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Gelation of suspension PVC with small amount of plasticizer compounds

RAPID COMMUNICATION

Summary — The course of gelation of suspension PVC-S (*K* values 58, 61 or 67) plastified with small amounts (0.5—4 phr) of dioctyl phthalate (DOP) was investigated in Brabender plastometer chamber. Rotational speed of rotors was 28 min^{-1}. On the basis of torque changes and the measurements of real temperature of gelating compound versus process time the curves of torque change versus this temperature were prepared for various plasticizer contents. It was found the higher DOP content the lower temperature corresponding to maximum torque, characterizing the gelation process. The dependence of real temperature of a compound in equilibrium state (T_E) on DOP content shows that gelation occurs when chamber temperature reaches 170 ^{o}C and plasticizer content is equal DOP_{min} = 2.5 phr. Effects of these parameters on the torque measured at equilibrium state are similar. Addition of 2.5 phr of DOP caused rapid increase in gelation degree (*G*) during processing of all the types of PVC tested, at temp. 175 ^{o}C.

Key words: suspension PVC, *K* value, plastogram, dioctyl phthalate, gelation degree.

The economical aspect, easy modifications and processing, usability and functional properties as well as progress in overcoming of ecological problems have an impact on continuous increase in PVC consumption [1, 2]. About 60 % of PVC production is used for rigid products, remaining part for soft products. The processing of the suspension PVC involves a transformation of virgin grains into the form of a final product. The conversion of PVC powder into a homogeneous material is described as a gelation effect [3, 4]. The gelation process may be described as a gradual disintegration of primary, original structure of PVC and creation by cooling of a new secondary physical crystal lattice [4—6]. Both, level and homogeneity of PVC gelation, by melt processing, play a key role in giving the final properties to the products.

The processing aids are used with the aim to achieve specific processing and functional properties [7—9], and usually a significant influence of the additives on PVC gelation may be observed. The plasticizers present a large group of PVC modifiers, which are in use for a long time. In practice, PVC compounds with a high content of plasticizer (10—50 phr and more) are used more often, and in special cases the content of plasticizer can reach even a value of 70 phr. PVC compounds with a plasticizer content lower than 5 phr are treated as unplasticized products, and rarely used.

The influences of plasticizers on PVC properties and on the processing were described in numerous works [6—10]. Using special processing equipment such as Brabender Plastograph, PVC plastifying effects have been analyzed by the measurement of the torque during mixing [8—12]. Temperature, rotor speed and composition are the major factors affecting the gelation of a rigid PVC compound in the Brabender mixing chamber [13]. For a define sample of the compound the analysis of typical torque curve allows to determine the influence of composition and temperature on the course of the gelation. Usually, the temperature of the processed compound is not taken into account. But it should not be forgotten that the real compound temperature during processing generally differs from that settled as invariable temperature of the chamber walls [13—16].

The main task of this work was to analyse the gelation of the compounds of suspension PVC with smalls amount of plasticizer during processing in a Brabender chamber, with regard to changes of the real temperature of PVC compound.

EXPERIMENTAL

Materials

Suspension poly(vinyl chloride) (PVC-S) grades (Anwil SA Włocławek, Poland) of *K* value 58, 61 and 67 (denoted PVC-S 58, PVC-S 61 and PVC-S 67, respectively) were processed. Tinorganic liquid stabilizer MOK Mark 17M (produced by Akcros) and plasticizer — dioctyl phthalate (DOP) trade name Ergoplast FTD (produced by Z. Ch. i T. S. Boryszew S.A.) were used.

Preparation of samples

The solution in ethanol of plasticizer (content varied between 0.5 and 4 phr) and stabilizer (3 phr) was carefully mixed with PVC powder. Next, the solvent was evaporated. This method allows to reach a high homogeneity of the dry blend. The compounds were dried at the room temperature for 72 h.

Methods

49 grams of the prepared mixture, was processed in the chamber of the Brabender kneader (Plasti-Corder Pl 2200-3), at adjusted temperature between 140 and 195 °C, at the constant rotation speed of the rotors 28 min^{-1}. The torque was examined as a function of the real compound temperature. This temperature was measured using sensor, isolated thermally from the chamber wall, located in the bottom plate, in the center position between both rotors.

After processing of the compound, PVC gelation level was determined by Perkin-Elmer DSC 7 calorimetric measurements, and evaluated according to the formula proposed by Potente and Schultheis, based on the melting enthalpies of the primary and secondary crystals [17].

RESULTS AND DISCUSSION

The torque rheometer curves were recorded for PVC compounds of various *K*-value, processed in the same conditions. As an example the torque curve of PVC-S 67 (without plasticizer) processed at adjusted temp. of 170 °C, recorded directly by the Brabender measuring mixer, is presented in Fig. 1. The characteristic points of such torque curve were described in [4, 15]. In this case we found that after first 6 min of kneading the temperature of the compound (Fig. 1a) reaches the value of 170 °C, and remains constant during continued mixing. After the first increase in torque, related to the loading of the chamber, the torque decreases slowly during continuous processing. The torque curve does not show any characteristic maximum correlated to the gelation of PVC. The compound processed in the conditions described above presents deformed, bonded grains, after final discharge [17]. The same effect was observed during PVC processing by rolling [18].

