

Shape memory effect in the epoxy polymer–thermoexpanded graphite system

V.A. Beloshenko*, Ya.E. Beygelzimer, A.P. Borzenko, V.N. Varyukhin

Donetsk Physics and Technology Institute, National Academy of Sciences of Ukraine, 72 R. Luxemburg, 83114 Donetsk, Ukraine

Received 26 October 2001; revised 15 February 2002; accepted 19 March 2002

Abstract

The peculiarities of shape recovery for deformed samples of the epoxy polymer–thermoexpanded graphite composition have been investigated. At specific concentrations of the filler, the shape memory effect accompanied by a significant increase in volume is observed. A number of technological schemes for obtaining products with unconventional shape memory effect and a physical model explaining the effect and specifying the boundaries of the region where it could be realized are proposed. © 2002 Published by Elsevier Science Ltd.

Keywords: A. Polymer–matrix composites (PMCs); B. Microstructure; C. Analytical modelling; Thermal shrinkage

1. Introduction

The shape memory effect in polymers (the thermal shrinkage) has been well studied, and widely used in producing insulating, constructional and packaging materials [1]. This is attained under polymer orientation when the stressed state is formed. The internal stresses relaxing under subsequent heating ensure the recovery of the product shape. The overwhelming majority of investigations relating to thermal shrinkage was carried out with homopolymers [2] or structurally heterogeneous polymer systems in which the interphase interaction is intensified by the chemical or physical modification methods [3,4]. The original shape of such objects is recovered with the conservation of volume. Recently [5], we have found that in the case of polymer systems with a weak interphase interaction (mixtures of thermodynamically incompatible polymers), the shape memory effect accompanied by an increase in volume can be observed. It is associated with the relaxation of microstresses at interfaces resulting in material loosening. The proposed thermoshrinkable products are of specific practical interest; however, their application is restricted by a relatively small value of the increase in volume and a complex character of the change in linear dimensions [5]. In spite of the restrictions mentioned, the results of Ref. [5] have made it possible to bring out a new trend in making thermoshrinkable polymer products. It is based on the realization of a

corresponding structurally heterogeneous state of the material and the deformation conditions under which the shape is recovered with the simultaneous increase in volume.

In this article, the material investigated is the epoxy composition filled with thermoexpanded graphite (TEG). The filler was chosen owing to its low bulk density and good compactibility. This allowed us to expect the development of the considered effect of volume increase not only at the expense of composite loosening at the polymer matrix–filler interface, but also due to the recovery of the original volume of TEG particles.

The use of matrix from the thermoreactive polymer was of special interest, since the shape memory effect had been mainly studied on thermoplastics till date. The reason is the low plasticity of thermoreactive and, in particular, epoxy polymers (EPs), which makes the realization of the above effects more difficult. However, as shown in Refs. [6–8], the problem could be solved at the expense of the formation of a definite structure under specific deformation conditions for the objects.

2. Experimental

The polymer matrix was a modified epoxy composition based on diglycidyl phthalic and hydrophthalic acid ester and blockoligomer from the aliphatic epoxy resin and acid oligoether cured by iso-methyltetrahydrophthalic anhydride [9]. The glass-transition temperature T_g of the above composition approximately equals 70 °C. TEG [10] was the result

* Corresponding author. Tel.: +380-622-55-02-81; fax: +380-62-3379018.

E-mail address: bel@hpress.dipt.donetsk.ua (V.A. Beloshenko).

of the interaction between cast graphite and sulphuric acid, in the presence of chromic acid, followed by the washing out till pH of the aqueous extract is equal to 6.5–7 and drying at 105 °C to a constant weight. The dried oxidized graphite was subjected to thermal shock at 1000 °C for 3 min that was enough for removing water from the inter-planar space. The bulk density of TEG was 0.02 g/cm³, and the carbon content was equal to 95.2%.

