STANISŁAW ZAJCHOWSKI
University of Technology and Agriculture
Faculty of Technology and Chemical Engineering
Department of Polymer Technology
ul. Seminaryjna 3, 85-326 Bydgoszcz
e-mail: stanislaw.zajchowski@atr.bydgoszcz.pl

# Mechanical properties of poly(vinyl chloride) of defined gelation degree

RAPID COMMUNICATION

**Summary** — The effect of processing temperature (140—205 $^{o}$C) on gelation degree (*G*) of unplasticized PVC of *K* value = 61, containing 8 wt. % of ethylene/vinyl acetate copolymer, has been studied using three various measuring tools: weight plastometer, capillary rheometer and screw capillary rheometer. It was found that independently on the method used all of measuring points lay on the one curve. The dependence of *G* value on the composition of the mixture of non-gelated (A) and fully gelated (B) PVC granulated products in the whole range of their compositions has been determined using the methods mentioned above. The following properties of the extrudates were tested: impact strength, tensile strength and relative elongation at break. There was found the possibility of determination of mechanical properties of an extrudate *via* proper selection of processing temperature and the composition of PVC granulated products, showing various gelation degrees.
**Key words:** poly(vinyl chloride), gelation degree, processing temperature, mechanical properties.

WŁAŚCIWOŚCI MECHANICZNE POLI(CHLORKU WINYLU) O ZDEFINIOWANYM STOPNIU ZŻELOWANIA

**Streszczenie** — Z zastosowaniem trzech różnych przyrządów pomiarowych: plastometru obciążnikowego, reometru kapilarnego oraz ślimakowego reometru kapilarnego Brabendera zbadano wpływ temperatury (140—205 $^{o}$C) na stopień zżelowania (*G*) nieplastyfikowanego PVC o liczbie K = 61, zawierającego 8 % mas. kopolimeru etylen/octan winylu. Stwierdzono, że wszystkie punkty pomiarowe niezależnie od zastosowanej metody pomiaru układają się na jednej krzywej (rys. 1). Powyższymi metodami określono zależność wartości *G* od składu mieszanin granulatu PVC niezżelowanego (A) i całkowicie zżelowanego (B) w pełnym zakresie ich składu (rys. 2). Otrzymane wytłoczyny poddano badaniom udarności bez karbu, wytrzymałości na rozciąganie oraz wydłużenia względnego przy zerwaniu (rys. 3—5). Stwierdzono możliwość ustalenia właściwości mechanicznych wytłoczyny poprzez odpowiedni dobór składu granulatów PVC o różnym stopniu zżelowania oraz temperatury przetwórstwa.
**Słowa kluczowe:** poli(chlorek winylu), stopień zżelowania, temperatura wytłaczania, właściwości mechaniczne.

Independently on many research works published for over 60 years, there are still unsolved problems concerning the processing of poly(vinyl chloride) (PVC) and its applications. It concerns also applications of PVC/wood flour composites. Recently, the growing interest in wood-polymer composites (WPC) has been observed and in majority it concerned the composites of polyolefins with wood flour [1—5]. There are only several papers on the composites of PVC with wood flour though, unlike polyolefin composites, PVC composites show wider possibilities of applications because of their high environmental ageing resistance [6—7]. One of characteristic features differentiating PVC from other thermoplastics is the structure of its grain as well as the structure of the products obtained of them. The conversion of the PVC powder into a homogeneous material, and properties changes related to this process, dependent on the processing conditions, an achieve which may be attributed to gelation occurrence [8—12].

The structure of PVC formed during gelation process determines its physical properties, including mechanical ones [13—18]. These problems were widely described in the Tomaszewska's doctor's thesis [19]. However, in the literature the data concerning gelation process of PVC in mixtures with wood flour are missing. The aim of this work was an estimation of the course of gelation process of PVC composition, selected on the basis of preliminary investigations done with wood flour. Especially mechanical properties of PVC dependently on gelation degree (G), defined by changing of parts of granulated products A and B showing gelation degrees 0 % and 100 %, respectively, were determined.

