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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Online publication date: 28 November 2010

To cite this Article Kotzev, G. , Touleshkov, N. , Christova, D. and Nedkov, E.(1998) 'Morphology of Polyethylene Foamed Crosslinked Specimens made by Hot Mold Injection Molding', *Journal of Macromolecular Science, Part A*, 35: 7, 1127 – 1135

To link to this Article: DOI: 10.1080/10601329808002106

URL: <http://dx.doi.org/10.1080/10601329808002106>

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MORPHOLOGY OF POLYETHYLENE FOAMED CROSSLINKED SPECIMENS MADE BY HOT MOLD INJECTION MOLDING

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ABSTRACT

Foamed and crosslinked specimens of polyethylene made by hot mold injection molding were investigated. A combination of PELD, dicumilperoxide and azodicarbonamide was used. The three components were mixed and granulated in an extruder-granulator at temperature 100–120°C. The degree of crosslinking was calculated by equilibrium strain ϵ_r determined at temperature 140°C and pressure stress $\sigma_p=0.045$ MPa. The same parameter was evaluated by thermomechanical curves. The degree of crystallinity was determined by DSC-kinetics of a nonisothermal melting and crystallization. The morphology was investigated by a polarized microscope MIN 8.

It is established that a part of polymer crystallizes as spherulites. The spherulites can be observed with crossed polarizers. The samples on the whole are not oriented. There exists only a local orientation around the edge of the bubbles which is proved by the observed bright regions. The number of the spherulites decreases with the increase of crosslinking degree. This also conforms with the degree of crystallinity which decreases with the increase of the crosslinking degree.

INTRODUCTION

Hot mold injection molding is a technique for producing foamed thermo-plastic low density specimens. Usually this method is combined with chemical modifications of polymers by adding crosslinking agents in the initial composition [1]. A concrete variant of the above described method was used for producing foamed crosslinked polyethylene specimens [2]. A homogeneous temperature field was created in the mold cavity. At this condition the viscosity of the foaming polymer melt remains for a long time suitable for the formation of highly foamed structure. The paper presents the initial data for the dependencies of the specimens overall density and tension strength on: mold temperature, crosslinking agent concentration, and blowing agent concentration.

As can be expected, the crosslinking results in a change of its molecular characteristics and hence, the properties of the product. Therefore, the aim of the investigation is to find out the effects of the crosslinking processes on the morphology of polyethylene foamed specimens made by hot mold injection molding.

EXPERIMENTAL

Materials

The object of investigation were centre-gate disk specimens (101 mm diameter and 12.5 mm height). The polymer used was LDPE (Ropoten FB-7-104), supplied by the Neftochim Company. It has high flowability (MFI = 6.3 g/10 min. at 190°C and load 21.2 N) and we expected its decrease as a result of cross-linking. Dicumylperoxide (Peroximon DC 40), supplied by ATO company, was used as a crosslinking agent. It is a 40 wt% concentrate in CaCO₃. Its decomposition temperature range is from 138 to 140°C. The blowing agent used was azodicarbonamide (Genitron EPA), supplied by the Fisons company, having a decomposition temperature range of 180-220°C.

Compounding and Injection Molding

The three components were blended and granulated in an extruder-granulator at cylinder temperatures in the zones - 100, 110, 120, 125°C. The weight concentrations of the blowing and crosslinking agents in the composites studied are as follows: azodicarbonamide - 5, 10, 15%; dicumylperoxide - 0.08, 0.24, 0.32, 0.40, 0.60%.

Test specimens were produced by hot mold injection molding on an in-line machine KuASY 800/250 at the following process conditions:

- temperature of the plasticizing cylinder in zones - 100, 125, 135, 130°C;
- mold temperature - 200°C;
- rate of screw rotation - 35.5 rev/min;
- rate of injection shot - 200 ccm/s.

Replaceable molds, placed consecutively on the machine, were used. Their forming cavities represents a disk which is connected to eight prismatic channels.

The hot mold injection molding process was effected by following operations:

- putting the mold between the moveable and statical platens of the machine and heating it for 15 minutes;
- injection of the polymer melt containing dicumylperoxide and azodicarbonamide into the mold cavity;
- decomposition of the crosslinking agent, crosslinking of LDPE, decomposition of the blowing agent and foaming of the polymer melt. The stage continued 10 minutes. During this time, if the foaming polymer melt completely fills the disk cavity it will enter into the prismatic channels;
- taking the mold out of the heated platens (the next mold was placed), cooling it in water to 80°C and taking the specimens out of the mold.

