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## The influence of temperature of poly(vinyl chloride) melt on the equilibrium state of gelation process

**Summary** — The final stage of PVC gelation during kneading until the moment of equilibrium state of the torque has been discussed. The processing of unplasticized PVC compounds was carried out in the Brabender mixing chamber at chamber temperature ( $T_{ch}$ ) 150, 160, 170, 175, 180, 185 or 200 °C and at rotational speed of the blades: 5, 10, 20, 30 or 40 min<sup>-1</sup> (for the temperature 150 °C also rotational speed 50 or 60 min<sup>-1</sup> was used). The shear rate values from 2.18 to 26.04 s<sup>-1</sup> corresponded with the range of rotational speed mentioned above. The change of the real temperature of the compound during kneading ( $T_E$ ) and its effect on PVC gelation degree ( $G$ ) were analyzed. A progress of gelation was studied using *MFR* measurements and SEM observations. It was found that  $T_E$  value affects the degree of gelation at the last stage of kneading while the effect of residence time of the compound in the chamber ( $t_E$ ) appeared to be insignificant. Apart from the high gelation level, revealed by DSC and *MFR* results, the processing at high shear rate leads to significant inhomogeneity confirmed by SEM method.

**Key words:** poly(vinyl chloride), gelation, mixing, torque, structure, melt flow rate.

### WPLYW TEMPERATURY POLI(CHLORKU WINYLU) NA STAN RÓWNOWAGI PROCESU ŻELOWANIA

**Streszczenie** — Przedstawiono wyniki badań przebiegu procesu żelowania (ugniatania) nieplastyfikowanej mieszanki poli(chlorku winylu) (PVC) do chwili osiągnięcia równowagi momentu obrotowego (punktu  $E$  na plastogramie). Ugniatanie prowadzono w komorze plastografometru Brabendera (Plasti-Corder PI 2200-3) w przedziale temperatury komory ( $T_{ch}$ ) od 150 °C do 200 °C, w warunkach szybkości ścinania ( $\dot{\gamma}$ ) od 2,18 s<sup>-1</sup> do 17,38 s<sup>-1</sup>, z wyjątkiem  $T_{ch} = 150$  °C, kiedy to stosowano również  $\dot{\gamma} = 21,72$  s<sup>-1</sup> i 26,04 s<sup>-1</sup>. Powyższym wartościom  $\dot{\gamma}$  odpowiadała szybkość obrotowa rotorów od 5 min<sup>-1</sup> do 60 min<sup>-1</sup>. Analizowano wartość odchylenia rzeczywistej temperatury ugniatanej mieszanki PVC ( $T_E$ ) od  $T_{ch}$  (czyli  $\Delta T_E$ ) w różnych warunkach ugniatania (rys. 1, tabela 1). Stopień żelowania ( $G$ ) określano na podstawie termogramów DSC (tabela 1). Postęp żelowania charakteryzowano na podstawie pomiarów wskaźnika szybkości płynięcia (*MFR*, rys. 2) i obserwacji elektronomikroskopowych (*SEM*, rys. 3). Stwierdzono, że stan żelowanej mieszanki PVC na końcowym etapie ugniatania w istotny sposób zależy od wartości  $T_E$ , natomiast wpływ czasu tego procesu jest pomijalnie mały. Niezależnie od dużych wartości stopnia żelowania wyznaczonych metodą DSC, przetwarzanie PVC w warunkach dużych wartości  $\dot{\gamma}$  powoduje znaczną niejednorodność struktury obserwowaną metodą SEM.

**Słowa kluczowe:** poli(chlorek winylu), żelowanie, mieszanie, moment obrotowy, struktura, wskaźnik szybkości płynięcia.

In numerous papers it was stated that poly(vinyl chloride) (PVC) gelation, occurring during processing, represents the transformation of primary morphological structure of grains into the secondary structure; this phenomenon includes also the crystalline phase which exists in the PVC grains [1–6].

The transformation of the primary grain morphology of the PVC compound during processing in the chamber of Brabender measuring mixer up to the equilibrium

state, was the subject of several studies [7–9]. Summers found that in PVC processed to the equilibrium state there were no primary particles — most of the crystallites were melted and the gelated compound was a continuous melt [7]. According to [9], the smooth texture seen in the SEM pictures after PVC fusion may probably be an indication of melting of the crystallites. Another authors propose, however, that unlike other polymers, PVC never attains a true homogeneous molten state at normal processing conditions [10].