## EXPERIMENTAL

### Materials

A composition of suspension PVC of *K* value 61, containing 8 wt. % of ethylene/vinyl acetate copolymer (EVAC), Ba/Cd stabilizers and system of lubricants and slip agents was examined in this work.

### Blends preparation

PVC dry blends were prepared in two-stage mixer. The mixing was carried out up to temperature 115 °C, and then in a low-speed mixer the blend was cooled to temperature 40 °C.

### PVC gelation

The PVC blend was extruded using a Brabender extrusiograph, characterized with a screw diameter D = 19 mm and a length 25 D, at screw rotational speed 28 rpm and screw compression ratio 1.8/1. The cross-section of an extruder head was 4x10 mm. A thermocouple measuring the actual melt temperature was placed between a screw and a head. For collecting and simultaneously cooling of extrudate the three-roller apparatus, giving possibility to control continuously the velocity of the extrudate take out transport, was used. The extrusion was carried out in the processing temperature range between 140 and 205 °C. The extrudates were granulated and gelation degree was determined. Granulated products obtained from the extrudates, produced at temperature of 140 °C (material A) or at 205 °C (material B) showed gelation degrees 0 % and 100 %, respectively.

Mixtures of A and B granulated products, in various ratios, were prepared in a laboratory mixer. These mixtures were extruded at temperatures between 170 and 205 °C, in conditions determined formerly for PVC compounds' gelation. Mechanical properies of finally obtained products with various gelation degree, were tested.

### Gelation degree

The gelation degree of all produced PVC extrudates was determined using a weight plastometer IIRT and WK 2000 capillary rheometer (Göttfert), according to procedures presented in the papers [8, 15, 16, 20—22]. In both cases the measurements were carried out at temperature 170 °C, using the die of L/D = 5/2. The piston load in a weight plastometer was 400 N. The piston displacement velocity in the capillary rheometer was in the range between 0.01 and 1 mm/s. To measure the gelation degree also screw capillary rheometer (Brabender) with the die L/D = 5/2 was used. The temperature of all cylinder heating zones was 150 °C while of head 170 °C. Screw rotational speed was 3 rpm. Pressure sensor has been placed before the entry to the die. The gelation degree has been evaluated from the difference of pressure for fully gelated B material, and non-gelated A granulated products, according to following formula:

$$G = \frac{P_x - P_{\min}}{P_{\max} - P_{\min}} \cdot 100\% \tag{1}$$

where: *G — gelation degree,* $P_x$ *— PVC melt pressure before the die entry,* $P_{min}$ *— pressure of PVC of gelation degree equal to 0 % (A material),* $P_{max}$ *— pressure of PVC of gelation degree equal to 100 % (B material).*

The methods used were selected taking into account the necessity of further estimation of gelation degree of PVC in composites with wood flour, foreseen for those materials. The capillary rheometer was used because this method allows to test big samples what is very useful by the estimation of average results, eliminating local inhomogeneities originating from possible differences in mixtures' compositions, composed of PVC with various gelation degree. The use of a screw capillary rheometer seemed to be advisable for the estimation of the gelation degree of PVC blends, especially filled ones. In case of two other methods it is necessary to consider the unsatisfactory repeatability of the results, obtained for in the case of composites with wood flour. This effect may by caused by an uncontrolled influence of a filler on the polymer behavior during transport from cylinder to the die, and by flow in the die [23—28]. In all three methods used the entry effect, being the basis of gelation degree measurement, was used. They are the bigger, the lower is a value of L/D ratio and the higher is the flow intensity [22—23]. The gelation degree is evaluated from the result of elastic strain measurement what in a case of processed PVC blends depends mainly on structure, related to processing temperature.

### Mechanical properties test methods

The following properties were tested: Charpy impact strength (unnotched) $a_n$ according to PN-81/C-89029 Standard, tensile strength $\sigma_M$ and relative elongation at break $\varepsilon_B$ in the static tension test, according to PN-EN ISO 527-1 Standard.

