

Deformations properties of glassy epoxy doped with SiO₂ and Al₂O₃ nanoparticles of different synthesis methods

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Abstract. The variation in the deformation properties of epoxy polymers doped with of SiO₂ and Al₂O₃ nanoparticles obtained by four different methods was experimentally investigated. It was shown that the doping of nanoparticles leads to structural changes in the polymer similar to the effect of plasticization (an increase in the mobility of the polymer chain). The variation of the types of nanoparticles contained in the composite significantly changes the process of the kinetics of microindentation stress relaxation. In particular, the complete recovery from microindentation (healing of the indentation) occurs at different concentrations by varying the method of nanoparticle synthesis.

Keywords: Microindentation, thermally stimulated relaxation, delocalization, epoxy polymer, nanoparticles

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Introduction

Polymers are currently used in many industries, including biomedicine, batteries, ceramics, composites, magnetism, electronics packaging, solid fuels, and adhesives [1,2]. The inclusion of various fillers [3,4] can significantly change such properties as mechanical strength [5,6], thermal [7] and electrical conductivity [8], thermal stability [9], magnetic characteristics [10,11], and other properties.

Based on polymers, in particular epoxy-polymer materials, composite materials are formed with granular fillers, dyes, or other additives that give the material specific properties. The properties of such composites depend on the size, shape, and nature of the particles, the interaction between their components, and the distribution of particles in the matrix [12,13]. Epoxy resins have a cross-linked structure; they have covalent bonds linking polymer chains together. In addition to them, the presence of other types of molecular interactions, such as hydrogen bonding, can also affect the properties of the epoxy resin [14].

Under mechanical stresses exceeding the yield pressure (plastic yield), in silicate and other inorganic glasses, plastic inelastic deformations occur, which can persist for a long time after the external pressure is removed. However, when the material is heated below the glass transition temperature (T_g), this deformation is restored to its original undeformed state. That is, it exhibits the behavior of reversible viscoelastic deformation [15-17].

Similar behavior is found in many amorphous polymers. After pressure is removed at room temperature, the deformation persists and is visually indistinguishable from residual plastic deformation. However, when heated below T_g, the deformed polymer returns to the

undeformed state [18-20], similar to inorganic glasses [21]. Consequently, the effect of plasticity turns out to be a universal property of such glassy materials.

Previously, it was assumed that a large "residual" deformation of amorphous polymers in the glassy state is fixed since thermal motion at room temperature is not enough to return distorted-chain macromolecules to their original state. Only during heating, when the intensity of thermal motion is high enough to give sufficient mobility to flexible macromolecules, can stress be relieved. Since this phenomenon also manifests itself in low molecular weight inorganic and metallic glasses, where chain macromolecules are absent, the "polymeric" approach to the nature of this deformation should be reconsidered.

Paper [19] developed an idea that a new structure arises in a region that is plastically deformed and subsequently relaxed as a result of thermal action; it is a structure different from the original one. The main carriers of these processes are local microshears, which appear under the action of external loads and disappear upon heating.

In the explanation given in [22], great importance was attached to the appearance of an interface in a deformable structure and the "healing" of interfacial boundaries during thermally stimulated strain relaxation. The elementary act of "plastic" deformation of glass was reduced to the displacement of the link from the equilibrium position associated with the rearrangement of the neighboring particles. In particular, in inorganic glass, this refers to the displacement of the bridge oxygen atom in the Si-O-Si bridging group, which leads to local deformations in the network of amorphous filaments. The process of delocalization of atoms in amorphous polymers corresponds to the displacement of a small portion of the main chain of the macromolecule (the main group of atoms in the crosslink) from its equilibrium position and is associated with the local deformation of intermolecular bonds [23,24]. An analysis of the recovery curves for the residual deformation of glasses during heating provides useful information both from a purely scientific and practical point of view.

