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On the jump-like creep of cross-linked polymers and composites based on them

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Abstract

The study on the jump-like character of creep of differing in their morphology polymers was continued. The creep processes were recorded using the method of laser interferometry, allowing investigations on strain rate inhomogeneity on micron level and determination of strain jump parameters. Polyester resins and filled composites based on them were used as objects of the investigation. It is shown that the characteristics of jump-like creep change considerably depending on material composition and strain stage. It is assumed that the strain jumps on micron level reflect the presence of ordered formations of the same scale in the structure, as well as their transformations. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Creep rate inhomogeneity; Polyester resin; Dispersely filled polyester resin

1. Introduction

General concepts concerning the levels of structure and deformation and the structural levels of deformation of different bodies have been accepted in reference literature at present [1,2]. The structural heterogeneity and the localised character of defects that are typical for all real solid bodies, imply a jump-like form of the displacements under the action of a force. However, the structural heterogeneity is not reflected in the conventional creep recording.

The applied new approaches to the study of creep kinetics provided the possibility of revealing the strain jumps in the form of periodic fluctuations in the rate for small increments, equal to the jump height. The resolution of the interferometric methodology applied in Refs. [3–11] allowed to establish the simultaneous development of several jump levels (parts of the micron and microns, tens of microns and a hundred and more microns). Using polyethylene fibres as an example, it has been shown that large jumps are formed by small ones just as big macrofibrilles are formed by microfibrilles, the corresponding sizes of jumps and microfibrilles being the same. The introduction of a cross-linking agent leads to the occurrence of more dense displacements at the microfibrille surface and the large strain jumps of the macrofibrille scale disappear [9,11]. Similar experiments with model structured polymers clearly exhibit the relationship between the structural heterogeneity and non-monotonous creep rate.

Jumps with micron sizes were first observed in amorphous polymers [4,5] and this provided grounds to assume the existence of ordered micron-level formations in the super-molecular structure of amorphous polymers, although there is no unambiguous morphological evidence in reference literature. Correlations proving the dependence of micron-scale jump characteristics on the parameters of the inhomogeneous polymer structure at molecular level are shown for amorphous polymers [5,7,11]. In this way, the initial jump-like form of movement originates, as might be assumed, at molecular level and is preserved at the higher levels according to the scale of inhomogeneity. The correlations shown in Refs. [5,7,11] refer to the jumps in the point ϵ_y of unstable equilibrium of structure when the plastic deformation is just starting to develop. Evolution of structure is observed for strains higher than ϵ_y and jump parameters change regularly according to the creep stage [4,5,11].

The problem concerning the correspondence between the strain jump parameters and the morphological characteristics of solid bodies is considerably new one and is not sufficiently well studied. It is necessary to investigate the kinetics of small deformations for polymers of different structure in order to understand clearly the nature of strain jumps. The jump-like creep was studied earlier for linear

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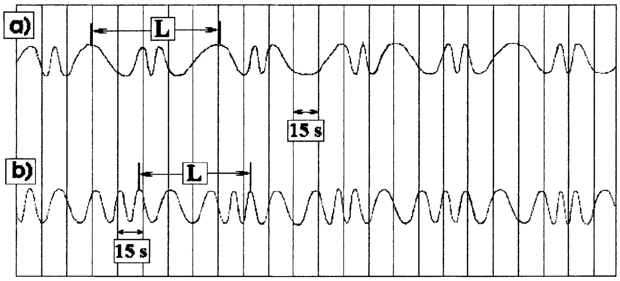

Fig. 1. Interferograms reflecting the jump-like creep of V550PE polyester resin under the action of a compressive stress $\sigma = 70$ *MPa* for creep strain $\epsilon = 7\%$ (a) and $\epsilon = 10.9\%$ (b). One beat corresponds to a displacement increment of 0.3 μm. *L* — period of rate change or height of the strain jump.

amorphous and crystalline polymer samples [5–11]. The present work treats materials with more complex structure: industrial polyester resins and composites based on them. It is expected that the changes in the composition of the filled resin composites as well as of the chemical composition of the polyester resins and the technologies for their production can exert influence on the average sizes of the typical for the resins ordered formations (globules) and hence on the strain jump characteristics.

The aim of this work is to make a comparative assessment of the values of strain jumps at micron level for polyester resin and polyester composites with dispersed fillers.

