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NANOSTRUCTURES IN CROSS-LINKED EPOXY POLYMERS AND THEIR INFLUENCE ON MECHANICAL PROPERTIES

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Abstract. The methods of nanostructures adjustment in cross-linked epoxy polymers were considered. The large potential of changing mechanical properties of these materials by nanoclusters relative fraction variation was shown.

1. Introduction

At present it is generally accepted [1] that macromolecular formations and polymer systems by virtue of their structure features are always natural nanostructural systems. In this connection the question of using this feature for polymer materials properties and operating characteristics improvement arises. It is obvious enough that for structure-properties relationships receiving the quantitative nanostructural model of the indicated materials is necessary. It is also obvious that if the dependence of specific property on material structural state is unequivocal, then there will be quite sufficient modes to achieve this state. The cluster model of polymer amorphous state structure [2, 3] is most suitable for this state structure description. It has been shown that this model's basic structural element (cluster) is a nanoparticle (nanocluster). The cluster model was used successfully for crosslinked epoxy polymers structure and properties description [5]. Therefore the purpose of the present paper is nanostructures regulation modes and the influence of the latter on rarely crosslinked epoxy polymer properties study.

2. Experimental

The studied object is an epoxy polymer on the basis of UPS-181 resin, cured by *iso*-methyltetrahydrophtaleic anhydride in the mass ratio of 1:0.56. After intermixing and exposure under vacuum of the components at room temperature and the pressure of 10–20 mm of mercury up to air bubbles disappearance during 15–30 min the mixture is poured into the heated up to ~ 343 K fluoropolymer molds and cured according to the experimentally selected temperature regime.

Testing specimens were obtained by the hydrostatic extrusion method. The indicated method choice is due to the fact that high hydrostatic pressure exertion in deformation process prevents the defects formation and growth, resulting in the material failure [6]. Hydroextrusion was realized for one passage on an apparatus of pistoncylinder system at room temperature. The extrusion strain e_e is equal to 0.14, 0.25, 0.36, 0.43 and 0.52. e_e value was calculated according to the formula [7]:

$$\varepsilon_e = \frac{d_1^2 - d_2^2}{d_1^2} \tag{1}$$

where d_1, d_2 are diameters of intermediate product and extrudate, accordingly (the latter is equal to 12 mm).

The stress-strain characteristics were studied under conditions of uniaxial compression on the Heckert FRZ-100/1 testing machine at the testing temperature of 293 K and strain rate $\sim 10^{-3}$ s^{-1} (the specimens diameter is equal to 10 mm, height – 15 mm). No less than five specimens were tested for each e_e value. The arithmetical mean of the obtained data totality was accepted as the measurements result.

Specimens' density was measured by hydrostatic weighing method to a precision of the fourth sign after comma. Further their values were expressed accounting for measurements of arithmetical mean error.

The obtained by hydrostatic extrusion specimens were annealed at maximum temperature of 353 K during 15 min, following which they were also tested on uniaxial compression.

3. Results and Discussion

The hydrostatic extrusion and subsequent annealing of epoxy polymer (EP) result in very essential changes of its mechanical behaviour and properties, moreover unexpected enough. The qualitative changes of EP mechanical behaviour can be monitored according to the corresponding changes of the stress-strain (s–e) diagrams, shown in Fig. 1. The initial EP shows the expected enough behaviour and its elasticity modulus E and yield stress s_Y are typical for such polymers at testing temperature T, which is about 40 K away from the glass transition temperature T_g [8]. The small (~ 3 MPa) stress decay Δs_Y behind yield stress is observed, which is also typical of amorphous polymers [5]. However, EP extrusion up to $e_e = 0.52$ results in stress decay Δs_Y ("yield tooth") disappearance and the essential E and s_Y lessening. Besides, the diagram σ–ε itself is more like analogous diagram for rubber, than for glassy polymer. This specimen annealing at maximum temperature $T_{an} = 353$ K gives a diametrically opposite effect – yield stress and elasticity modulus increase sharply (the latter increases about 2 times in comparison with the initial EP and more than one order in comparison with the extruded specimen). Besides, a pronounced "yield tooth" appears. It is necessary to note that specimen shrinkage at annealing is small (~ 10 %) and equal to about 20 % of e_e.
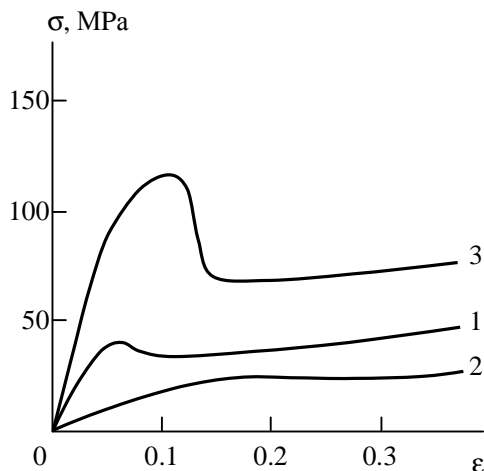
Fig. 1. The stress-strain (s–e) curves for initial (1), extruded up to $e_e = 0.52$ (2) and annealed (3) EP