The run of PVC gelation process significantly depends on the processing temperature [2, 11]. By the analysis of the effects related to PVC gelation, where the most often discussed value is the degree of gelation, the influence of shearing conditions is generally not taken into account; on the contrary, the shearing is indicated

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by the description of the device in which the processing is carried out.

In our previous paper [12], the significant rise of the real temperature of gelating PVC compound ( $T_E$ ) and a shortening of time to reach the equilibrium state ( $t_E$ ), with the increase of shear rate during kneading in the chamber of Brabender mixer, were presented. Therefore, the main task of this paper is to analyze separately the effects of the real compound temperature and of the time to reach the equilibrium state values on the structure and properties of PVC compound at the state of torque equilibrium.

## EXPERIMENTAL

### Material

The composition of PVC compound and the parameters of mixing of the dry blend were the same as described in [12]. So, the material used in this study was the PVC compound containing PVC S-61 Polanvil ( $M_n = 47\,500$ ,  $M_w/M_n = 2.25$ ), produced by Anwil Wloclawek (Poland) (100 parts) mixed with tinorganic stabilizer MOK Mark 17M, produced by Acros (4 parts), and paraffin wax Loxiol G22, produced by Henkel (1 part).

### Processing

The dry blend compound (54 g), as previously, was processed in the Brabender mixing chamber (Plasti-Corder PI 2200-3), at chamber temperature ( $T_{ch}$ ) 160 °C, 170 °C, 175 °C, 180 °C, 185 °C or 200 °C and the torque was registered as a function of time. The processing was performed always to the time when the equilibrium state of torque was achieved, *i.e.* the point *E* at the torque-time curve (description of the characteristic points at the torque curve according to [13–15]). The rotational speed of the blades was: 5, 10, 20, 30 and 40  $\text{min}^{-1}$ , and the applied friction was 1:1.5. Additionally, the experimental temperature range was completed with the chamber temperature of 150 °C, at which the measurements also for the rotational speed 50 and 60  $\text{min}^{-1}$  were realized. The shear rates ( $\dot{\gamma} = 2.18, 4.34, 8.69, 13.03, 17.38, 21.72$  or  $26.04 \text{ s}^{-1}$ ) were evaluated as the average values from the highest and the lowest shearing, in the same way as in [12].

We have analyzed the value of the real compound temperature at the point *E* [12]. This real value of  $T_E$  was determined by means of the resistance temperature detector (RTD) situated between the rotors isolated from the walls of the chamber, directly in the kneaded PVC compound. As RTD the Pt100 sensor was applied and the measurement resolution was about 0.5 °C.

### Measurements

The cryogenic fractured surfaces of fused PVC samples (prepared in nitrogen) were observed using the

scanning electron microscope (SEM) — LEO 14-39 VP. The surfaces were covered with gold prior to the observation.

The thermal transitions, related to the melting of primary and secondary crystallites were determined by means of differential scanning calorimetry, using the Perkin Elmer DSC 7 apparatus, operating with a heating rate of 10 °C/min, from 60 °C to 250 °C in a nitrogen as an inert atmosphere. The average weight of the sample was 15 to 20 mg.

The gelation degree (*G*) was estimated according to the formula proposed by Potente [16], based on the melting enthalpy (in J/g) of the primary ( $\Delta HA$ ) and secondary ( $\Delta HB$ ) crystallites:

$$G = \frac{\Delta HA}{\Delta HA + \Delta HB} \cdot 100 \% \quad (1)$$

A typical run of the DSC thermogram of PVC sample was already presented in our previous paper [6].

The rheological measurements of PVC compound were accomplished using a specially constructed MFR apparatus [17], giving the possibility to apply very high pressure. The experimental conditions of the melt flow rate (MFR) measurements were as follows:

- temperature of barrel 170 °C;
- piston load 800 N;
- diameter of piston 9.5 mm;
- length of capillary die 6 mm;
- diameter of capillary die 2 mm;
- time of material heating 10 min.

## RESULTS AND DISCUSSION

The differences ( $\Delta T_E = T_E - T_{ch}$ ) among the real temperature of gelating compound at *E* point ( $T_E$ ) and the adjusted temperature of the chamber ( $T_{ch}$ ), for the whole temperature range and for all shear rates applied in this study, are presented in Fig. 1.