Characterization of the Crosslinked Foamed LDPE

As a result of the crosslinking, chemical changes were studied by:

- equilibrium strain ϵ_p . The test was performed on a modified apparatus for determination of Vicat heat resistance at temperature 140°C and pressure stress of 0.045 MPa (load of 9 N on an area of 16 mm diameter). Tablets of diameter 19.5 mm and height 10 mm were used. They were produced by pressing finely cut specimens at temperature 180°C. A measurement of equilibrium strain was done 15 minutes after loading.

In compliance with the classic rubbery theory [3], the concentration of segments of the network can be defined by the value ϵ_p according the formula:

$$N = \sigma_p (100 - \epsilon_p)^2 / \epsilon_p (200 - \epsilon_p) kT \quad (1)$$

where N is the numbers of segments in cubic meter, σ_p is the pressure stress in Pa, k is the Boltzman constant, T is the absolute temperature;

- thermomechanical curves obtained in the range of 50-150°C at a heating rate of 1°C/min. The test specimens, pressure stress, and apparatus were the same as those for determination of equilibrium strain. The measurement was done 15 seconds after loading.

The degree of crystallinity α was calculated by the formula:

$$\alpha = \frac{1}{\Delta H_m^0} \int_{T_1}^{T_2} \left(\frac{dH}{dT} \right)_{T_n} dT. \quad (2)$$

where T_1 and T_2 are the initial and final temperatures of phase transition, T is the absolute temperature, H is the enthalpy, ΔH_m^0 is the melting enthalpy of the ideal PE crystal (4110 J/mol) and the values $\left(\frac{dH}{dT} \right)_{T_n}$ were taken from DSC-graphics obtained by differential scanning calorimeter Perkin-Elmer DSC-7 at heating and cooling rates of 10°C/min..

The microscopic observations were made with the MIN-8 polarizing light microscope. Microtome cuts with the thickness about 40 μm were used.

RESULTS AND DISCUSSION

Crosslinking Degree

The concentration of the polymer network segments calculated by Equation 1 is a measure for the crosslinking degree. As seen in Table 1, the number of the segments in cubic meter increases with the increase of the concentrations of dicumylperoxide (*DCP*) and azodicarbonamide (*ACA*). As expected, the crosslinking degree results in deformation processes. At temperatures higher than the melting temperature, the presence of intermolecular links considerably decreases the plastic strain component as a result of the rubbery strain becoming dominating. The thermomechanical curves (Figure 1) show that above 120°C, with the increase of the crosslinking degree, the irreversible plastic deformation, characteristic both for the initial and slightly crosslinked polyethylene (curve 1), gradually decreases and a "rubbery plateau" appears in the curves 2, 3, 4 and 5. Hence, it follows that the crosslinking processes occurred in the polymer can be estimated by height of this plateau.

TABLE 1. Concentration of the Segments of LDPE Network

| ACA % | DCP % | Concentration Numbers in m ³ |
|----------|----------|--|
| 5 | 0.08 | 1.6x10 ²² |
| 5 | 0.24 | 2.1x10 ²⁴ |
| 5 | 0.32 | 3.9x10 ²⁴ |
| 5 | 0.40 | 4.0x10 ²⁴ |
| 5 | 0.60 | 1.35x10 ²⁵ |
| 10 | 0.32 | 4.4x10 ²⁴ |
| 15 | 0.32 | 8.3x10 ²⁴ |