The investigation samples were prepared by mixing the epoxy composition and TEG powder components in a required proportion. Then the polymer billet was cured in a cylindrical or pipe-like mould at 120 °C for 4 h. Next, the cured billet state was deformed in the high elastic state and cooled, under load, to the temperature lower than T_g , so as to ‘freeze’ the attained non-equilibrium state. The deformation was realized by the uniaxial compression in a cylindrical mould or the radial reduction with the hydrostatic pressure, as well as by mandrelling in a cylindrical mould (pipe-like billet). The resulting rods were 8–20 mm in diameter and 12–30 mm long, as well as bushes with the external diameter of 10 mm, internal one of 3 mm, 15 mm long. The hydrostatic pressure of up to 250 MPa was built up in a high-pressure chamber by using a pipe-type setup [11]. The polymer billet was isolated from the liquid by an elastic casing and placed in a special device to prevent from pressure action on its end faces. The billet in a high-elastic state was deformed and subsequently cooled under load to a temperature lower than T_g . So, the products were in the form of rods or bushes of about 20 mm diameter. The degree of deformation ε and the degree of recovery S are calculated by the formulas: $\varepsilon = (l_i - l)/(l_i)100\%$, $S = (l - l_i)/(l)100\%$ (for the rods); $\varepsilon = (d - d_i)/(d)100\%$, $S = (d_i - d)/(d_i)100\%$ (for the bushes). Here, l_i and d_i are the initial length or internal diameter, respectively; l and d are the current length or internal diameter.

The shape was recovered by heating samples to $T > T_g$ and holding them at that temperature for 15 min.

The strain–strength characteristics were studied by compressing cylindrical samples, which were 15-mm long and had a diameter of 10 mm, under the room-temperature conditions. Microhardness H was measured by indenter load 0.5 N. The H value was the average of 15–20 measurements.

The microstructure was investigated and microphotography was done using a light reflection microscope. The structure was examined at the rod end faces in the non-etched state and after etching by concentrated sulphuric acid. To analyse the microstructure quantitatively its image was fixed using an electronic digital camera of a 480–640 pixel resolution. The results were processed by an ‘Image-Tool’ application package as well as ‘Sigma’ and ‘Excel’ programs.

3. Results and discussion

Table 1 shows the results of investigation of the

cylindrical rod behaviour under deformation in a mould followed by heating, in the free state, to $T > T_g$. As was expected, the EP samples failed at negligible values of ε .

The TEG possessing high compactibility ensures the realization of high value of deformation as it changes from a powder to a solid shape. Nevertheless, the shape memory effect was observed in this case. At the same time, there is the synergism effect with the EP–TEG system. At specific TEG concentrations, a composite is produced which is not only well deformed, but also capable of complete recovery of the shape. With such a scheme, the deformation is increased by length with the diameter remaining unchanged. The attention is directed to value of the effect: the change in length (volume) may reach 45%. This is not the limiting value for the investigated TEG concentrations. The limiting value of ε attained by us is defined by technical potentialities of the experimental setup.

The table shows how the character of shape recovery depends on the proportion of the ingredients in the composite under study. At low TEG concentrations (3 wt%), there is incomplete relaxation in volume in all the investigated ranges of ε . Only a partial recovery of the shape occurs also with 15 wt% TEG. In the range of 6–15% concentration, the $S(\varepsilon)$ dependence deviates from the linear one at ε values close to the limiting value. As a result, it is easy to find that

Table 1
Characteristics of the EP–TEG composition

TEG (wt%)	ε (%)	S (%)	Comment
0	10	0	
3	10	6.9	
	20	13.5	
	30	18.05	
	40	0	Failure under straining
6	10	10	
	20	20	
	30	30	
	40	40	
	45	45	
8	10	10	
	20	20	
	30	30	
	40	40	
	45	43.8	
12	10	10	
	20	20	
	30	30	
	40	36	
	45	0	Failure under straining
15	10	2.7	
	20	0	
	30	0	Failure under straining
18	10	0	
	20	0	
	30	0	Failure under straining
100	10	0	
	40	0	

