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Assessment of the influence of mineral fillers on polyethylene crosslinking process in the presence of peroxide by rheometric method

RAPID COMMUNICATION

Summary — The investigation results of the influence of mineral fillers on low-density polyethylene (PE-LD) crosslinking process taking place in the presence of dicumyl peroxide (DCP) have been presented. The fillers used in the study were particulate materials (talc, chalk, magnesium hydroxide and alumina trihydrate) and layered organoclays (commercial as well as experimental products). The content of DCP was 2 wt. % and of a filler — 0 or 5 wt. %. The whole experiment (polymer melting, compounding and crosslinking) was carried out as a single run in the chamber of the measuring mixer — Haake PolyLab QC. In order to assess the influence of the fillers on crosslinking process quickly, we proposed the method basing on subtraction of torque values obtained during the process for two-component system (PE-LD/DCP) from analogical values obtained for three-component system (PE-LD/DCP/filler). We consider this method being a very usefull tool, well supplementing the results obtained with use of other analytical methods.

Key words: low density polyethylene, crosslinking, dicumyl peroxide, rheometric measurements, modified layered organoclays.

ZASTOSOWANIE METODY REOMETRYCZNEJ DO OKREŚLENIA WPŁYWU NAPEŁNIACZY MINERALNYCH NA PRZEBIEG PROCESU SIECIOWANIA POLIETYLENU WOBEC NADTLENKU

Streszczenie — Przedstawiono wyniki badań przebiegu procesu sieciowania polietylenu małej gęstości (PE-LD) wobec nadtlenku dikumylu (DCP), zachodzącego w komorze plastografometru PolyLab QC firmy Haake. Stwierdzono, że zastosowana metoda umożliwia uzyskanie podczas procesu sieciowania danego materiału powtarzalnych zależności momentu obrotowego, koniecznego do utrzymania na stałym poziomie szybkości obrotowej rotorów plastografometru. Kształt tej zależności jest cennym źródłem informacji o przebiegu procesu sieciowania (rys. 1). Analogiczne pomiary przeprowadzono także w układach z napełniaczem. Zawartość DCP stanowiła 2 % mas., a napełniacza mineralnego 0 lub 5 % mas. próbki. W roli napełniacza stosowano kredę, talk, wodorotlenek magnezu, wodorotlenek glinu, a także modyfikowane glinokrzemiany warstwowe (produkty handlowe Dellite firmy Laviosa Chimica Mineraria S.p. A.) oraz krajowe produkty eksperymentalne NanoBent (otrzymane z Zakładów Górniczo-Metalowych "Zębiec" S.A.). Stwierdzono, że dodatek napełniacza mineralnego w bardzo istotny sposób wpływa na kształt krzywej zmiany momentu obrotowego w czasie procesu sieciowania. Powoduje on znaczny wzrost wartości momentu obrotowego, przy czym o ile w przypadku kredy, talku oraz obu wodorotlenków maksymalna wartość momentu obrotowego nie zmieniała się po zakończeniu procesu sieciowania (rys. 2), o tyle zastosowanie wszystkich badanych modyfikowanych glinokrzemianów warstwowych powodowało spadek wartości momentu obrotowego po zakończeniu tego procesu (rys. 3).

Słowa kluczowe: polietylen małej gęstości, sieciowanie, nadtlenek dikumylu, pomiary reometryczne, modyfikowane glinokrzemiany warstwowe.

Crosslinked materials based on polyolefins, especially polyethylene and ethylene copolymers, are of great importance in industry. Crosslinked polyolefins are used mainly for the production of insulation of power electrical cables, heat-shrinkable materials or hot water pipes [1]. Crosslinking process is a very radical method of thermoplastic polymers' modification, because it changes main characteristics of the polymer, rendering it non melting and insoluble. There are three methods of crosslinking of polyolefin materials used by the industry, two of them being chemical and one with the use of radiation [2]. Nevertheless the most popular is

the method involving organic peroxides as the source of free radicals necessary to initiate crosslinking process.