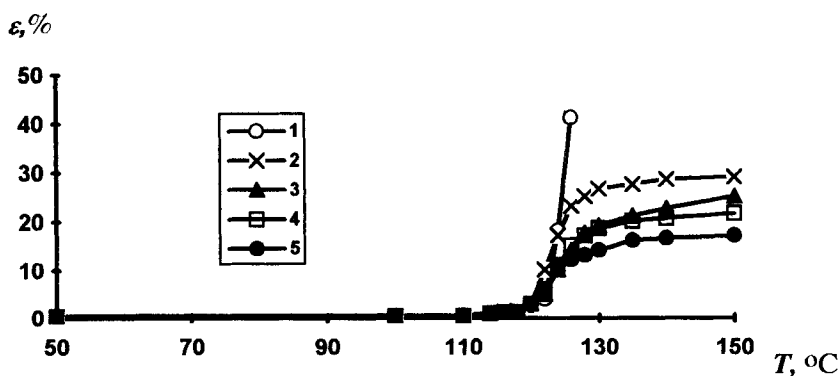


Figure 1. Thermomechanical curves of specimens produced by ACA = 5 % and DCP (1 - 0.08; 2 - 0.24; 3 - 0.32; 4 - 0.40; 5 - 0.60).

Morphology

From the observations of microtome cuts of the specimens, it can be seen that the bubbles become more homogeneous in shape and size with the increase of the quantity of crosslinked agent, and they are distributed almost uniformly. The increasing of the blowing agent content leads to formation of a heterogeneous foamed structure. It occurs as very large pores, and also as very small pores (Figure 2). The size of the bubbles was measured with a micrometric scale eyepiece. The

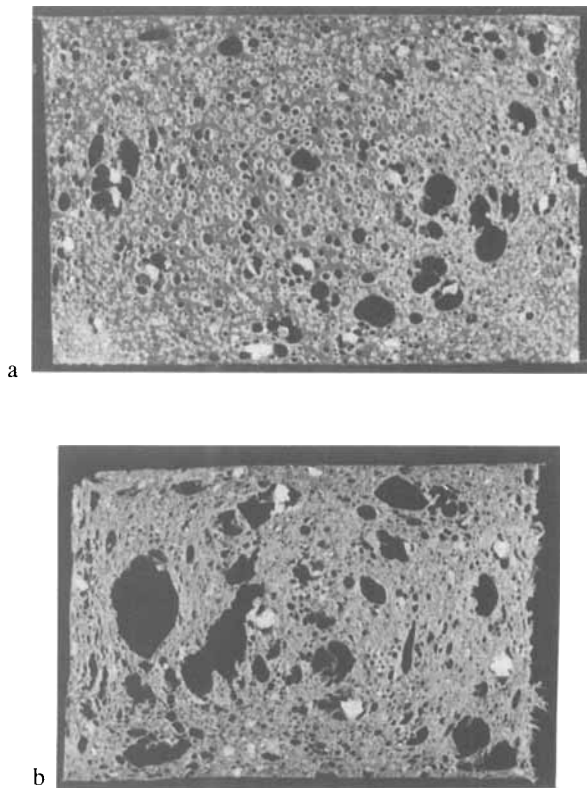


Figure 2. Microtome cuts of specimens produced by **DCP** = 0.24 % and various azodicarbonamide concentrations in percent (a -5; b - 10).

largest bubble size is about 2 mm, and the smallest one is approximately 40 μm . The pores with an average size in the order of 130-180 μm predominated.

Most of the bubbles have a spherical form. The largest bubbles are of irregular form. The walls of the bubbles are mainly smooth. Smaller bubbles with a prolonged (flattened) form were observed around the large pores in some samples. Probably, the expansion of the large pores exert influence on the near disposed smaller pores.

It is seen that a part of polymer crystallizes as spherulites (Figure 3). They are lightened in crossed polarizers. The number of spherulites round the edges of the pores are very small. The surface of the bubbles is not able to create a spherulite nuclei.