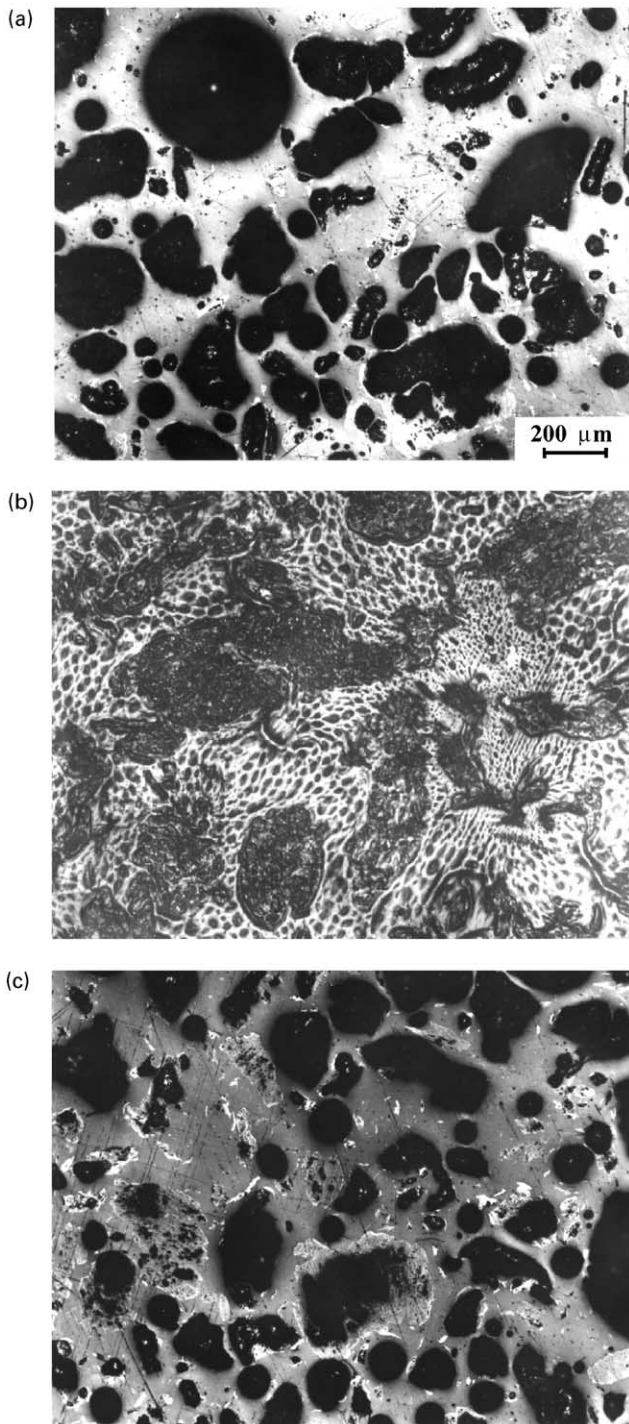


Fig. 1. Microstructure of the EP–6 wt% TEG: (a) initial state; (b) after 50% deformation; (c) after 50% deformation and shape recovery.

the 6–8% concentration range relates to the optimal, in this respect, TEG concentrations.

Taking account of this fact, we have investigated the shape memory effect using samples such as bushes. It has been found that with 6 wt% TEG in the composite, nearly a 60% deformation of a tubular sample is possible. Next, under heating in the free state the inner diameter decreases

down to the initial value. The external diameter and the length remain unchanged.

The hydrostatic reduction of cylindrical samples with the locked ends at 50–100 MPa has made it possible to produce articles in the form of rods, which when heated increase in diameter, the length being conserved. Such rods can be utilized in manufacturing disks with the radial increase in volume.

The study of the microstructure at different stages of the influence of deformation-temperature influence on samples with the 6 wt% TEG concentration has shown the following. In the initial state, the composite has a two-phase structure with the clear phase separation (Fig. 1a). In microphotographs, the dark phase corresponds to TEG and the light one to EP. The deformation results in filler compaction and a peculiar orientation of the polymeric matrix. This develops better on the etched surface of the cut, where a vortex-like structure with expanded EP globules is observed (Fig. 1b). After shape recovery (Fig. 1c), the size and location of TEG particles differ from those in the initial sample (the compared microphotographs have been obtained for one and the same surface area).

Quantitative changes occurring in the structure of EP–TEG composite are well seen on histograms of the TEG-particle distribution by size (Fig. 2). In the initial material, fraction of the dark phase makes 53%; after a 50% deformation and shape recovery, it varies insignificantly. The average size of TEG particles decrease from 0.157 to 0.129 mm, respectively.

