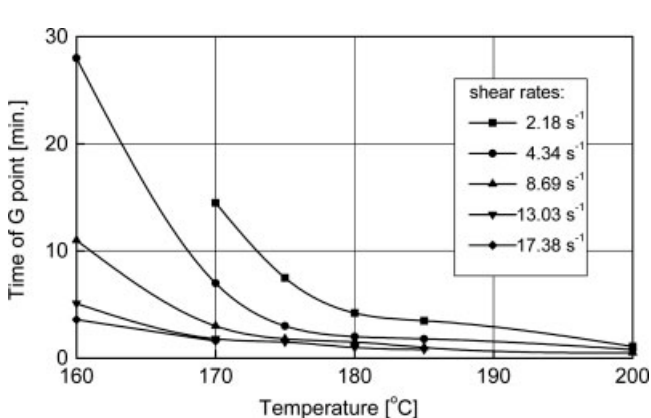


Figure 4 The time of reaching the inflection point of torque curve as a function of the processing temperature at various shear rates.

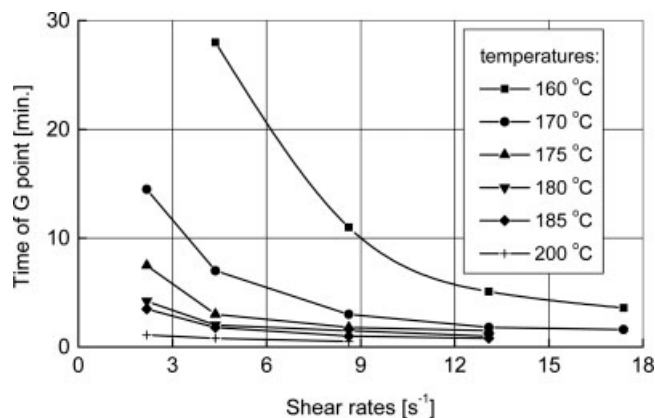


Figure 5 The time of reaching the inflection point of torque curve as a function of the shear rate at various processing temperatures.

This time (t_G) decreases with the rise of the temperature of the chamber; the decrease is more evident for the temperature of the chamber of 160 and 175°C. In the range of the temperature between 180°C and 200°C, the time necessary to attain M_G is the shortest (from 0.5 to 5 min).

The most significant t_G time shortening, with an increase of shear rate, was observed for the temperature of the chamber of 160°C and 170°C. Above 180°C, the time necessary to attain M_G is only 2 min and practically does not depend on shear rate (Fig. 5).

The conclusions of SEM observations were confirmed by the analysis of changes of value of torque (M_G) in the inflection point, as a function of the temperature and of the shear rate (Figs. 6 and 7). For all processing conditions used in this work, the torque M_G reaches the values between 18 and 30 N m, and increases relatively slow with the rise of shear rate (Fig. 6). The lowest value of the torque in the point G was observed for the composition processed at the lowest shear rate of 2.18 s^{-1} . By this shearing rate, the value M_G is practically identical (from 18 to 20 N m) for the temperatures of the chamber between 160 and 200°C.

The highest differences between the values of M_G for the composition processed at various temperatures were obtained at the shear rate of 8.69 and 13.03 s^{-1} . The kneading process of the PVC composition at the temperature of the chamber between 185 and 200°C causes a more sudden growth of M_G as a function of the shear rate.

It was found that the values of torque at the point G, for the PVC compound processed at the temperature of 185°C and at the shear rate of 13.03 s^{-1} , as well as at 200°C and 8.69 s^{-1} , are practically the same and reach the highest value (Fig. 7). Thus, if the temperature growth is about 15°C, similar value of torque at the point G, for the composition processed at the lower shear rate, are observed.

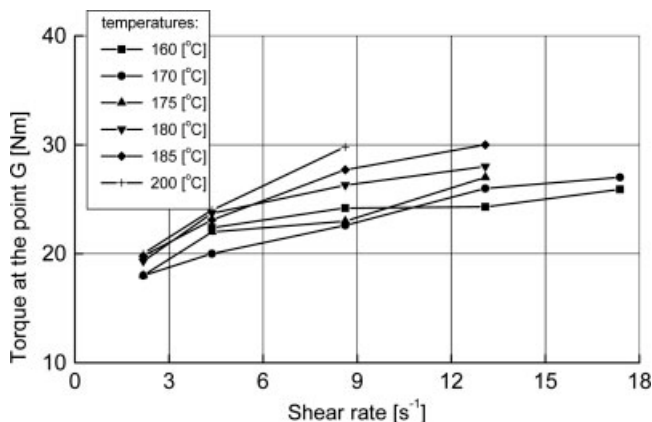


Figure 6 The torque of inflection point as a function of the shear rate at various processing temperatures.