The main role of a dispersed filler is to create an additional force that prevents the displacement of the macromolecule chain fragments. The feature of nanoparticles is that their surface has a significant number of active sites, which depend on the conditions and method of particle synthesis. The presence and strength of the active sites of the filler surface play a decisive role here since the active sites resist indentation and contribute to the healing of cracks. Strengthening effects can be observed when using the same nanoparticles in combination with different matrices or different nanoparticles with the same matrix. It was shown that different synthesis methods form nanoparticle surfaces with different properties while maintaining the phase composition of the material [25,26]. The relationship between the types of surface sites, their strength, and the interaction of nanoparticles with a dispersion medium was also shown. In particular, there was a significant difference in the strength of the active sites for the studied samples, which was reflected in the rheology of nanofluids based on epoxy resin and water.

Materials and methods of experiment

Table 1 lists the properties of the nanoparticles used.

To study the kinetics of deformation, an industrial epoxy resin ED-20 (PolyMax (Russia)) was used. After doping nanoparticles into it, the suspension was subjected to ultrasonic treatment for 30 minutes in an ultrasonic bath Sapphire (Russia) as a measure for particle deagglomeration. After that, the PEPA hardener was added in a ratio of 1:10 to the resin weight. The mixtures were then poured into molds lightly lubricated with silicone grease. Curing took place within 24 hours at room temperature. ED-20 is a commercial cross-linked polymer in a glassy state at room temperature ($T_g \approx 80^\circ\text{C}$) [14]. For microscopic analysis, it was cut into pieces $10 \times 10 \times 3$ mm in size and additionally polished. Ten samples were prepared and tested for each concentration.

Table 1. Samples under study

Sample	Origin	Producer	Average particle diameter, nm
Aluminum oxide			
Aa	Flame hydrolysis of a mixture of aluminum chloride, hydrogen, and air	Evonik Industries AG, (Germany)	27.7
Ta	Evaporation of material by an electron beam	Bardakhanov LLC, (Russia)	34.3
La	Liquid phase synthesis	Nanjing XFNANO Materials Tech Co., (China)	27.2
Ea	Electric explosion of a thin wire in an argon atmosphere	Advanced powder technologies LLC, (Russia)	64.3
Silicon dioxide			
As	Flame hydrolysis of high-purity SiCl ₄	Evonik Industries AG, (Germany)	22.7
Ts	Evaporation of material by an electron beam	Bardakhanov LLC, (Russia)	28.2
Ls	Liquid phase synthesis	Nanjing XFNANO Materials Tech Co., (China)	24.3
Ps	Plasma-chemical synthesis in arc plasma	Plasmotherm, (Russia)	23.8

The samples were subjected to microindentation and visualization on an HVS-1000A microhardness tester with a Vickers quadrangular diamond pyramid (apex angle 136 degrees). The samples were indented with a load of 1.96 N (200 g) for 20 s. After indentation, the samples were placed on a hot plate (the indentation surface was in contact with the hot plate) at a given temperature for a given period of time, and then photographed again. The temperatures used were 20, 60, 70, 75, and 80°C. At temperatures above 80°C, the samples began to break down.

When microindentation is performed on a sample at room temperature, a square imprint with concave sides is formed (Figs. 1(a), 1(d)). However, for current samples with some elasticity, when the indenter is removed, part of the samples returns to the space occupied by the indenter resulting in an imprint with concave sides. However, full recovery was prevented by "plastic" deformation.

When the samples were heated, the filling of the cavity was observed, as shown in Figs. 1(a-c). The recesses were deformed inward from the sides, and the corners of the recess were not deformed. Thus, to quantify the deformation, the width of the central point between the two walls of the microindent (L) was measured (Fig. 1(d)).