Multiple cycling (to 10 times) according to the scheme: deformation recovery of sample shape neither breaks its integrity nor causes noticeable damage. At the same time, the cut area occupied by the dark phase (TEG) reduces to 27%. By quantitative structural analysis, a decrease in the amount of dark phase (TEG) is apparently explained by the crushing and redistribution of graphite particles under deformation. It was not possible to reveal a contribution from those fine particles, as they are beyond the sensitivity threshold of the method.

The microhardness of polymer matrix of the EP–6 wt% TEG composite is lower than in the basic EP, there is a wide spread in its values (Table 2). In the deformed composite, H value is the highest, still it does not reach the same of the EP.

The strain–strength properties of the composite under consideration are comparatively high. Thus, for the system with the 6 wt% TEG concentration, the yield strength under compression is 22 MPa, the modulus of elasticity, 220 MPa, flow strain, 12%.

Let us consider the kinematics of polymer composite deformation at the initial stage and under shape recovery. This will help us in obtaining a better understanding of the physics of the shape memory effect in such objects and in outlining the boundaries, where the effect can be realized.

The investigated material was a polymer-based porous body with the pores filled with TEG. Let us suppose that the high-elastic material in the form of a cube has been in a

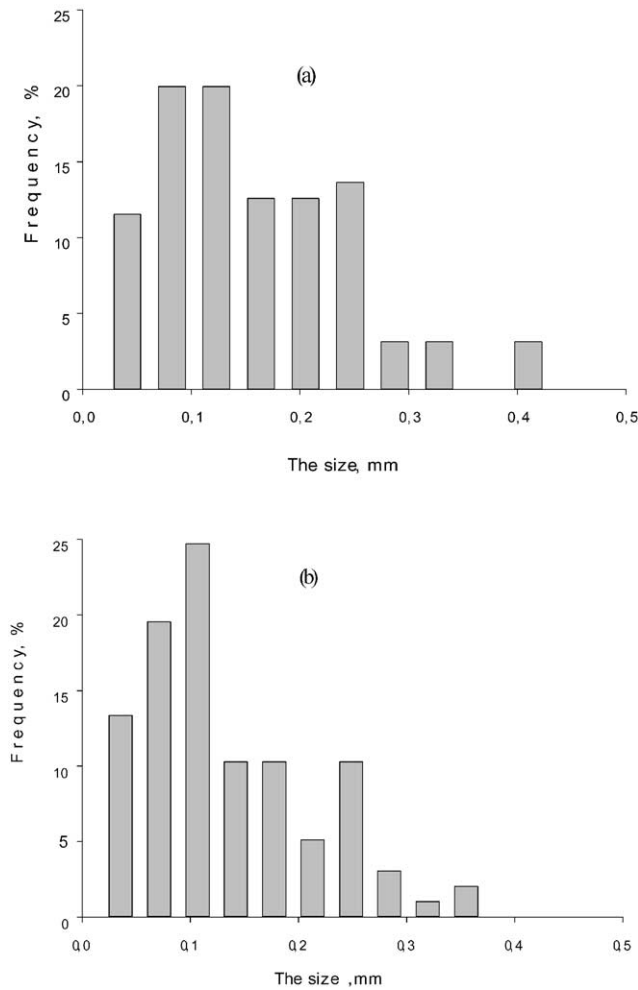


Fig. 2. Histograms of TEG particle distribution by size: (a) initial state; (b) after a 50% deformation and shape recovery.

state of strain ε_i ($i = 1, 2, 3$) along the edges and transformed to a rectangular parallelepiped. As a result, in the structure the following transformations have taken place: the pores have changed the initial shape and size, graphite in the pores has been partly compacted, and polymer has undergone high-elastic strain. If now the temperature is decreased to $T < T_g$, the entire sample will be ‘frozen’ in the form of a rectangular parallelepiped. The subsequent heating, which transforms the polymer into a high-elastic state will result in reversible strain under which the sample takes the cubic shape.