So, in the range of the chamber temperature between 150 °C and 185 °C the  $T_E$  values are higher than adjusted. The highest increase in  $T_E$  (above  $T_{ch}$ ) occurred for the compound processed in the chamber at the temperature

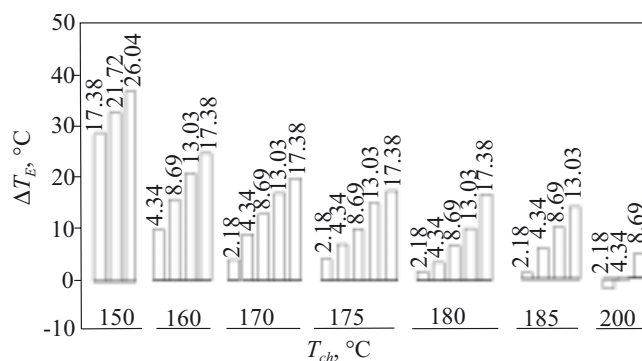


Fig. 1. Difference ( $\Delta T_E$ ) between real temperature of compound (PVC S61) and chamber temperature as a function of shear rate ( $\dot{\gamma}$  on  $\text{s}^{-1}$ ) and chamber temperature ( $T_{ch}$ )

150 °C; mainly between 29 °C for the shear rate 17.38 s<sup>-1</sup> and 37 °C for the shear rate 26.04 s<sup>-1</sup>. With increasing temperature of the chamber the increase in  $T_E$  is smaller. At the chamber temperature of 200 °C the temperature of PVC compound  $T_E$  does not even attain the adjusted value, or in certain cases ( $\dot{\gamma} = 8.69$  s<sup>-1</sup>) only exceeds it slightly.

The occurrence of two endotherms of the fusion of primary and secondary crystallites was observed in all DSC thermograms, and similar observation was reported in the literature [2, 3, 16]. The degree of gelation ( $G$ ) of PVC compound was estimated basing on the values of the enthalpy of fusion of crystallites ( $\Delta H_A$ ,  $\Delta H_B$ ) found in DSC thermograms. The values of the degree of gelation  $G$  dependent a shear rate, and, consequently, on the melt temperature  $T_E$  and time  $t_E$  are compared in Table 1.

**Table 1.** Dependence of degree of gelation ( $G$ ), the real temperature ( $T_E$ ) and time ( $t_E$ ) on shear rate ( $\dot{\gamma}$ ) and chamber temperature ( $T_{ch}$ )

$T_{ch}$ , °C	$\dot{\gamma}$ , s <sup>-1</sup>	$T_E$ , °C	$t_E$ , min	$G$ , %
150	17.38	179	36	99
	21.72	183	22	99
	26.04	187	15	99
160	4.34	170	48	56.5
	8.69	176	24	72
	13.03	181	18	95
	17.38	185	15	98
170	2.18	174	36	56.5
	4.34	179	21	62
	8.69	183	15	75.5
	13.03	187	15	91
	17.38	190	14	96
175	2.18	179	24	59
	4.34	182	18	74
	8.69	185	15	87.5
	13.03	190	15	96
	17.38	193	14	98
180	2.18	182	20	69
	4.34	184	18	87
	8.69	187	15	92.5
	13.03	191	15	98
	17.38	197	13	99
185	2.18	186	18	75
	4.34	191	16	87.5
	8.69	195	15	94.5
	13.03	199	15	99
200	2.18	198	12	91
	4.34	200	12	94
	8.69	205	11	99

It was found that the degree of gelation increased with the rise of the shear rate, for the temperature of the chamber in the range 160–200 °C. Particularly visible is the influence of the shear rate on  $G$  value in the case of

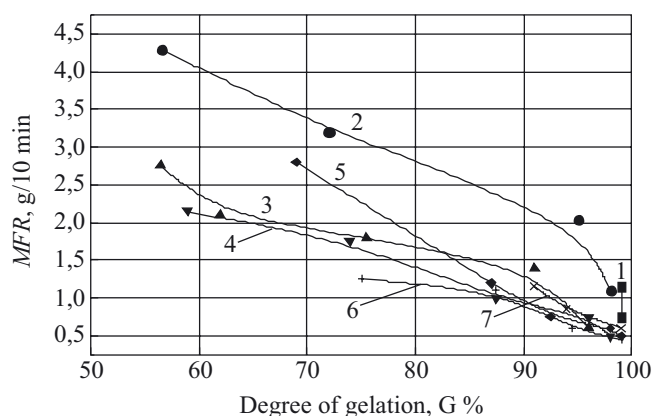
lower  $\dot{\gamma}$  values *i.e.* from 2.18 s<sup>-1</sup> to 13.03 s<sup>-1</sup>. The increase in shear rate above 13.03 s<sup>-1</sup> does not cause any considerable change of the degree of gelation — the values of  $G$  in these conditions are in the range 96–99 %.