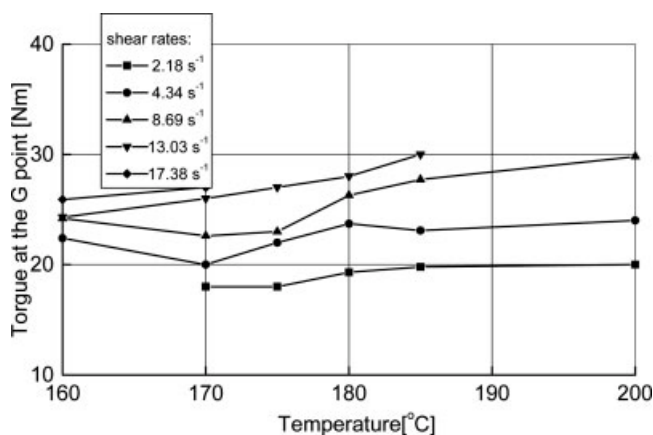


Figure 7 The torque of inflection point as a function of the processing temperature at various shear rates.

Therefore, taking into consideration the results discussed above, it may be concluded that the increase of the temperature of the chamber and the growth of the range of shear rate, as used in this work, cause only a small rise of the value of the torque at the point G and, simultaneously, a considerable shortening of the time of reaching this point on the torque curve.

CONCLUSIONS

Essential transformation of the morphology of PVC grains occurs during the kneader processing of an unplasticized composition of PVC S61, in the time when the inflection point G of the torque curve is reached. The dynamics of this transformation depends especially on the shear rate: the higher the shear rate the shorter is the residence time of the composition in the Brabender mixing chamber. Rapid transformation of the morphology of grains, observed by this type of PVC processing, are not accompanied by the changes in the PVC crystal structure. This effect was confirmed by the degree of gelation, which practically remained independent from the shear rate.

Thus, it may be concluded that the explanation of the effect of the PVC transformation in the particular inflection point G requires both, the microscopic observation of the fractured surface and gelation degree determination, as it was done in our studies. The SEM observation has indicated the occurrence of partly gelation in a form of braked grains. On the contrary, as well the results of DSC as MFR measurements proved that the gelation induced changes of heat of fusion, and of viscosity occurred only to a very low extend at this stage of PVC processing. Therefore, the inflection point may not be treated as a stage where the gelation of PVC was completed.

References

1. Zajchowski, S.; Piszczek, K.; Tomaszewska, J. *Polimery* 2001, 46, 232.
2. Terselius, B.; Jansson, J. F. *Plast Rubber Proc Appl* 1985, 5, 193.
3. Gilbert, M. *Plast Rubber Int* 1985, 10, 16.
4. Portingell, G. C. In *Particulate Nature of PVC, Formation, Structure and Processing*; Butters, G., Ed.; Applied Science: London, 1982; Chapter 4.
5. Covas, J. A.; Gilbert, M.; Marshall, D. E. *Plast Rubber Proc Appl* 1988, 9, 107.
6. Gilbert, M.; Hemsley, D.; Miadonye, A. *Plast Rubber Proc Appl* 1983, 3, 343.
7. Covas, J. A.; Gilbert, M. *Polym Eng Sci* 1992, 32, 743.
8. Potente, H.; Schultheis, S. M. *Kunststoffe* 1987, 77, 401.
9. Piszczek, K.; Tomaszewska, J.; Sterzyński, T. *Polimery* 2004, 49, 646.
10. Faulkner, P. G. *J Macromol Sci Phys* 1975, B11, 251.
11. Bortel, K.; Szewczyk, P. *Polimery* 1993, 38, 578.
12. Chen, C. H.; Wesson, R. D.; Collier, J. R.; Lo, Y. W. *J Appl Polym Sci* 1995, 58, 1107.
13. Berard, M. T. *J Vinyl Add Technol* 2002, 8, 246.
14. Pedersen, T. C. *J Vinyl Technol* 1992, 14, 54.
15. Chen, C. H.; Mao, C. F.; Lo, Y. W. *J Appl Polym Sci* 2001, 81, 3022.
16. Tomaszewska, J.; Sterzyński, T.; Piszczek, K. *J Appl Polym Sci* 2004, 93, 966.
17. Hawkins, T. *J Vinyl Technol* 1982, 4, 110.
18. Piszczek K. University of Technology and Life Science (UTP), Bydgoszcz, Poland, to appear.
19. Piszczek, K. *Polimery* 2005, 50, 441.
20. Piszczek, K.; Skraga, J.; Zajchowski, S. *Polimery* 1981, 26, 170.