So, we obtain a simple relation between strain ε_i at the

Table 2
Microhardness of EP and composite EP–6 wt% TEG

Object	H (MPa)
EP	187
Matrix of initial composite	100–150
Inclusions in initial composite	< 100
Strained composite ($\varepsilon = 50\%$)	140–160

stage of the initial shape change and strain ε_i^* at the stage of sample shape recovery:

$$\varepsilon_i^* = -\varepsilon_i. \quad (1)$$

At first glance, expression (1) looks the same as the relation between strains in direct and reverse directions for a highly elastic polymer. However, this is not so. The difference is that, when strained, the EP volume may change only insignificantly, whereas the composite under consideration has higher possibilities due to the presence of pores filled with TEG.

The ability of a material for changing volume is reflected upon relations between strain components and this conditions the difference in kinematics of polymer and polymer composite deformation. Let us specify the above-mentioned relations between the components of strain ε_i ($i = 1, 2, 3$) along different axes. It is easy to show (see, e.g. Ref. [12]) that under straining the relative change in volume ε of the cube can be calculated by the formula:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 + \varepsilon_3. \quad (2)$$

Thus, for TEG in the first approximation

$$\varepsilon_1 + \varepsilon_2 + \varepsilon_3 = 0 \quad (3)$$

and for the composite

$$\varepsilon_{\text{lim}} < \varepsilon_1 + \varepsilon_2 + \varepsilon_3, \quad (4)$$

where ε_{lim} is the limiting value of the relative change in volume, when the volume of pores is reduced so that the filler (graphite) becomes compacted to a theoretical density ($\varepsilon_{\text{lim}} < 0$).

Quantity ε_{lim} is estimated as follows: Let V_p and V_{g0} be the volumes of polymeric matrix and TEG, respectively, prior to deformation. After deformation with the maximum possible compaction of graphite, the resulting change in volume of the polymer matrix will be much less than that in volume of the composite, and volume of graphite will be equal to V_{g1} . As a result, the relative change in the volume of the composite is

$$\varepsilon_{\text{lim}} = \frac{V_{g1} - V_{g0}}{V_p + V_{g0}}. \quad (5)$$

By introducing the volume fraction of graphite $\delta_v = V_{g0}/V_p$ and assuming, in the first approximation, that TEG filling the composite pores had, prior to deformation, the bulk density $\vartheta = V_{g1}/V_{g0}$, we obtain the following relation for ε_{lim} :

$$\varepsilon_{\text{lim}} = -\frac{\delta_v(1 - \vartheta)}{1 + \delta_v}. \quad (6)$$

The limitations of Eqs. (3) and (4) arise from the permissible changes in volume for corresponding materials. There are some other limitations on ε_i ($i = 1, 2, 3$) caused by the limiting deformations of the polymer. To describe such limitations, in the mechanics of a deformable solid, it is customary to introduce the so-called limiting surfaces in

the space of deformations or stresses [12]. The mentioned surfaces restrict the region where the material is deformed without failure. Let us try to represent, even if schematically, such a surface for the polymeric composite. To this end we first give the following reasoning.

First, from the three equitable deformations it follows that the limiting surface should have the axis of symmetry of the third order at the minimum, equally inclined to the three coordinate axes of the deformation space.

Second, it is clear that both the shear and cubic strain of the entire composite result in deformations of the polymeric matrix. Thus, the higher the cubic strain, the lower are the limiting values of the shear strain. It is known [12] that in the space of strains, the measure of the cubic strain is a value by which a representative point is distant from the origin of coordinates along the line equally inclined to the coordinate axes. For the shearing strain the measure is a distance between the representative point and the straight line. It follows that the distance from the limiting surface to the line equally inclined to coordinate axes should decrease with distance from the origin of coordinates. This means that the cut of the limiting surface by the plane normal to the above straight line should be ‘contracted’ to that line with distancing from the origin of coordinates. In the limiting case, it should turn into a point corresponding to the case when the polymer matrix has failed as a result of the cubic strain of the composite.

Fig. 3 illustrates a construction drawn in correspondence with the above reasoning. The pyramidal surface represents schematically the limiting surface of a porous composite. This is the simplest surface satisfying the above conditions. The OO -line equally inclined to the three coordinate axes is the third-order axis of symmetry for that structure. The A -point corresponds to the failure of the composite under cubic strain only. For all points of plane S_0 the material is deformed with no changes in volume. Plane S_1 corresponds to the limiting compaction of the porous material.