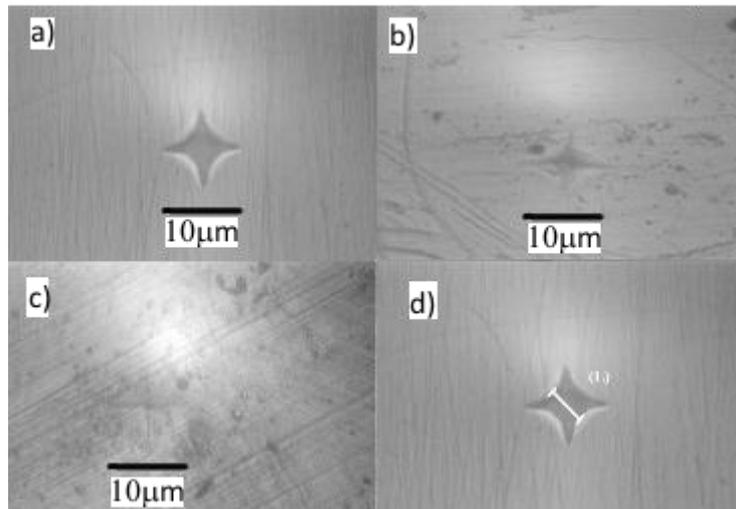


Fig. 1. Microindentation of ED-20 with Ts (1.6 wt %) at 75°C after a) 0 s, b) 5 s, c) 30 s, d) measured value L, imprint width

Results

Figure 2 shows the deformation kinetics of ED-20 without additives (control sample) at various temperatures. L_0 is the initial width after indentation, and ΔL is the change in width after heating. At room temperature, no change in the imprint size with time was observed. At 60°C, slight shrinkage is observed. When the temperature was within 10°C of T_g , a stronger indentation deformation was observed. However, none of the temperatures resulted in a complete recovery of the imprint.

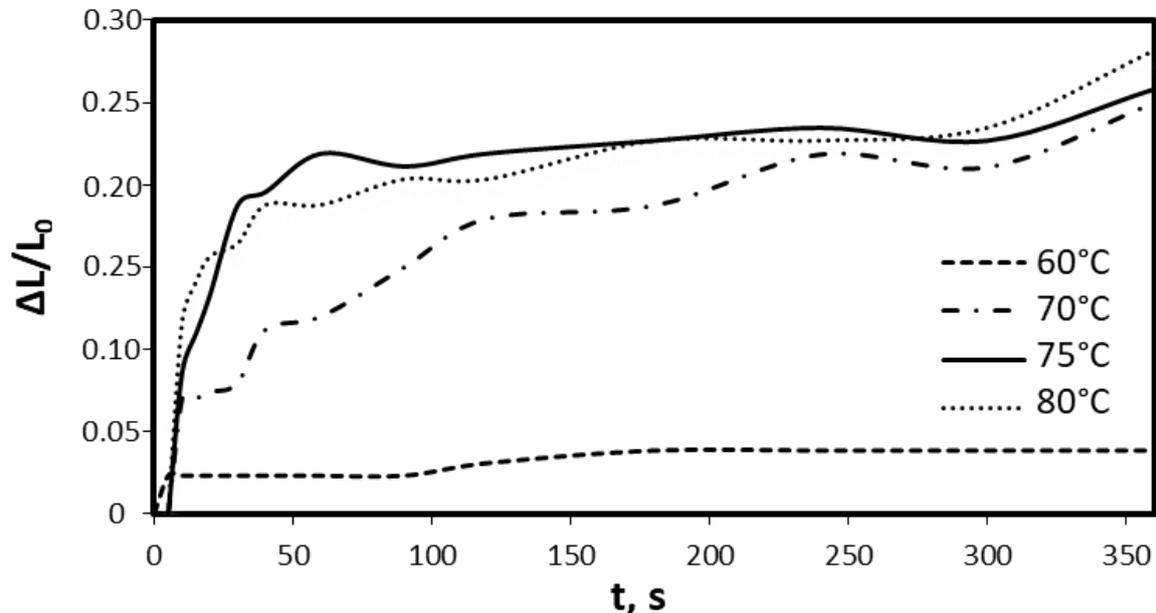


Fig. 2. Thermal permanent deformation of imprints on epoxy resins at different temperatures

When nanoparticles were added to the epoxy resin, the recovery performance improved, as shown in Fig. 3, for 75°C. As with the control, maximum recovery occurs within 10°C of the T_g of the epoxy; although the amount of the recovery is much larger.