2. Materials and methods

The studied two brands of unsaturated polyester resin were Jotun ChS Polyester 122 (JChS122) and Vinalkid 550 PE (V550PE). Two test series were prepared under laboratory conditions using the JChS122 resin with 20 volumetric percent of a 'hard' (marble powder) and 'soft' (powdery PVC) disperse filler. The modulus of elasticity of the hard filler is about 15 times higher than the resin matrix one, and the modulus of elasticity of the soft filler is commensurate with the matrix one.

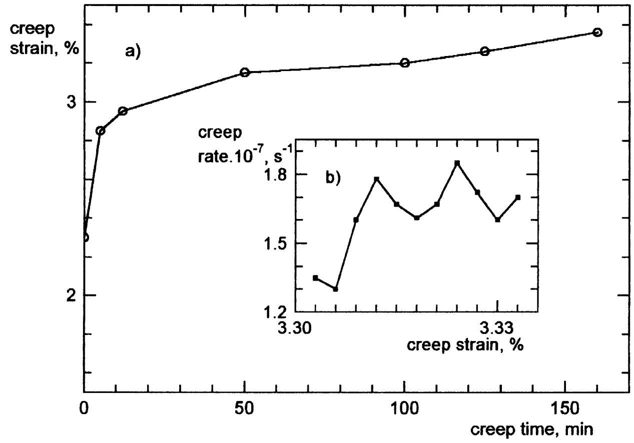

Fig. 2. Creep curve of JChS122 polyester resin for compressive stress $\sigma =$ 40 *MPa* (a) and creep rate fluctuations for small sections of the creep curve (b). $T = 16$°C. Each point of the creep rate fluctuation curve refers to a strain increment of 0.003%. Parameters of the jump-like strain: $L =$ 1.2 *μm*, $h = 1.2$.

The polyester resin (with no filler) and the composites based on it were cured under normal temperature and pressure with the conventionally used curing system (accelerator — cobalt naphtenate, initiator — cyclohexanon peroxyde). The test samples were small cylinders cast under laboratory conditions (diameter of 5 mm, height 10 mm, the cylinders for the V550PE resin being 6 mm high).

Creep under compression was investigated. The strain during the creep process was recorded using a laser interferometer [3–11], one of the mirrors being fixed at the movable clamp to follow the sample deformation.

The creep information was recorded in the form of a sinusoid (Fig. 1), its frequency ν determining the strain rate, $d\epsilon/dt = \lambda\nu/2l_0$, and the number of beats N determining the strain value, $\epsilon = \lambda N/2l_0$ ($\lambda = 0.63$ μm — laser wavelength, l_0 — sample length).

The interferometric manner of recording the process in the form of beats provided the possibility of more precise rate analysis according to the beat frequency. Each beat in the interferogram corresponded to a displacement increment of 0.3 μm. In this way, the lowest strain for rate determination was 0.0015% for the sample length of 10 mm and 0.0025% for the sample length of 6 mm, or equal to half a beat of 0.15 μm. The beat frequency can also be determined using a frequency metre and by automatic rate recording depending on time and strain.

Since rate periodicity was not always clearly exhibited, the rate inhomogeneity was usually studied, measuring it in different points (small sections) of the creep curve at successive strain increments of 0.003% (for 10 mm long samples) and 0.005% (for 6 mm long samples), corresponding to displacements of 0.3 μm. Then the rate dependence was plotted for the successive strain increments equal to 0.003 (0.005)%.

Two quantities were introduced to characterise the jump-like deformation: the height of the strain jump L corresponding to the period of fluctuation and ratio h between the maximum and minimum of the rate in the period of the same fluctuations (the jump slope). The regular changes in the L and h parameters [4,7,11] provide evidence about the physical nature of the jumps related to the chemical structure of the polymer and the rearrangement of structure in the course of the strain process. The L and h values in the present work represent the arithmetic mean of five L_i, respectively, h_i values.

3. Results and discussion

The deformation in the initial viscoelastic creep stage of polymers proceeds with a decreasing rate and is recoverable

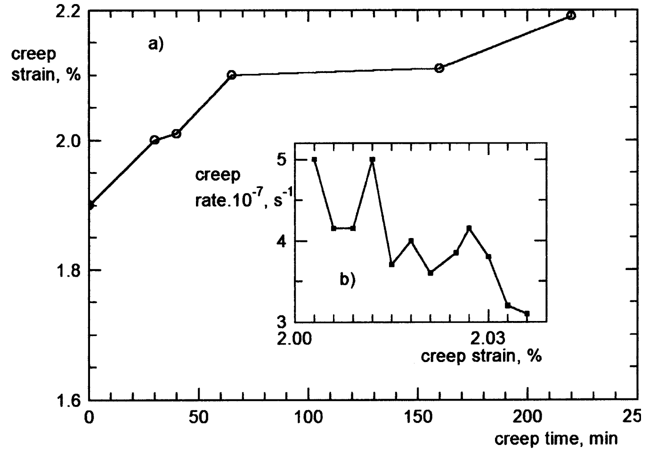

Fig. 3. Creep curve of JChS122 polyester resin composite with 20 vol% of marble powder for compressive stress $\sigma = 40\ MPa$ (a) and creep rate fluctuations for small sections of the creep curve (b). $T = 16$°C. Each point of the creep rate fluctuation curve refers to a strain increment of 0.003%. Parameters of the jump-like strain: $L = 1$ μm, $h = 1.3$.