One of the problems associated with the crosslinking technology is the question of proper assessment of crosslinking degree. The most widely used in the industry as well as in the science measure for quantitative description of crosslinking degree is so called gel index. But gel index measurements have several limitations. First of all, time needed for the measurement is very long, it takes *ca.* 5 hours at least. In addition, physical crosslinking effects are neglected [3]. Another analytical method often used for investigation of crosslinking or gelation processes is based on rheometric principles [5, 6]. It let not only one-point measure of crosslinking degree value, as is the case of gel index, but also obtain the full characteristics of viscosity changes taking place during the whole crosslinking process. Various rheometers are used for this purpose. There are Monsanto-type rheometers available, but using them we need another equipment necessary for preparation of the mixture of polymer with curative and other additives in appropriate shape (disc usually). As an alternative the measuring mixers, called also internal mixers or plastographs, can be used. They allow to measure the changes during crosslinking and raw materials can be feed as received, without any preliminary preparation.

In the paper we intend to present our results concerning an assessment of the influence of different mineral fillers, including particulate materials and layered organically modified clays, on the process of low-density polyethylene crosslinking in the presence of organic peroxide. The work was done with the use of one apparatus only — measuring mixer. The main goal of the work was to find reliable and relatively rapid method of evaluation of the influence of fillers, especially nanoclays, on the crosslinking process in order to prepare recipes of new, innovative kinds of crosslinked polymer materials of nanocomposites type [6—8].

EXPERIMENTAL

Materials

The materials used in this study were as follows:
— low-density polyethylene (PE-LD, trade name Malen E type FGNX 23D022, Basell Orlen Polyolefins Sp. z o.o.) characterized by density 0.925 g/cm^3 and melt flow rate MFR = 2.0 g/10 min;
  — dicumyl peroxide (DCP, reagent grade);
  — chalk and talc (technical grade);
  — aluminum trihydrate (ATH, trade name Martinal OL 107C, Albemarle);
  — magnesium hydroxide (MDH, trade name Magnifin H10A, Albemarle);
  — two types of organically modified montmorillonite with trade names Dellite 67G and Dellite 72T (Laviosa Chimica Mineraria S.p.A., Italy);

— experimental series of organoclays "NanoBent" (ZS-1, ZR-1 and ZW-1, Z.G.-M. "Zębiec" S.A., Poland).

All materials were used as received, without any additional treatment. The fillers used were in the form of macroscopic powders; no particle size distribution measurements were made.

Processing

The proportions of reagents were constant at all experiments: DCP — 2 wt. %, mineral filler — 0 or 5 wt. % and PE-LD — 98 wt. % (samples without a mineral filler) or 93 wt. %.

The experiments were carried out using Haake PolyLab QC internal mixer equipped with Rheomix 600 chamber (Roller Rotors). Samples in amounts of 63 g were used. All ingredients were introduced into the chamber at once at the beginning of each experiment. Controlling of the experiment and data sampling (torque and melt temperature) were done by computer software (PolySoft OS). Temperature probe was protruding from the bottom part of the mixer into polymer melt. The data were acquired every second. The programmed parameters of the process were as follows: 130 °C/30 rpm/5 min (step I) then switched to 3 rpm/heating up to 180 °C (β = 10 °C/min)/15 min (step II). So, the shear stress during the crosslinking process was kept relatively low.