In our experiments the lowest chamber temperature where the gelation has been reached was  $T_{ch} = 150$  °C; surprisingly, a high value of the degree of gelation was observed for PVC compound processed in the Brabender kneader at this temperature of the chamber. Kneading PVC compound at the temperature of 150 °C and at high shear rate (above 17.38 s<sup>-1</sup>) leads to a very high  $G$  namely 99 %. For the compound gelating in these conditions, a relatively long time for reaching the equilibrium of the torque ( $t_E = 15$ –36 min), was necessary.

Such a long residence time  $t_E$  of the compound in the chamber might be a reason of the high  $G$  value. Although, for the compound processed at higher chamber temperature  $T_{ch}$ , especially in the lower range of the shear rate from 2.18 to 13.03 s<sup>-1</sup>, also a comparable time of reaching the equilibrium state is needed; however in this case the degree of gelation is smaller.

From the analysis of the values presented in the Table 1 it follows that for the chamber temperature of 150 °C the rise of the real temperature  $T_E$  is definitely the highest — an observation similar to the changes of the temperature  $T_X$  in the point corresponding to the maximum torque, as described in detail at our previous work [15]. Thus, the effect of a spontaneous self heating of PVC compound may be a reason of the surprisingly high value of the degree of gelation, noticed particularly at the relatively low temperature of the chamber. So, the real residence time of the compound in definite conditions of temperature and mechanical charges seems to be less important for the high gelation state of PVC compound.

According to the literature, the transformations of the morphological structures of grains, due to PVC gelation,



**Fig. 2.** MFR versus gelation degree ( $G$  from DSC) for unplasticized PVC compound after processing to equilibrium state of torque at various chamber temperature ( $T_{ch}$ ): 1—150 °C, 2—160 °C, 3—170 °C, 4—175 °C, 5—180 °C, 6—185 °C, 7—200 °C