The general picture of parameters E and s_Y change as a function of e_e is presented in Figs. 2 and 3, accordingly. As one can see, both indicated parameters showed common tendencies at e_e change: up to $e_e \approx 0.36$ inclusive E, and s_Y weak increase at e_e growth is observed, moreover their absolute values for extruded and annealed specimens are close, but at $e_e > 0.36$ the pronounced antibatness of these

parameters for the indicated specimen types is displayed. The cluster model of polymers amorphous state structure and elaborated within its frameworks polymers yielding treatment allows to explain such behaviour of the studied samples [2, 3].

The cluster model supposes that polymers amorphous state structure presents the local order domains (nanoclusters), surrounded by loosely-packed matrix. Nanoclusters consist of several collinear densely-packed statistical segments of different macromolecules and due to this they offer the analogue of crystallite with extended chains. There are two types of nanoclusters: stable, consisting of a relatively large segments number, and unstable, consisting of a smaller number of such segments [9]. At temperature increase or mechanical stress application unstable clusters are disintegrated in the first place, which results in the two well-known effects. The first of them is known as two-stage glass transition process [10] and supposes that at $T_g' = T_g - 50$ K disintegration of unstable clusters restraining loosely-packed matrix in glassy state occurs, which defines devitrification of the latter [2, 3]. The well-known rapid polymers mechanical properties decrease at approaching to T_g is the consequence of this effect [8]. The second effect consists in unstable clusters decay at s_Y under mechanical stress action, loosely-packed matrix mechanical devitrification and as a consequence glassy polymers rubber-like behaviour on cold flow plateau [9]. The stress decay Δs_Y behind yield stress is due to namely unstable nanoclusters decay and therefore Δs_Y value serves as characteristic of these nanoclusters fraction [9]. Proceeding from this brief description, the experimental results adduced in Figs. 1-3 can be interpreted.

The rarely cross-linked polymer on the basis of resin UPS-181 has low glass transition temperature T_g, which can be estimated according to shrinkage measurements data as equal to ~ 333 K. This means that the testing temperature $T = 293$ K and its T_g' are close, which is confirmed by small Δs_Y value for the initial EP. This supposes nanoclusters' (nanostructures') small relative fraction j_{cl} [2, 3] and since these nanoclusters have arbitrary orientation, e_e increase rapidly results in their decay, which defines loosely-packed matrix mechanical devitrification at $e_e > 0.36$. Devitrified loosely-packed matrix gives insignificant contribution in E [11], equal practically to zero, which results in sharp (discrete) elasticity modulus decrease. Besides, at $T > T_g'$ j_{cl} rapid decay is observed, *i.e.* segments number decrease in both stable and unstable nanoclusters [3]. Since just these parameters (E and j_{cl}) are defined s_Y value, then their decreasing defines sharp lessening of yield stress. Now extruded at $e_e > 0.36$ EP presents a rubber with high cross-linking degree which is reflected by its diagram σ–ε (Fig. 1, curve 2).
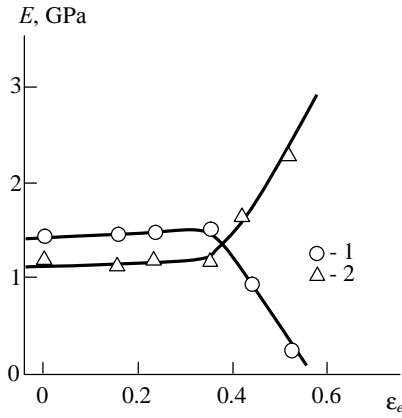
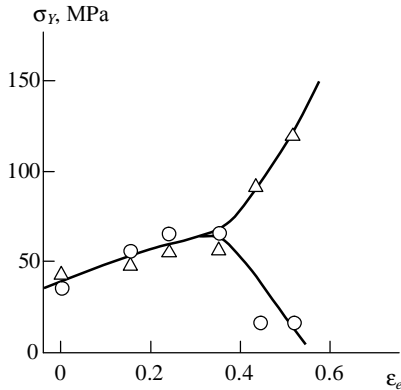**Fig. 2.** The dependences of elasticity modulus E on extrusion strain e_e for extruded (1) and annealed (2) EP

Fig. 3. The dependences of yield stress s_Y on extrusion strain e_e for extruded (1) and annealed (2) EP

Fig. 4. The dependences of nanoclusters relative fraction j_{cl} on extrusion strain e_e for extruded (1) and annealed (2) EP

Fig. 5. The dependence of specimens density r on extrusion strain e_e for extruded (1) and annealed (2) EP

The polymer oriented chains shrinkage occurs at the extruded EP annealing at a temperature higher than T_g. Since this process runs in a narrow temperatures range and during a small time interval a large number of unstable nanoclusters are formed. This effect is intensified by the available molecular orientation, *i.e.* by preliminary favourable segments building, and it is reflected by Δs_Y strong increase (Fig. 1, curve 3). j_{cl} increase results in E growth (Fig. 2) and j_{cl} and E combined enhancement – in s_Y considerable growth (Fig. 3).