RESULTS AND DISCUSSION

Figure 1 presents typical plastogram obtained for the process of PE-LD crosslinking in the presence of DCP. The moment when raw materials are placed into the mixer chamber heated previously to 130 °C, with rotors turning at 30 rpm, and the mixer is tightly closed is defined as start or "zero" point. Step I takes 5 minutes; as a result of polymer melting the torque value rapidly decreases. After *ca.* 2 minutes the mixture is homogeneous on the macroscopic level — the value of torque is practically constant in time, which also confirmed that prema-
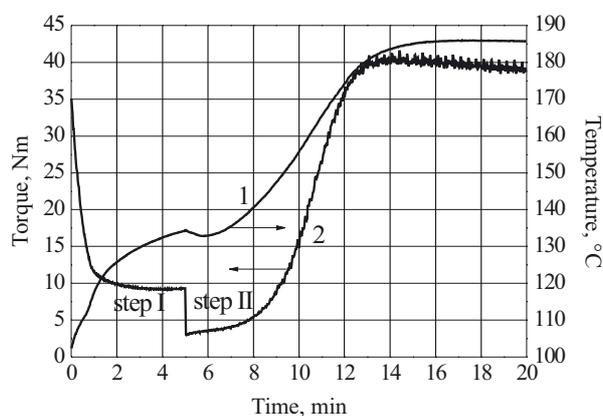

Fig. 1. Melt temperature (curve 1) and torque (curve 2) changes during two-step process of PE-LD crosslinking

ture crosslinking (scorching) does not occur. The temperature of the content of mixers chamber increases rapidly up to *ca.* 135 °C, that is *ca.* 5 degrees above the programmed temperature. After that step II starts. The machine slows down rapidly (practically within 2 s) the rotors to 3 rpm and heating of the mixer chamber begins, with the increment of 10 degrees per minute. As a result of lower shear rate, value of the torque decreases, too. As time of the step II goes on, the temperature of the melt drops slightly at the beginning (weaker mechanical source of heat) and soon begins to rise. It is worth noting that there are three sources of heat: mechanical (friction), convectional (generated with programmed speed by heater) and chemical (after reaction start). As we can see in Fig. 1, the value of the torque during the step II increases very slowly at first 2—3 minutes and than significantly accelerates. The maximum value of the torque is reached after additional 5 minute and then begins to decrease very gently. After reaching a maximum value the torque curve shows subtle "structure" but that problem is beyond the scope of the paper. One important remark is, that judging by torque value only, the crosslinking process starts at relatively low temperature of *ca.* 135— 140 °C. This statement is in good agreement with the results described in [9].

Analogical measurements were done for three-component systems: PE-LD/DCP/mineral filler. In general the characteristics were similar but there were important quantitative differences. As a rule, torque values for three-component systems were significantly higher than analogical values measured for two-component PE-LD/DCP system. So, the first conclusion is that mineral fillers affect crosslinking process and the structure of crosslinked polymer network. There is a question what is the right parameter which can be used as a measure of the influence of additive (mineral filler in this case) on crosslinking process. After analyzing results of the experiments described above we are of opinion that worthy information could be obtained using the equation:

$$\Delta M(t) = (M_{3,t} - M_{3,0}) - (M_{2,t} - M_{2,0}) \qquad (1)$$

where: $\Delta M(t)$ — *difference between corrected torque value measured for three-component system* ($M_{3,t}$) *and corrected torque value measured for two-component system* ($M_{2,t}$), *at time t denoting time passed since the beginning of step II,* $M_{3,0}$ *and* $M_{2,0}$ — *torque values measured at the very beginning of the crosslinking process (we have used the averaged value for the first 5 seconds of the step II here) of three-component* ($M_{3,0}$) *and two-component* ($M_{2,0}$) *systems, respectively.*

We can see the shapes of $\Delta M(t)$ function for samples with mineral fillers like talk, chalk, ATH and MDH in Figure 2 and for samples containing five types of organoclays in Fig. 3. Assuming that the presence of any mineral filler does not cause any changes in the crosslinking system, the function $\Delta M(t)$ should be a straight, horizontal line with value dependent on thickening or thinning effect of the filler only. We can observe those
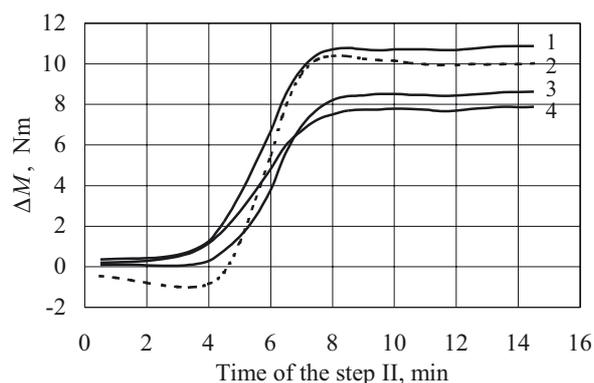