## RESULTS AND DISCUSSION

The average values of the gelation degree, evaluated on the basis of the results of the measurements obtained by three methods used, versus polymer temperature dur-

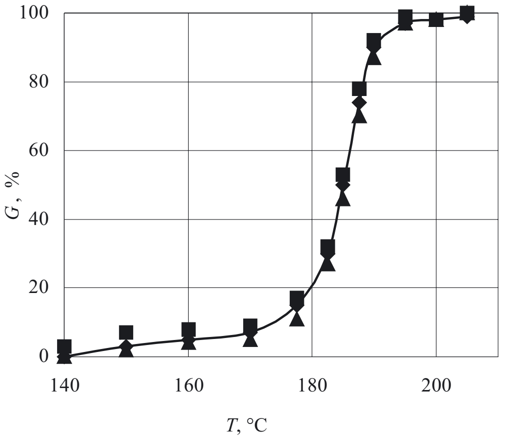

*Fig. 1. Dependence of average gelation degree (G) of PVC mixture on polymer temperature in molten state (T), determined by:* ■ *— weight plastometer,* ▲ *— capillary rheometer,* ♦ *— screw capillary rheometer*

ing extrusion in molten state, lie in one curve (Fig. 1). A less or more gelated PVC is often considered as a system in which two phases: a non-gelated and a gelated exist [16, 18, 20]. So, the question is now how far the mutual parts of non-gelated and gelated materials affect the average value of gelation degree. To answer this question the rheometric investigations of PVC blends were done in the whole range of concentrations of both granulated products: A obtained by extrusion at temperature of. 140 °C and B extruded at temperature 205 °C.

The linear dependence of the value of gelation degree (evaluated on the basis of three methods used) on the concentrations of A and B granulated products, has been found (Fig. 2). Therefore, the PVC of any gelation degree can be considered as a system consisting of non-gelated and gelated areas.

To determine the effect of the PVC gelation degree on its mechanical properties, the defined mixtures of A and B granulated products were tested versus temperature of extrusion. The results of investigations of impact strength of extrudates produced in a processing temperature range between 170 and 205 °C are presented in Fig. 3. It may be stated that the courses of impact strength changes versus processing temperature, for the extrudates obtained from A (100/0) (curve 5) and B (0/100) (curve 1) granulated products, are equivalent. With the temperature increase the impact strength first increases, reaching the maximum at processing temperature of 185 to 190 °C, dependently on the composition. Further increase in temperature causes impact strength decrease, showed especially at temperature above 200 °C. The highest values of impact strength, equal to 40 kJ/m$^2$, were found for 50/50 A/B mixture (curve 3). It was also found that independently on the initial composition of A/B mixture, impact strength of all samples extruded at temperature 205 °C was the same.

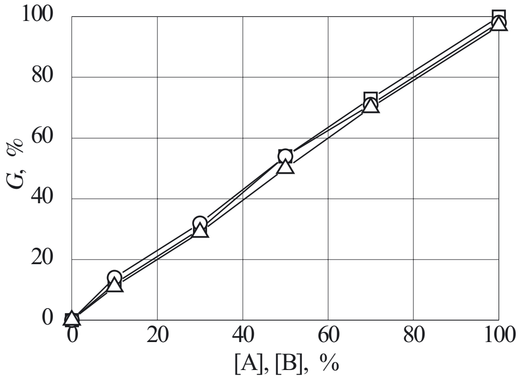

*Fig. 2. Dependence of gelation degree (G) determined by:* □ *— weight plastometer,* △ *— capillary rheometer,* ◊ *— screw capillary rheometer, on the composition of A and B granulated products' mixture*