So, the polymer can only be deformed within the limits of the S_0 -plane triangle. The polymer fails at boundaries of that region. The porous polymeric composite can be deformed within the limits of a truncated pyramid with the lower base

lying on S_0 and the upper one on S_1 . On the lateral surface of that region the polymer matrix is failed and on the upper base there occurs the limiting compaction of graphite in pores.

Fig. 3 clearly shows the difference in the kinematics of porous-composite deformation and polymer deformation, it illustrates the region in the space of deformation where the shape memory effect with the change in volume of the composite is observed. The whole of the region can be used for the engineering applications of the effect.

Let us analyse some features of the effect of shape recovery by using the proposed geometrical model. First, we note that when, in the composite, a TEG volume fraction is high the absolute magnitude of the ε_{lim} value may become so high that the S_1 plane will be drawn over the vertex A of the limiting surface. In this case, the reversible deformation of the composite is limited by the pyramid of the limiting surface. In an attempt of further compaction of the composite at the stage of initial straining, the polymer matrix will be failed and the recovery of the sample under heating will be incomplete. This means that there are maximally permissible graphite concentrations which should not be exceeded.

A very interesting phenomenon is observed in the porous composite near the plane of the limiting compaction S_1 . Graphite being compressed by the walls, starts crushing and penetrating into the polymer matrix under high pressure and shear strain. The photographs of microstructures (Fig. 1) demonstrate the phenomenon. If prior to deformation the polymer matrix was light-coloured, then after the deformation and subsequent relaxation it becomes grey-coloured. This can only be the result of the introduction of fine graphite particles into the matrix, since the deformation of the EP proper does not result in colour change. Since with a $\times 1000$ magnification microscope it is impossible to identify the isolated TEG particles introduced into the polymer matrix, it can be concluded that they are less than 100 nm in size.

Now we generalize relation (1) to the non-uniformly deformable samples of arbitrary shape. For this, we use the approach, which is on the basis of the mechanics of a rigid deformable body. The introduction of the so-called representative element of the material is taken into consideration [12]. A representative element is understood as a volume of the material that is, on the one hand, sufficiently small to be considered as a material point and to neglect the changes in macrodeformation while considering the entire sample on the macroscopic level. On the other hand, the element should be large enough for having the properties of a material, in particular, to contain sufficient pores.

We consider the above-mentioned cube as the representative volume of the material. Then, according to Eq. (1), for an arbitrary material point of the macrosample we have the following relation between the strain tensor ε_{ik} at the stage of the initial shape change and the strain tensor ε_{ik}^* at the stage of shape recovery:

$$\varepsilon_{ik}^* = -\varepsilon_{ik}. \quad (7)$$

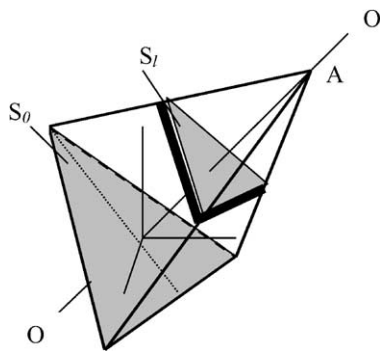


Fig. 3. A geometrical model of limitations (3) and (4) and limiting surface of porous composite in the space of deformations.

As was stated above, it is only valid in a definite region in the space of porous-composite strains.

Relation (7) makes it possible to explain the following typical peculiarity in the change in the shape of the samples during the free heating: if at the stage of straining any dimension is kept fixed, then under heating the dimension remains constant. Let us consider, for example, the uniaxial compression of the sample in a mould. We introduce the cylindrical coordinate system (r, φ, Z) with the Z-axis coinciding with the axis of the mould. For all points of the sample deformed in the mould with rigid walls $\varepsilon_{rr}^* = \varepsilon_{\varphi\varphi}^* = 0$. Hence, according to Eq. (7), if heating $\varepsilon_{rr}^* = \varepsilon_{\varphi\varphi}^* = 0$, then the diameter of the sample should remain unchanged. Since $\varepsilon_{zz}^* \neq 0$ and $\varepsilon_{rr}^* = \varepsilon_{\varphi\varphi}^* = 0$, the composite behaves as if its Poisson's ratio is zero during shape recovery. At the microlevel this is provided by polymer–matrix possibility of ‘entering’ the pores of the composite under straining and ‘going out’ of them when the sample is recovered.