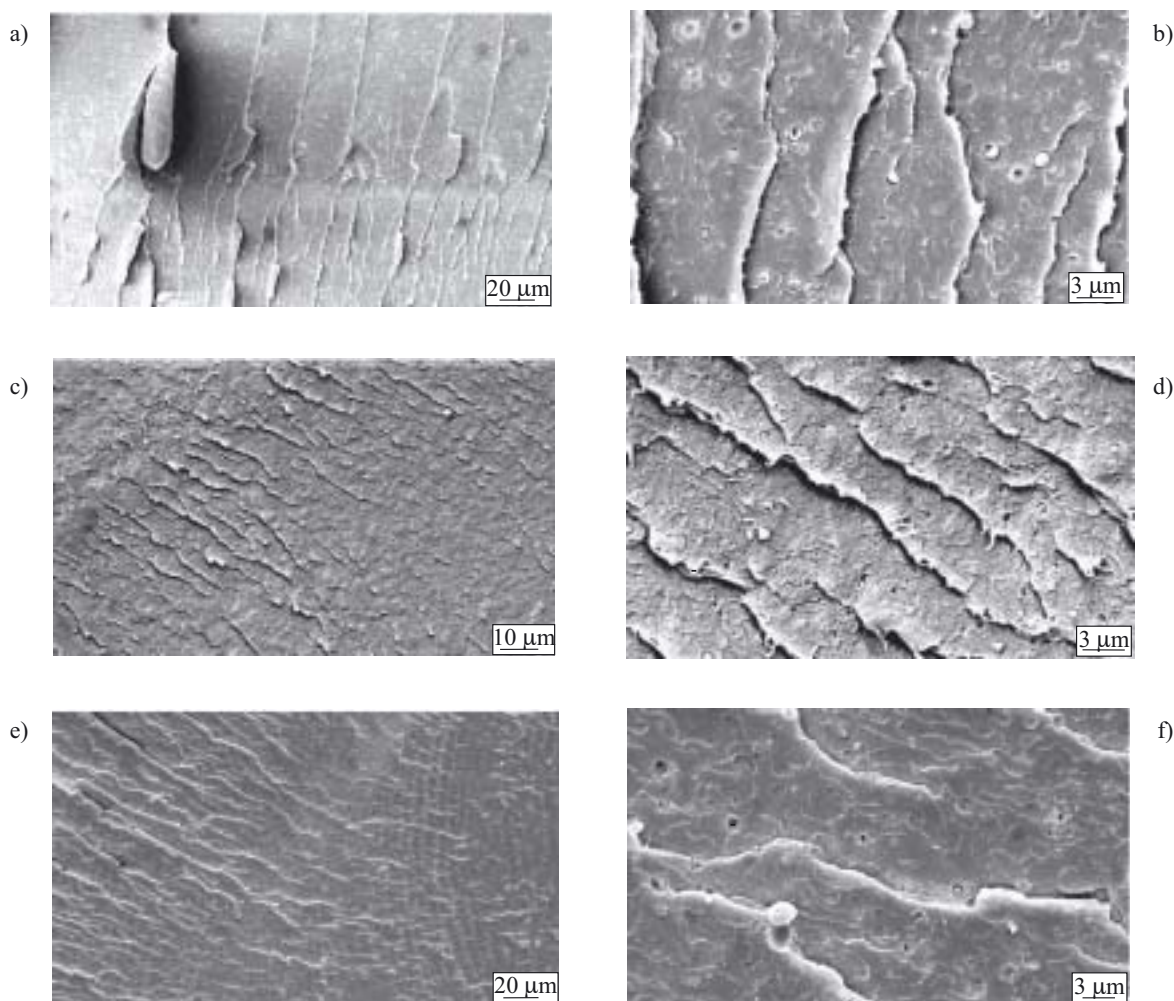


Fig. 3. SEM images of PVC-S61 after processing to equilibrium state of torque in the Brabender measuring mixer in the following conditions: a, b — 150 °C, 17.38 s<sup>-1</sup>; c, d — 170 °C, 2.18 s<sup>-1</sup>; e, f — 170 °C, 17.38 s<sup>-1</sup>

may indirectly be analyzed by the changes of *MFR* values [6, 18, 19], where a similar interpretation of these changes as in the case of estimation of gelation level by means of DSC method, may be suggested. In the Fig. 2 the relation between gelation degree *G* (as evaluated from DSC measurements) and *MFR* values for PVC compound kneaded at various shear rates is presented. A general and obvious tendency may be observed, as observed already before [6], that with increasing gelation degree a lowering *MFR* value may be noted.

However, it is known that the high value of degree of gelation, as observed before, is not always directly reflected by the application properties related to the homogeneous structure, *i.e.* free from grain elements — an effect which may be confirmed by microscopic observation [11].

The fracture surfaces of PVC compound, processed until the equilibrium state of the torque, does not differ significantly from the structure of the compound processed to the point X [15], mentioned already in this paper. The grain elements with a diameter of about 1 μm or smaller, corresponding to the size of domains [1, 10, 20], are visible at the fracture surface of all samples (Fig. 3),

however, the smallest quantity of remaining grain elements may be seen for the samples processed by 170 °C and 2.18 s<sup>-1</sup> (Fig. 3c, d), it means the lowest applied shear rate. In the case of the remaining samples processed in the chamber at  $T_{ch} = 150$  °C or 170 °C and at the shear rate 17.38 s<sup>-1</sup> the presence of particles with a diameter even of about 3 μm was observed, what may confirm that at these processing conditions the most inhomogeneous structures were produced. It may be suggested that the rest of the grain elements in the homogeneous structure of gelated material results probably from the durability of grains, caused by a rapid increase in real temperature of PVC compound processed in Brabender mixer.

Nevertheless, the SEM images of fractures of samples processed at  $T_{ch} = 170$  °C, at shear rate 2.18 or 17.38 s<sup>-1</sup> (Fig. 3c—f) are very similar, the *MFR* values for these samples are considerably different. The almost 80 % decrease in *MFR* value for the sample processed at the high shear rate indicates (Fig. 2, curve 3) a significant enlargement of the durability of the structure, what is probably related to a rise of durability of the formed physical network of secondary crystallites.

## CONCLUSION

The real temperature of PVC compound determines its degree of gelation in the last stage of the gelation while, on the contrary, the influence of the residence time of the compound in the chamber seems to be less significant.

The degree of gelation evaluated by DSC traces shows a considerable agreement with MFR values, characteristic for the state of gelation [2, 6, 18, 19].

The PVC samples processed at high shear rate show significant inhomogeneity (observed by SEM), though DSC and MFR measurements confirm a high level of gelation in this case, similar to an effect described in our earlier work [15] for samples at the X point in the plastogram. This may be explained by an insufficient grinding (disintegration) of grains at the earlier stage of the processing, *i.e.* by reaching the minimum value of the torque.

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