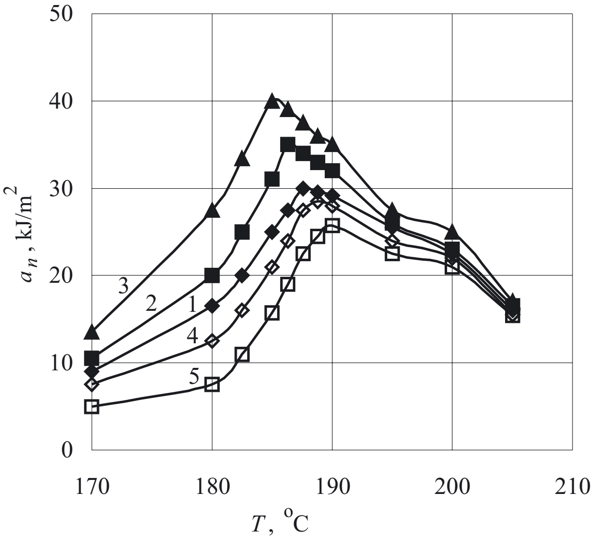

*Fig. 3. Dependence of impact strength ($a_n$) of the extrudate obtained from the mixture of A/B granulated products on the processing temperature (T): 1 — 0/100; 2 — 25/75; 3 — 50/50; 4 — 75/25; 5 — 100/0*

The analyze of the values of relative elongation at break (Fig. 4) let clearly conclude the effect of A and B granulated products contents on this property. Maximal elongation, equal 120 %, occurs in the case of B material, extruded at temperature 185 °C (curve 1). Maximum of elongation occurs also for all other samples. The elongation gradually decreases over the polymer processing temperature 185—189 °C. Independently on the compositions of the extruded mixtures, the values of elongation of the extrudates obtained at temperature 205 °C are identical and equal to 58 %.

The dependence of the tensile strength of the PVC extrudate on processing temperature looks differently (Fig. 5). For A/B mixtures extrudates produced at 170 °C the tensile strength clearly depends on both granulated products parts. The higher A concentration (non-gelated PVC) the lower tensile strength value. An increase in the polymer temperature during processing only slightly decreases the differences. The tensile strength grows

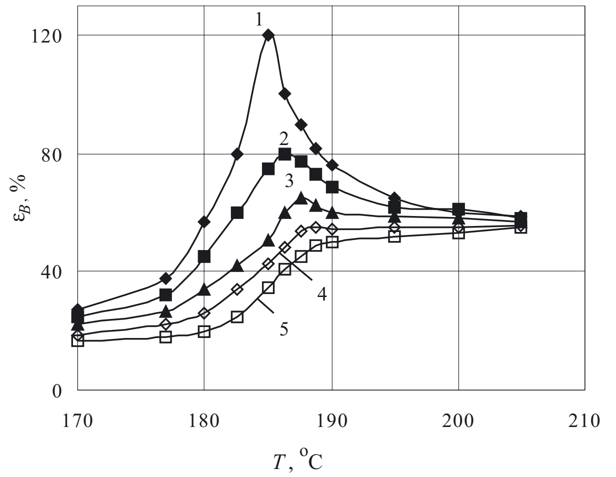

*Fig. 4. Dependence of relative elongation at break ($\varepsilon_B$) of the extrudate obtained from the mixture of A/B granulated products on the processing temperature (T): 1 — 0/100; 2 — 25/75; 3 — 50/50; 4 — 75/25; 5 — 100/0*

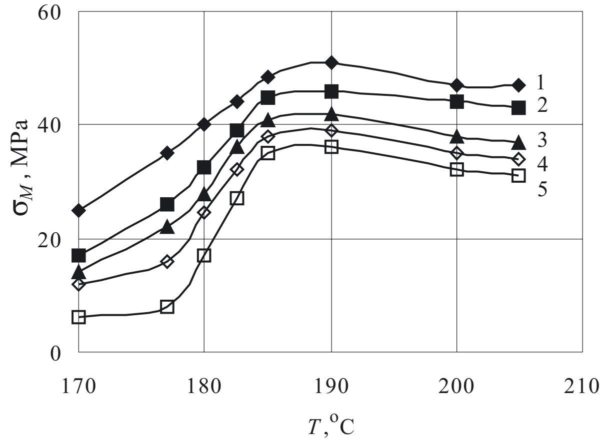

*Fig. 5. Dependence of tensile strength ($\sigma_M$) of the extrudate obtained from the mixture of A/B granulated products on the processing temperature (T): 1 — 0/100; 2 — 25/75; 3 — 50/50; 4 — 75/25; 5 — 100/0*

gradually with processing temperature, reaching the maximum at about 190 °C; followed by a slight decrease in the tensile strength. The differences of $\sigma_M$ up to the temperature 205 °C, dependent only on initial A/B ratio. The extrudates produced only of A material show the lowest $\sigma_M$ values in the whole range of processing temperatures, on the contrary, those obtained of B material — the highest ones.