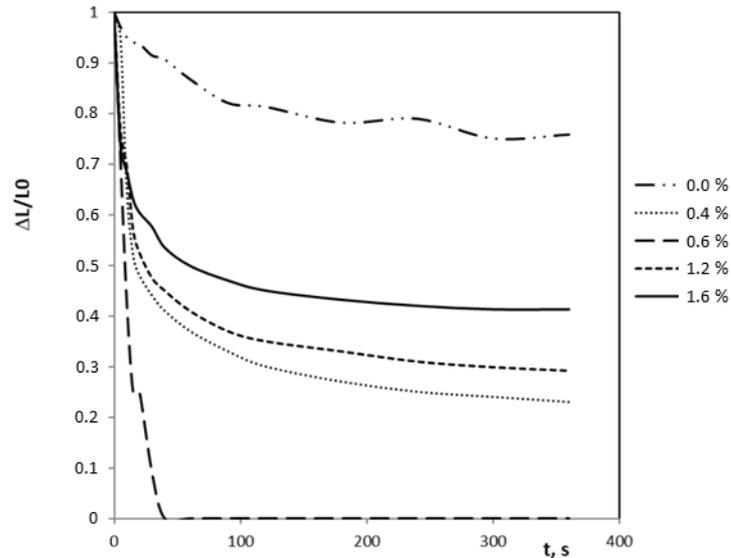


Fig. 3. Thermal residual deformation of indentations on epoxy resins ED-20 with As nanoparticles at 75°C

However, only the composite with a concentration in a small range showed complete recovery after microindentation at 75°C (Fig. 1(c)). Although all other concentrations of nanoparticles increased their recovery in comparison with the control, they reached a maximum recovery of only about 30%. This indicates that there is an optimal concentration of nanoparticles that ensures complete recovery. At 80°C, the range of concentrations where complete recovery occurred somewhat expanded, but still remained limited.

Figures 4 and 5 show the specific behavior of permanent deformation at a certain concentration, which varied depending on the nanoparticles doped in ED-20.