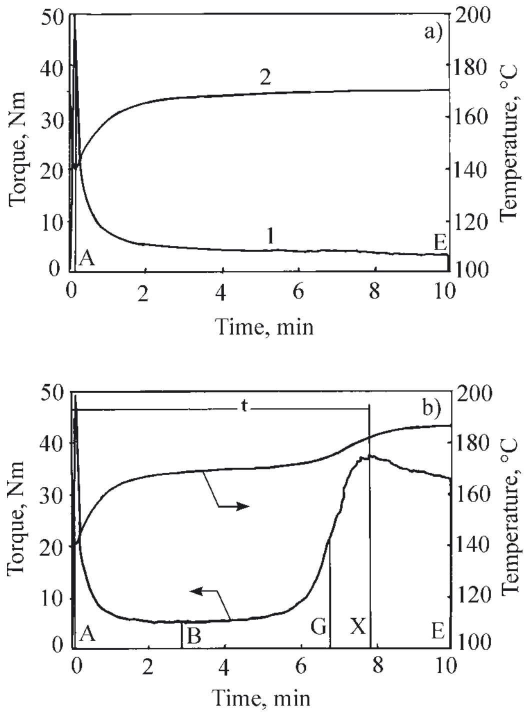

Fig. 1. Torque rheometer process curves of PVC-S 67 compound processed at adjusted temperature 170 °C: a) without plasticizer; b) with 2.5 phr of DOP

The torque curve of the compound containing 2.5 phr of DOP is presented in Fig 1b. The temperature of the

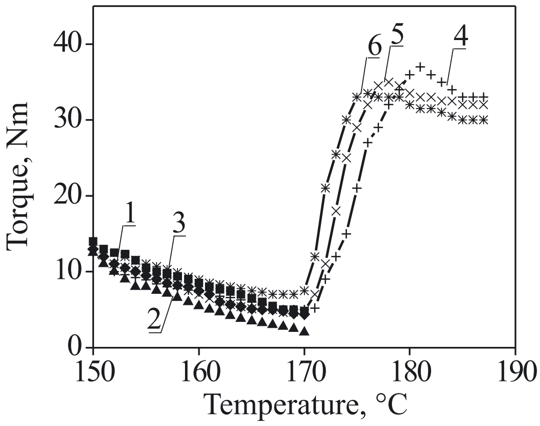

Fig. 2. Torque of PVC-S 67 with different content of DOP, processed at adjusted chamber temperature 170 °C, as a function of the real temperature; contents of DOP: 1 — without DOP, 2 — 1 phr, 3 — 2 phr, 4 — 2.5 phr, 5 — 3 phr, 6 — 4 phr

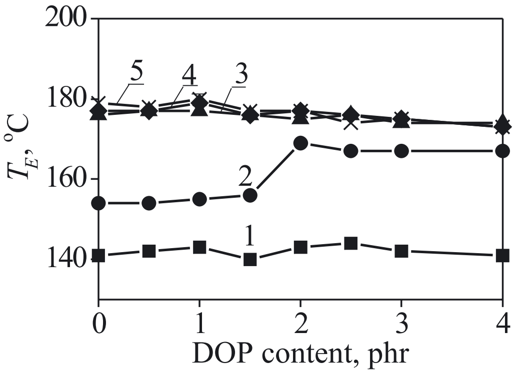

Fig. 3. Real temperature of gelation in point E (T_E) for PVC-S 58 compounds as a function of DOP content and adjusted chamber temperature: 1 — 140 °C; 2 — 155 °C; 3 — 170 °C; 4 — 188 °C; 5 — 195 °C

kneaded compound increases to adjusted 170 °C during first 5 min, and in the course of the next 2 min raises still about 13 °C. In this time the torque grows significantly, and reaches the maximum corresponding to the point of PVC gelation (point X). The further processing leads to the reduction of the torque to the state of its equilibrium (point E).

The results of analysis of torque of PVC compounds with different content of DOP, as a function of the real compound temperature using method described in [13] are presented in Fig 2. In PVC compounds with DOP content lower than 2.5 phr the gelation was not observed. The torque curves of the compounds processed with higher DOP content, demonstrate the characteristic maximum of torque (point X) occurred always in the gradually decreasing temperature (T_X). The similar consequence of DOP addition may be observed for the Brabender processing of PVC-S 58 and PVC-S 61. The effect of addition of DOP on the real compound temperature at the point E (T_E at the end of test, which is considered as equilibrium state), depending on the adjusted temperature of the kneader, for PVC-S 58 is presented in Fig. 3. If the adjusted temperature was 140 °C, independently on the DOP content, no gelation effect was observed (curve 1). In this case the real compound temperature was almost constant. For the highest adjusted temperature, over 170 °C, all PVC compounds without and with DOP showed a gelation effect; on the contrary, a decrease in the real temperature (curves 3 to 5) for rising DOP content, was noted. Finally, it was found if the kneading temperature was adjusted as 155 °C the gelation effect depended significantly on the plasticizer content (curve 2).