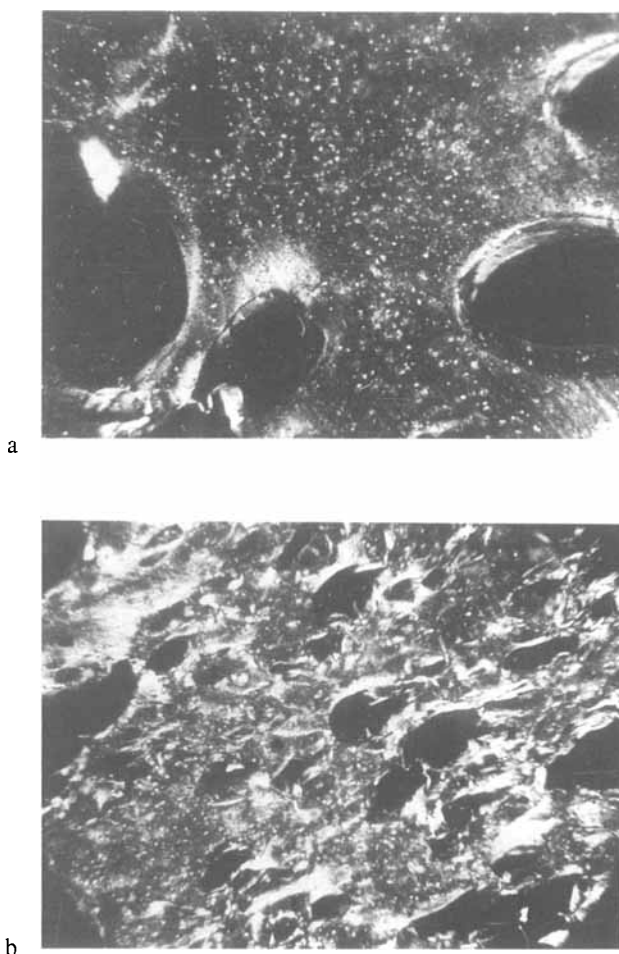


Figure 3. Polarized light micrographs of microtome cuts of foamed and crosslinked PE at ACA = 5% and DCP: a - 0.40%; b - 0.60%.

The size of the spherulites is very small. It is of the order of some micrometers. The reasons may be as follows: the crosslinks create spherulite nuclei. The crosslinking shortens the effective crystallizable length of the molecules. The last decreases the dimension of the crystallizing lamellae and the size of the spherulites. The number of spherulites is greater in the samples with a smaller quantity of a crosslinked agent. There, they are grouped together in the space between the pores. The number of the spherulites decreases with the increase of the crosslinking degree

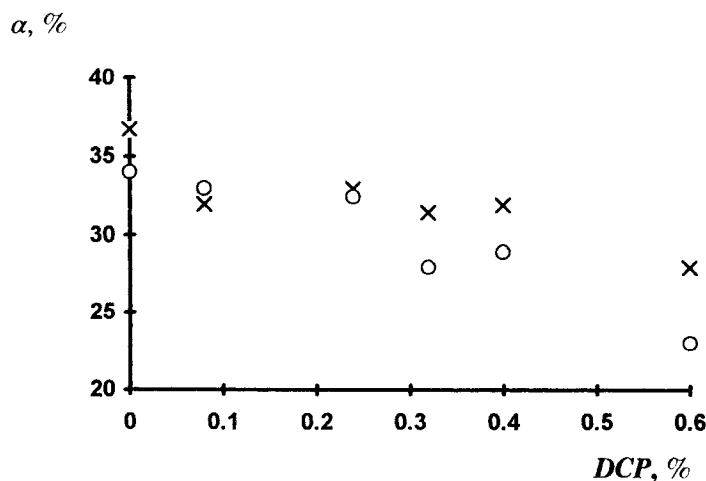


Figure 4. Degree of crystallinity vs. dicumylperoxide content (x-melting; o-crystallization).

(Figure 3). This is in agreement with the degree of crystallinity, which also decreases with the increase of the crosslinking degree (Figure 4).

An attempt was made to try and measure the birefringence coefficient. It turns out that it is impossible. Therefore, the orientation as a whole is very weak, below 0.001. There exists only a local orientation around the edge of the bubbles caused from the expanded pores. The observed brightly-lit regions around the edges of the bubbles are proof of this. Probably, that is a strongly-oriented semicrystalline region.

CONCLUSIONS

The paper studies the structure of foamed crosslinked specimens of low density polyethylene produced by hot mold injection molding. The chemical processes occurring during molding have a radical mechanism, and they affect one another. This results in the formation of a specific structure. It is found that the crosslinking degree of the foamed polyethylene increases with the increase of the concentrations of dicumilperoxide and azodicarbonamide and the flowability of the foamed polyethylene melt decreases correspondingly. The crosslinked foamed PELD form spherulites. The crosslinking of the polymer affects its morphology. The crystalline phase decreases with the increasing of the crosslinked degree. The

samples as a whole are not oriented. There exists only a local orientation around the edge of the bubbles. The increasing of the blowing agent and the decreasing of the crosslinked agent leads to formation of the heterogeneous foamed structure.

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