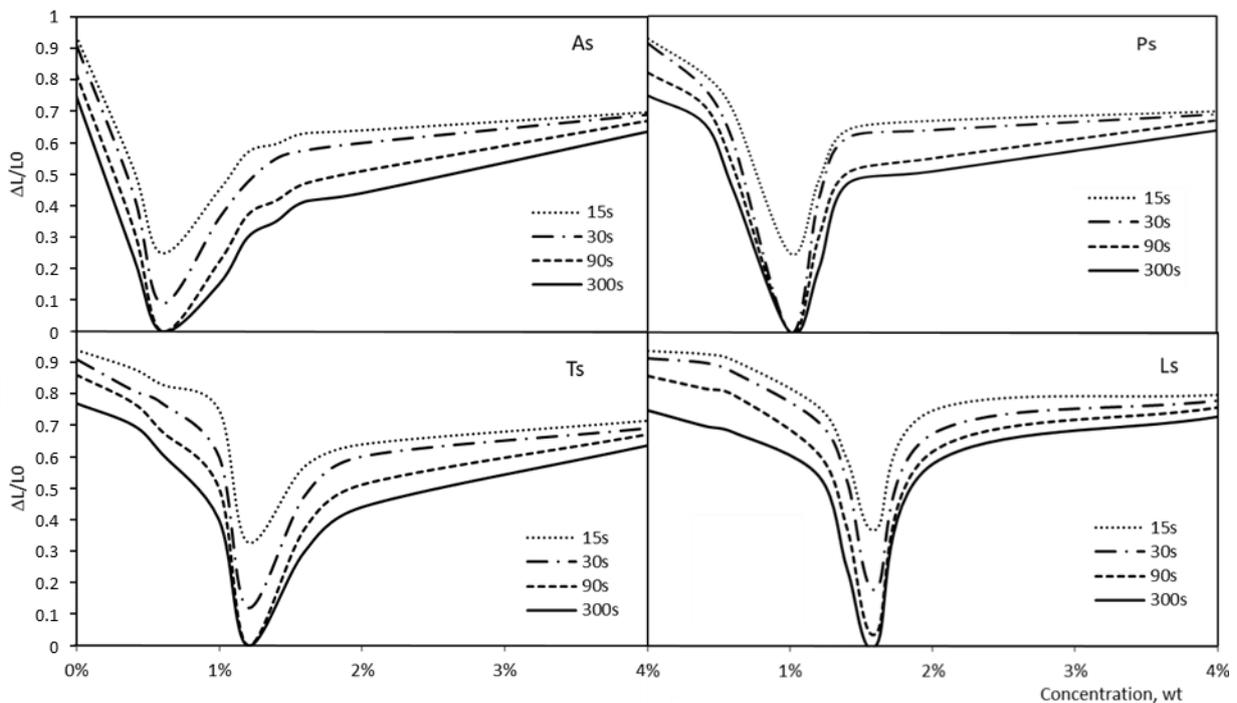


Fig. 4. Thermal residual deformation of imprints on epoxy resins ED-20 with SiO₂ nanoparticles depending on the concentration at 75°C

It can be seen from the obtained data that the minimum residual deformation of the composites is located at different concentrations of nanoparticles. That is, the particle-resin interaction has a different meaning for particles obtained by different synthesis methods. The intensity of the interaction introduced by nanoparticles coincides with the assumptions obtained in [26], i.e., it is due to the strength of surface sites formed during the synthesis of nanoparticles. The fastest hardening effect among silica is produced by As particles having strong Lewis acid sites. While the weakest and most delayed effect is shown by Ls particles, the surface of which has only Brønsted main sites.

A similar situation arises for samples containing aluminum oxide nanoparticles. The Aa particles, having a more active surface [26], strengthen the composite faster than other particles. At the same time, La particles having the most passive surface strengthen the composite at the highest concentration of particles. In the same way, the efficiency of the particle-resin interaction can be traced when changing the method of particle synthesis [27,28]. The variation in the activity of the particle surface leads to a change in their concentration at which the maximum recovery of the deformation is achieved.