The considered structural changes can be described quantitatively within the frameworks of a cluster model. The nanoclusters relative fraction j_{cl} can be calculated according to the methods stated in paper [12]. The $j_{cl}(e_e)$ dependences shown in Fig. 4 have the character expected from the adduced above description and are its quantitative confirmation. The dependence of density r of EP extruded specimens on e_e, adduced in Fig. 5, is symbate to the dependence $j_{cl}(e_e)$, that should be also expected since densely-packed segments fraction decrease should be reflected in r lessening.
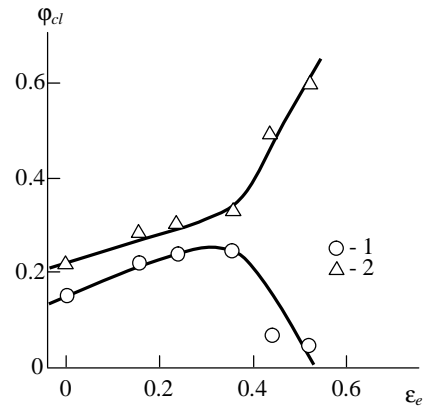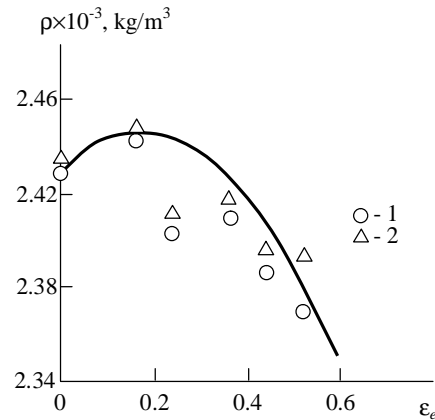
In paper [13] the supposition was made that r change can be due to microcracks network formation in the specimen, that results in r lessening at large e_e (0.43 and 0.52), which are close to the limiting ones. r relative change (Δr) estimation according to the equation is:

$$\Delta r = \frac{r^{max} - r^{min}}{r^{max}} \qquad (2)$$

where r^{max} and r^{min} are the greatest and the lowest density values, accordingly, shows that $\Delta r \approx 0.01$.

This value can be reasonable for free volume increase, which is necessary for loosely-packed matrix devitrification [3] (accounting for closeness of T and $T_g^{'}$), but it is obviously small if to assume as real microcracks formation. As the experiments have shown, EP extrusion at $e_e > 0.52$ is impossible owing to specimens cracking in extrusion process. Therefore the critical dilatation Δd_{cr} value, which is necessary for microcracks cluster formation, can be estimated [14] as follows:

$$\Delta d_{cr} = \frac{2(1+n)(2-3n)}{11-19n} \qquad (3)$$

where n is Poisson's ratio.

Accepting the average value $n \approx 0.35$, we obtain $\Delta d_{cr} \approx 0.60$ that is essentially higher than the estimation Δr made earlier. These calculations assume that r decrease at $e_e = 0.43$ and 0.52 is due to unstable nanoclusters decay and corresponding to EP structure loosening.

The stated above data give a clear example of large possibilities of polymer properties operation through its nanostructure change. From the plots in Fig. 2 it follows that annealing of EP extruded up to $e_e = 0.52$ results in more than 8 times elasticity modulus increase and from data in Fig. 3 6 time increase of yield stress follows. From the practical point of view extrusion and subsequent annealing of rarely cross-linked epoxy polymers allow to obtain materials which are just as good as densely cross-linked EP by stiffness and strength, but exceeding the latter by plasticity degree. Let us note that besides extrusion and annealing other modes of polymers nanostructure operation exist: plasticization, filling, films obtaining from different solvents, and so on.

4. Conclusions

The present paper results demonstrated that neither cross-linking degree nor molecular orientation level define crosslinked polymers final properties. Those properties are defined by a state of supersegmental (nanocluster) structure, which, in turn, can be directly regulated by molecular orientation and thermal treatment application.

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НАНОСТРУКТУРИ У ЗШИТИХ ЕПОКСИДНИХ ПОЛІМЕРАХ ТА ЇХ ВПЛИВ НА МЕХАНІЧНІ ВЛАСТИВОСТІ

Анотація. *Розглянуто методи коректування нанострук-тур у зшитих епоксидних полімерах. Показана можливість зміни механічних властивостей таких матеріалів внаслідок відповідного розділення нанокластерів.*

Ключові слова: *епоксидний полімер, наноструктури, механічні властивості, екструзія у твердому стані, відпал.*