Fig. 2. Changes of torque values (ΔM) during peroxide crosslinking of PE-LD in binary PE-LD/DCP and ternary PE-LD/DCP/mineral filler systems for different types of mineral fillers: 1 — MDH, 2 — talc, 3 — ATH, 4 — chalk

effects at first 2—3 minutes of the step II indeed (Fig. 2 and 3), but when the process of peroxide decomposition accelerates and crosslinking of macromolecules reaction starts, the values of $\Delta M(t)$ function increase rapidly. The main difference among the results obtained for samples containing particulate fillers, *i.e.* talk, chalk, ATH or MDH (Fig. 2) and samples with layered organoclays (Fig. 3) is that in the former case values of $\Delta M(t)$ function did not change after reaching its maximum (with slight exception for talc maybe) whilst in the latter case the values of $\Delta M(t)$ function reach its maximum and after that decrease more or less rapidly. This statement is in good correlation with the results described in [10], where was said that DCP might initiate grafting between the polymer and the clay, supported by information of limited thermal stability of organoclays [8]. The behavior of $\Delta M(t)$ function for the sample containing Dellite 67G (Fig. 3, curve 5) is of particular interest since after reaching maximum, the function drops to zero and then rises again.
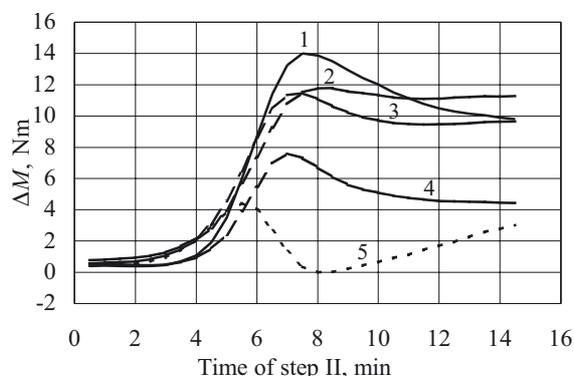

Fig. 3. Change of torque values (ΔM) during peroxide crosslinking of PE-LD in binary PE-LD/DCP and ternary PE-LD/DCP/organoclay systems for different types mineral fillers: 1 — ZS-1, 2 — ZW-1, 3 — ZR-1, 4 — Dellite 72T, 5 — Dellite 67G

CONCLUSIONS

The results of investigations of peroxide initiated crosslinking process of low-density polyethylene with the use of internal mixer let conclude as follows:

— Apparatus of the type used in the study, in conjunction with appropriate software, allows to conduct very precise measurements of changes taking place in polymer matrix during chemical processes, crosslinking in this case.

— All mineral fillers under consideration affect peroxide initiated crosslinking process of low-density polyethylene, as it is evident from torque measurements.

— Layered organoclays exhibit different behavior during crosslinking process conducted in low-density polyethylene matrix than particulate fillers; one explanation of the unusual effect of layered organoclays presence, especially at the end of crosslinking process *i.e.* when the temperature of crosslinked material is relatively high (above 180 °C), may be assigned to insufficient thermal stability of investigated organoclays. On the other hand, the effect of exfoliation of organoclays in polymer matrix could not be excluded. More precise statements on the character of changes taking place during crosslinking processes described in the paper can be possible only after confrontation of obtained results with the results reached with the use of different analytical methods.

— The method described here seems to be very effective and rapid tool for assessment of usability of various additives as components of crosslinkable materials.

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