It is possible to produce samples, which could have their dimensions increased (both height and diameter), and the composite would behave like a material with the negative Poisson's ratio. This is easily realized with the help of a step-like mould, in which the deformed sample is moved from the section of large diameter to that of smaller diameter.

The given analysis shows that with the restraining of the investigated composite, structures can be formed, which when recovering their shape imitate the materials with different, including negative, Poisson's ratios, more exactly, with different coefficients of proportionality between longitudinal and lateral strains. What is the real Poisson's ratio of the composite and how does it depend on a pretreatment of the material are topics for future investigations. But already now it can be stated that in the composite this coefficient is much lower than that of the polymer (both in the highly elastic and glass states).

4. Conclusion

For the EP–TEG system, with a specific content of the latter, an unconventional shape memory effect has been revealed, which is accompanied by a considerable increase in volume. Technological schemes for the formation of the

above effect are proposed making it possible to have products with an unusual behaviour under heating: the rods increasing in length with diameter kept constant; bushes increasing in internal diameter with length and external diameter kept constant; disks increasing in diameter with height kept unchanged. A physical model has been elaborated to explain the effect and determine the regions of its realization. It is shown that in polymer composites with a compactible porous filler, the kinematics of shape recovery can be widely varied by straining.

References

- [1] Ryan D, Kraus R. Advances in heat-strink technology. IEEE Elec Insul Mag 1988;4(3):31–4.
- [2] Trznadel M, Kryszewski MJ. Thermal shrinkage of oriented polymers. Macromol Sci—Rev Macromol Chem Phys 1992;32(4):259–300.
- [3] Zicans J, Kalnins M, Bocoka T, Kalkis V, Bledzki AK. Studies of morphology, rheological, mechanical and thermorelaxation properties of chemically and radiation modified PE/EPDM copolymer blends. J Macromol Sci, Pure Appl Chem 1998(7/8):1217–37.
- [4] Kalkis V, Maksimov RD, Kalnins M, Zicans J, Bocoka T, Revjakin O. Thermomechanical and adhesive properties of radiation-modified polymer composites for thermosetting products. Mech Compos Mater 2000;36(3):379–94.
- [5] Beloshenko VA, Beygelzimer YaE, Varyukhin VN. Thermal shrinkage of polymer mixtures obtained by solid state extrusion. Polymer 2000;41(10):3837–40.
- [6] Beloshenko, VA, Stroganov, VF, Sheludchenko VI. A method to produce thermal-shrinkage devices. Patent No. 10299, Ukraine, 1996.
- [7] Beloshenko VA, Askadskii AA, Varyukhin VN. Promising ways of structural modification of polymers and polymer composites with the use of high pressure. Uspekhi Khimii 1998;67(11):1044–67 (In Russian).
- [8] Beloshenko VA, Beygelzimer YaE, Stroganov VF, Sheludchenko VI. Thermal shrinkage couplings from thermoset polymers and their application for pipeline joints. Engng Mech 2000;7(3):231–7.
- [9] Beloshenko VA, Stroganov VF, Sheludchenko VI, Amosova EV. A method of adhesive-coupling connection of pipes, an epoxy composition for manufacturing connecting units and a method of their fabrication. Patent No. 2141600, Russia, 1999.
- [10] Yaroshenko OP, Shapranov VV, Savoskin MV, Popov AF. A method of thermoexpanded graphite production. Patent No. 18065, Ukraine, 1997.
- [11] Beloshenko VA, Pacter MK, Beresnev BI, Zaika VI, Zaika TP. Structural and kinetic aspects of hydrostatic pressure effect on polymer network formation. High Press Res 1991;6:203–12.
- [12] Hill R. The mathematical theory of plasticity. Oxford, England: Clarendon Press, 1998. p. 368.