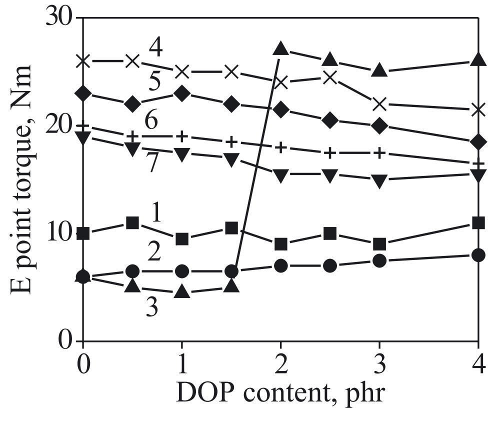

Fig. 4. Torque at equilibrium state (point E) for PVC-S 61 compounds as a function of DOP content and adjusted chamber temperature: 1 — 140 °C; 2 — 155 °C; 3 — 170 °C; 4 — 175 °C; 5 — 180 °C; 6 — 188 °C; 7 — 195 °C

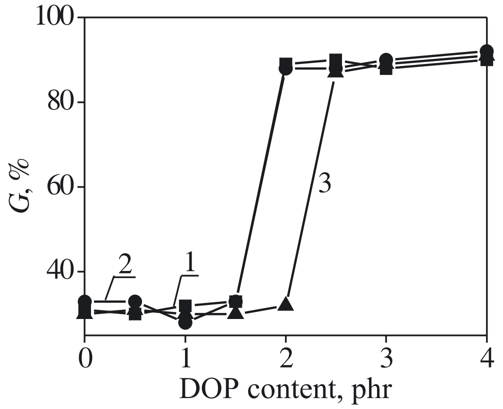

Fig. 5. Gelation degree (G) of PVC after processing at adjusted temperature 175 °C as a function of DOP content and K value: 1 — PVC-S 58; 2 — PVC-S 61; 3 — PVC-S 67

The smallest amount of the plasticizer which creates the PVC gelation, for given *K* value, may be defined as plasticizer minimum content (DOP_{min}). Similar dependence of torque for compounds in the equilibrium state (point E) on adjusted temperature of chamber and content of DOP was observed (Fig. 4). Important consequence of the addition of DOP_{min} amount of plasticizer at temp. 175 °C was a rapid growth of gelation degree (*G*) of PVC what is shown in Fig. 5.

CONCLUSION

A significant influence of DOP addition on the lowering of the temperature, corresponding to gelation point, as well as a modification of torque for a defined processing temperature was found. The lowest temperature limiting the gelation of PVC rigid compounds can be reached by small addition of plasticizer. The addition of DOP_{min} (about 2.5 phr) to a rigid PVC compound, allows lowering the gelation temperature of about 5 °C. Basing on the investigations of unplasticized PVC-S 61 compound it follows that the trace of torque depends on the speed of the rotors but the effect of gelation temperature decrease probably depends only on *K*-value and plasticizer content [13, 15]. Therefore, such investigations may present an industrial advantage in PVC processing.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

- Otrzymywanie i niektóre właściwości multiblokowych kopoli (amido-*b*-amidów)
- Poliamidy aromatyczne zawierające segmenty chalkonylowe podstawione *m*-fenylenodiaminą (*j. ang.*)
- Polieterole z pierścieniem purynowym
- Nowa metoda syntezy poli(kwasu asparaginowego) w warunkach promieniowania mikrofalowego
- Rozpuszczalne w wodzie karbamoiloetylowane pochodne skrobi ziemniaczanej. Cz. I. Synteza i struktura
- Synteza nowych, rozpuszczalnikowych, akrylowych klejów samoprzylepnych charakteryzujących się małym skurczem (*j. ang.*)
- Reakcja utwardzania żywicy epoksydowej na podstawie mezogenicznej pochodnej naftalenu (*j. ang.*)
- Procesy relaksacyjne i struktura fazowa kopolimerów estrowo-eteroamidowych
- Wpływ organicznych rozcieńczalników i rozpuszczalnika na właściwości reologiczne plastizoli PVC
- Wpływ bezhalogenowej modyfikacji żywic epoksydowych na ich poziom uniepalnienia
- Badania odporności błon z wulkanizatów kauczuku butylowego na przenikanie mieszanin rozpuszczalników organicznych
- Związki powierzchniowo czynne z grupy polioksyetylenowanych estrów kwasów tłuszczowych. Cz. II. Podstawowe wielkości lepkościowe a równowaga hydrofilowo-lipofilowa produktów oksyetylenowania estrów metylowych kwasów tłuszczowych oleju rzepakowego
- Wpływ rozwiązań konstrukcyjnych ślimaków układów uplastyczniających oraz warunków procesu wytłaczania na właściwości kompozytu polipropylenowego