after removing the load. When a certain strain (the so-called yield point ϵ_y) is reached the rate passes through a minimum and then starts to increase. This corresponds to the rearrangement of the initial super-molecular structure and to the development of 'plastic' deformation (forced elastic, recoverable under heating above the glass-transition temperature). It has been shown for linear polymers that the strain jumps are manifested as early as during the first stage in the ϵ_y proximity, and that bigger and more abrupt jumps are formed during the second stage [4,5,11]. Cross-linked polymers exhibit not so pronounced second stage but it is observed for sufficiently high stresses and is supposed to be related with the inhomogeneity of the three-dimensional network and the presence of not-linked structure, analogical to the structure of linear polymers [12].

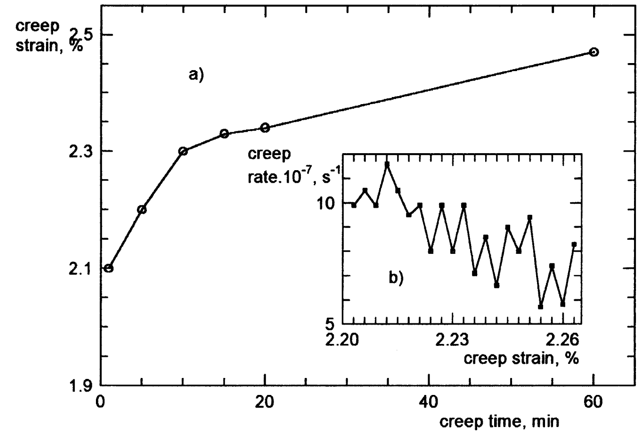

Fig. 4. Creep curve of JChS122 polyester resin composite with 20 vol% of powdery PVC for compressive stress $\sigma = 40\ MPa$ (a) and creep rate fluctuations for small sections of the creep curve (b). $T = 16$°C. Each point of the creep rate fluctuation curve refers to a strain increment of 0.003%. Parameters of the jump-like strain: $L = 0.6$ μm, $h = 1.2$.

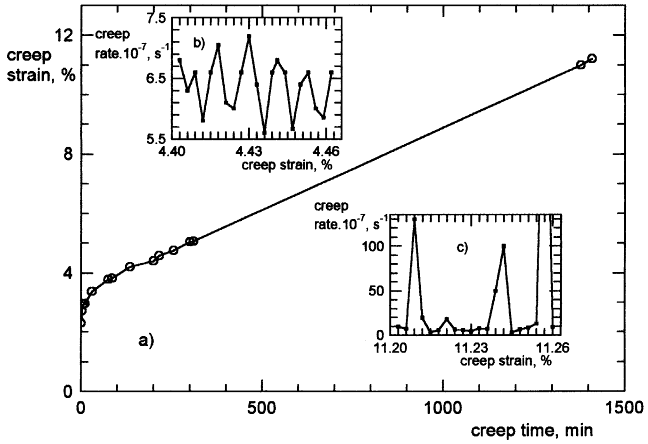

Fig. 5. Creep curve of JChS122 polyester resin for compressive stress $\sigma = 70\ MPa$ (a) and creep rate fluctuations for two small sections of the creep curve in the proximity before the yield strain ϵ_y (b) and after the yield strain ϵ_y (c). $T = 16$°C. Each point of the creep rate fluctuation curve refers to a strain increment of 0.003%. Parameters of the jump-like strain: $L = 1.2$ μm, $h = 1.2$ (b) and $L = 1.35$ μm, $h = 20$ (c).