Hence, from the investigations presented follows that applying of a PVC processing temperature in the range 185—190 °C leads to PVC products revealing advantageous properties. This observation agrees with the results given in papers [15—19], where also this processing temperature range has been found as leading to optimal properties of an unplasticized PVC.

Summarizing, one can say that there is a possibility of straight controlling of PVC mechanical properties *via* a selection of a composition of PVC of different gelation degrees, as well as *via* selection of an appropriate processing temperature.

*The research was realized in the frame of the project No. 4 T08E 04822, financially supported by Polish State Committee for Scientific Research.*

## REFERENCES

1. Materiały konferencyjne, "Wood-Plastic Composites", Wien 2003.
2. Materiały konferencyjne, "5th Global Wood and Natural Fibre Composites Symposium", Kassel 2004.
3. Patuszyńska I., Zajchowski S., Patuszyński K.: *Inż. i Ap. Chem.* 2005, **44**, 3, 57.
4. Kuciel S., Liber A.: *Polimery* 2005, **6**, 436.
5. Zajchowski S., Patuszyński K.: *Kompozyty (Composites)* 2005, **5**, 3, 35.
6. Zajchowski S.: *Chemik* 2004, **57**, 1, 15.
7. Zajchowski S, Głowacka L.: "Nowe kierunki modyfikacji i zastosowań tworzyw sztucznych", red. J. Jurga, B. Jurkowski, T. Sterzyński, Wyd. Politechniki Poznańskiej, Poznań 2004, 71.
8. Zajchowski S.: "Wpływ charakteru ziaren poli(chlorku winylu) na właściwości reologiczne i strukturę morfologiczną plastyfikatów", praca doktorska, UMK Toruń 1977.
9. Świerz-Motysia B., Pielichowski K.: *Polimery* 2005, **50**, 601.
10. Piszczek K., Tomaszewska J., Sterzyński T.: *Polimery* 2004, **49**, 646.
11. Obłój-Muzaj M., Świerz-Motysia B., Szabłowska B.: "Polichlorek winylu", WNT Warszawa 1997.
12. Abramowicz A.: *Polimery* 2005, **50**, 593.
13. Benjamin P.: Conference "PVC Processing", Egham 1978, B5.1.
14. Piszczek K.: *Polimery* 2005, **56**, 441.
15. Zajchowski S., Tomaszewska J., Piszczek K.: IX Seminarium "Tworzywa sztuczne w budowie maszyn", Kraków 2000, 377.
16. Tomaszewska J., Piszczek K., Zajchowski S.: IX Seminarium "Tworzywa sztuczne w budowie maszyn", Kraków 2000, 341.
17. Zajchowski S., Piszczek K., Tomaszewska J.: *Polimery* 2001, **46**, 232.
18. Menges G., Parey J., Zajchowski S.: Raport z prac, Institut für Kunststoffverarbeitung RWTH, Aachen 1980.
19. Tomaszewska J.: "Reometryczna i strukturalna analiza procesu żelowania nieplastyfikowanego polichlorku winylu", praca doktorska, Politechnika Poznańska, 2005.
20. Parey J., Zajchowski S.: *Plastverarbeiter* 1981, **32**, 724.
21. Zajchowski S., Parey J.: Raport z prac, Institut für Kunststoffverarbeitung RWTH, Aachen 1981.
22. Lamberty M.; *Plast. Modern. Elast.* 1974, **26**, 82.
23. Sikora R.: Podstawy przetwórstwa tworzyw wielkocząsteczkowych, Wydawnictwa Uczelniane, Politechnika Lubelska, Lublin 1992.
24. Kloziński A., Sterzyński T.: *Polimery* 2005, **50**, 455.
25. Stabik J.: *Polimery* 2004, **49**, 712.
26. Stabik J.: *Polimery* 2004, **49**, 634.
27. Jeziórska R.: *Polimery* 2004, **49**, 623.
28. Stasiek J.: *Polimery* 2003, **48**, 443.

*Received 25 VII 2005.*