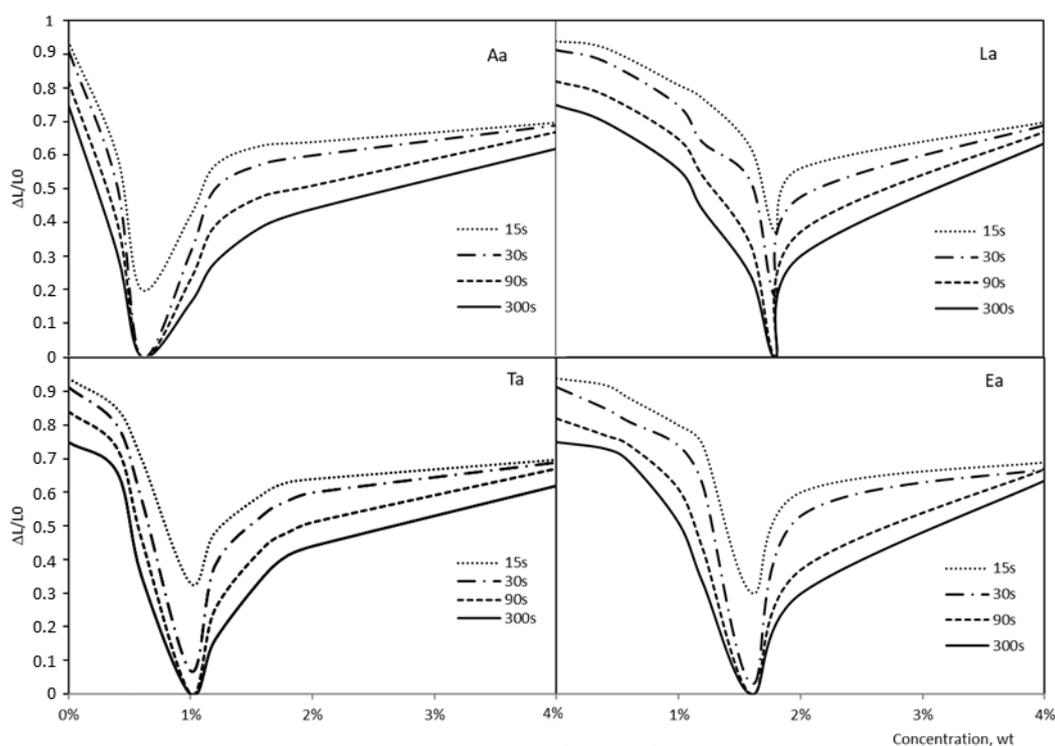


Fig. 5. Thermal residual deformation of imprints on epoxy resins ED-20 with Al₂O₃ nanoparticles depending on the concentration at 75°C.

In [29], a correlation was traced between the dependences of the activation energy of the deformation process and the microindentation deformation itself on the concentration of nanoparticles. Both values have a clear minimum at the concentration, when there is maximum healing of the deformation and a much smaller change in the activation energy at other concentrations. Apparently, at such a concentration, a change in the structure of the polymer occurs. At low concentrations, there are few additional polymer-nanoparticle bonds, and the polymer is relatively easily deformed. As the concentration increases, the number of strengthened bonds increases, reaching a maximum at the optimum value. That is, the number of doped nanoparticles can use all the free bonds of the polymer creating an additional structural network. With a further increase in concentration, forced bonds appear between

nanoparticles (agglomeration), which are much weaker. It is important to note that the number of additional polymer-nanoparticle bonds depends on the activity of the nanoparticle surface [26] and varies depending on the method of their synthesis.

Within the framework of the model of delocalized atoms [23], the relaxation of plastic deformation during heating (thermal stimulation) is explained by the return of exciting delocalized atoms to their main undeformed state [17]. The volumes of delocalization of atoms for pure ED-20 and the one consisting of 1.6 wt% SiO₂ [29] were approximately 97 and 63 Å³, respectively.

Therefore, it can be assumed that a group of atoms in the conjugation site of the system of covalent bonds is responsible for the viscous strain of epoxy polymers. Its molecular mechanism is reduced to local displacements (delocalization) of the bridge oxygen atom in the Si-O-Si bond [16,17]. Depending on the activity of the surface of nanoparticles and the intensity of the bonding of O-Si or O-Al groups, which can be determined using IR spectroscopy [30,31], the activation energy of composites with particles of the same chemical composition but different synthesis methods may vary. A smaller volume of delocalization of atoms means that in a given volume, where the polymer has been deformed, there are more units of delocalization, i.e. the volume of fluctuations is larger at any given temperature.

Conclusions

The kinetics of thermally stimulated relaxation of inelastic strains in an epoxy polymer with SiO₂ and Al₂O₃ nanoparticles was studied by restoring imprints in epoxy resin samples at elevated temperatures. For all samples, the maximum relaxation value was observed at 75°C, which is 10°C below the glass transition temperature.

We showed that although pure epoxy samples received a maximum recovery of 20%, samples with certain concentrations of nanoparticles had complete relaxation (disappearance of imprints). At higher concentrations, complete relaxation was not achieved.

It is shown that a change in the method of nanoparticle synthesis leads to a change in the concentration at which the relaxation maximum is reached.

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