The investigated materials refer to cross-linked structures and exhibit some specific features of the jump-like creep. The creep curves of three materials — polyester resin JChS122 (Fig. 2a) and composites based on it with 20 vol% of marble powder (Fig. 3a) and 20 vol% of powdery PVC (Fig. 4a) are determined for the stress causing deformations within the viscoelastic range. The rate fluctuations are shown in Figs. 2b, 3b and 4b for the same materials and for almost equal deformations. The fluctuation period L corresponding to the average jump values differs to a certain extent for the different materials, the lowest values being observed for the polyester resin containing polyvinyl chloride (Fig. 4b). In the case of the polyester resin (Fig. 2b) and the marble-powder containing composite (Fig. 3b), the jump difference is negligible. It is supposed that the movable polyvinyl chloride molecules play the role of a plasticiser and contribute to the emerging of lower-scale ordered formations by increasing the flexibility of the polyester molecules. When the filler represents hard marble powder particles, the deformation takes place in the polymer layers and for this reason the rate inhomogeneity of the composite reflects the heterogeneity in the polyester, as is the case with compression of the resin itself.

The data shown in Figs. 2–4 refer to the viscoelastic range since the chosen materials, temperature and stresses, do not allow reaching the critical strain ϵ_y after which the irrecoverable flow takes place. The initial arrangement of the macrochains is not yet destroyed in the viscoelastic region and for this reason the strain jumps characterise the scale of morphological inhomogeneities closest to the initial arrangement, inherent to the initial medium.

The creep of the most plastic of the studied materials — the JChS122 and V550PE polyester resins, is considered for high stresses $\sigma = 70$ MPa in order to study the irrecoverable deformation. The comparison of the creep curves in Figs. 5a

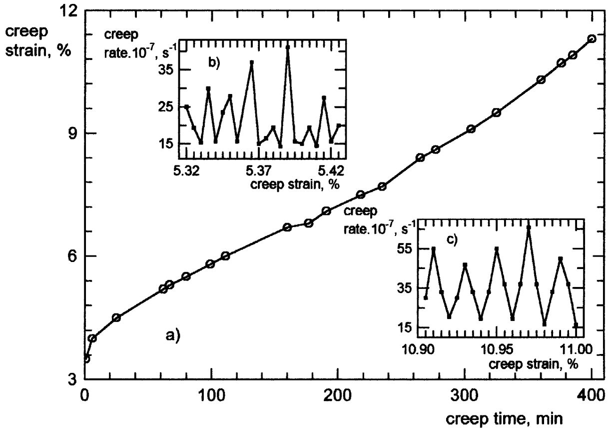

Fig. 6. Creep curve of V550PE polyester resin for compressive stress $\sigma = 70\ MPa$ (a) and creep rate fluctuations for two small sections of the creep curve in the proximity before the yield strain ϵ_y (b) and after the yield strain ϵ_y (c). $T = 16°C$. Each point of the creep rate fluctuation curve refers to a strain increment of 0.005%. Parameters of the jump-like strain: $L = 0.75\ \mu m$, $h = 2.2$ (b) and $L = 1.2\ \mu m$, $h = 2.7$ (c).

and 6a proves that the V550PE resin is more deformable than the JChS122 one, possibly because of its more inhomogeneous or loose cross-linking. The rate dependencies for a number of consecutive beats (increment of 0.3 μm) in the interferogram are plotted in Fig. 5b,c and Fig. 6b,c for two points (small sections) of the creep curves, showing the typical rate fluctuation or jump-like creep deformation. The plots in Figs. 5b and 6b are done in the vicinity before the yield strain ϵ_y and in Figs. 5c and 6c after ϵ_y, at the stage of macroscopic plastic deformation. (The characteristic transition point ϵ_y of the polyester creep curve is within the 5–6% deformation range).

The comparison of the data shown in Figs. 2–6 has revealed the following regularities:

1. The stress changes have not affected jump parameters at the first stage of creep (see Fig. 2b and Fig. 5b). This result corresponds to the idea that the jumps at the first stage are determined by the scale of inhomogeneities of the initial undeformed structure, for example the macroglobule size [13].
2. The amplitude of rate changes (the degree of rate inhomogeneity or the jump abruptness *h*) for high stresses and strains (Figs. 5c and 6c) is bigger than that of the same resin for lower strains (Figs. 5b and 6b), which is typical for linear polymers too [4,5]. The observed increase *h* above ϵ_y is especially significant for the JChS122 resin (Fig. 5c). It is supposed that the jump-like creep is related with the periodicity of the strong and weak interactions between the molecule groups in the shear planes. The experiments proved [14] that the initial system of strong (hydrogen) bonds is destroyed above the yield point, the display and development of more distinct jump-like creep as well as the organisation of new more ordered structure being connected with this fact too.
3. The comparison of the jumps for the two polyesters (Figs. 5 and 6) leads to the conclusion that the average size of the ordered formations in the V550PE resin is smaller than that in the JChS122 one.
4. It is seen in Figs. 5c and 6c that for deformations during the second stage (after ϵ_y) the jumps become more abrupt and the values of the parameters *L* and *h* increase. It is known that the flow stage in amorphous polymers is related with orientation processes and is accompanied by the emergence of big strain jumps [5–9]. The activation analysis proved that the irrecoverable strain, if any, in cross-linked polymers proceeds according to the mechanism of flow of linear structures. Hence, the augmentation of the jumps in this case corresponds to the beginning of the orientation rearrangement of structure.

In this way, the observed transition to plastic deformation in cross-linked systems as well as in linear polymers proceeds with increasing jumps. The considered materials do not represent an exception from the number of solid bodies for which regular jump-like creep has been established. This confirms the common features of this phenomenon.

Some general features of jump-like deformation could be summarised as follows:

The deformation above the yield strain corresponds to the formation of macroscopic instability manifested as 'necking' under tensile and 'barrel-like' shape formation under compressive loading. The further deformation proceeds as a movement of the instability boundary along the test sample. Consequently, the jumps represent the form of development the boundaries of barrel-like shape under compression (or narrowing under tension) at a micron scale in the present case. The highest (macro-) level of the jumps is the formation of necking and barrel-like shape formation themselves on sample scale, as well as the well-known phenomenon of jump-like strain in metals and crystals under helium temperatures [15,16]. The deepest level is that of dislocations and disclinations [17], their origin and movement having a jump-like, localised character. The resolution of the interferometric method of rate measurement and the application of new approaches provided the possibility of observing jumps on sub-micron and micron level during creep of various solid bodies at room temperature [11]. Polymer creep has been studied in most detail and the non-accidental regular character of the jumps has been established depending on rate fluctuations, i.e. an order is observed in the rate value scattering. The correlations determined for polymers confirm the assumption that the initial reason for the jumps consists in the inhomogeneity of potentials of the intermolecular interaction, overcome during the acts of deformation. The most abrupt jumps are observed in polymers in which the formation of strong non-chemical (polar, hydrogen) bonds — the so-called 'physical nodes', is possible. At present not only single bonds but also ordered formations of molecule chain sections oriented in parallel or zigzag direction are considered as physical nodes that could originate in the form of fluctuations [18]. It has been shown for different polymers [10] that high rates within the limits of the period L correspond to lower value of the relative activation energy q_i compared to the same values for low rates. Hence the activation analysis confirms the model of breaking of physical nodes during the jump formation: the overcoming of the high potential barrier (node) corresponds to a higher relaxation time, i.e. lower rate of the jump. In the present work treating polyesters, the abruptness of the jump (h) in the ϵ_y proximity is small that corresponds to low polarity of the polymer groups.

So the jump-like deformation is inherent to different solid bodies, different creep stages and different strain levels. It has been show using model polymers that correspondence exists between the jump scale and the size of the ordered formations in the direction of force action [9]. The found correlations have many things in common with the wave theory of plasticity where the wavelength is juxtaposed to the grain size in metals [18]. It is more difficult to explain the strain jump scale in amorphous bodies where there is no distinct idea about the structural formations. It can be supposed in the present case that under the action of the applied forces and strains the polymer chain sections are oriented under shear along the planes of the maximum tangential stresses (directed to 45° toward the sample axis). Ordered formations on a micron level emerge and this means that the strain itself organises the structure determining the jump size. The length of the ordered formations can depend on molecule length. It is relevant to mention here the dislocation models that were not initially applied to amorphous bodies, including polymers. The ideas about instability formation as a dislocation shear loop propagating under the action of tangential stresses through the sample cross-section were developed later by Gilman, Argon and Bowden. Taking under consideration the experimental results, a jump-like character of the dislocation movement should be assumed.

The phenomenon of jump-like creep is undoubtedly connected with the collective co-operative behaviour of molecules and reflects most clearly the self-organisation in a complex system in the form of instability development.

The structural nature of jumps should be further investigated but the results already obtained lead to the conclusion that creep on micron level exhibits the inhomogeneities in the structure of solid bodies.

4. Conclusions

Investigations have been carried out on the creep of polyester resins and dispersely filled composites based on them on micron level. A jump-like character has been established for the creep rate of these materials. The mean values of the parameters L and h have been determined. It is shown that during the first creep stage (before reaching the yield strain ϵ_y), the stress changes do not exert influence on L and h. During the second creep stage (after reaching the yield strain ϵ_y), the jumps become more abrupt and the L and h values increase. The creep on micron level provides evidence for the structural inhomogeneity of polyester resins and composites.

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