Creep and relaxation of polyester acrylate composites

Vladimir Erofeev, Nikolay Fomin, Viktor Ivlev, Vyacheslav Yudin and Anton Myshkin
National Research Mordovian State University, Saransk, Russian Federation

a464aa@gmail.com

Abstract. It is shown that creep and relaxation are the most important properties for structural materials. This research presents the results of a study of filled polyester acrylate composites’ creep and relaxation. The comparison of mechanical indicators with similar for unfilled materials is shown in this work. Investigation of mechanical properties of the samples was carried out on a universal testing machine Shimadzu Autograph AG-X Series at room temperature. It was revealed that the intensity of stress and creep relaxation in the composite is much weaker than in pure resin. It was found that composites are characterized by a logarithmic time dependence of stress relaxation and creep. Logarithmic dependences for the studied parameters are of the same nature. Changes in indicators are mainly due to the properties of the binder.

1. Introduction
Information on the properties of polymer composite materials is contained in numerous works of domestic and foreign authors [1-4, 8-20]. It is known that under the influence of long-acting loads, the behavior of the composites is inelastic. With loads that do not change over time, the deformations of the composites increase, while stresses can decrease. An increase in deformations and a drop in stresses under constant loads are called creep and relaxation, respectively. These are important characteristics of concrete intended for the manufacture of products that during operation will be subjected to prolonged exposure to loads [6,7]. The creep of the material determines the performance of the product for load-bearing structures.

The results of compressive and bending strength tests of composites based on polyester acrylate (PEA) MGF-9 are presented in work [5]. Tests were conducted in order to optimize the composition and technology of obtaining these materials. Despite numerous studies of polymer composites, the question of the effect of various fillers in polyester acrylate polymer concrete has not been clarified until recently. The properties of filled polymer composites should be considered in comparison with the properties of unfilled polymer composites. The results obtained are analyzed to obtain additional information about the mechanisms that affect their mechanical relaxation.

In this work, experimental studies of the creep and stress relaxation of unfilled polyester acrylate composites, as well as composites with quartz filler, were carried out. Creep was studied on samples $1 \times 1 \times 3$ cm.

2. Materials and Methods
To obtain the composite material the following were used: as binder - oligoester acrylate of the MGF-9 brand, hardening initiator - cyclohexanone peroxide (PCON-2) and curing accelerator - cobalt
octoate (OK-1). The filler was ground quartz sand of different fractions of the Smolnensky deposit of the Republic of Mordovia. Mixtures were prepared manually. Samples were made in metal forms pre-lubricated with paraffin. To study the mechanical properties, rectangular samples with dimensions of 10×10×30 cm were used.

The mechanical properties of the samples were determined on a Shimadzu Autograph AG-X Series universal testing machine. Test process management and pre-processing of data obtained on this machine are performed using the TRAPEZIUM X*1 software. The measurements were carried out with a constant velocity of movement of the active capture of 3 mm / min. The compression force was directed along the long axis of the sample.

To study the relaxation of mechanical stresses, the sample was stepwise loaded to a predetermined stress level, then the machine grips were fixed (constant deformation remained) and the dependence of stress on time was recorded for 1800 seconds. Then the load increased to the next level and the relaxation curve continued to be recorded.

To study creep, the sample was stepwise loaded at a constant speed of 3 mm / min to a predetermined force, which was held for 1800 s. During this time, the creep curve (time dependence of deformation) was recorded. Then the load increased to the next value. At each fixed load, a creep curve was recorded.

All measurements were performed under normal conditions.

3. Results
Creep is directly related to the accumulation of irreversible plastic deformations in a composite loaded with constant loading. Over time, an increase in elastic, highly elastic and plastic deformations is observed. When the load is removed at a certain point in time t1, the elastic deformation e0 is instantly restored, after which a slow decrease in deformation in time occurs — relaxation of the deformations (the opposite consequence), [6,7,16]. Relaxation of tension is directly related to the response of the material structure to prolonged mechanical stress in the constant deformation mode and is important in the development of new composite materials [6,7]. In our experimental studies, unfilled and filled polyester acrylate (PEA) polymer composites were considered.

Typical creep and tension relaxation curves of polyester acrylate composites are shown in Fig. 1 (screenshots from the control computer).

![Figure 1](screenshots from the control computer).

Plastic deformation of polymeric materials is carried out mainly due to the irreversible movement of fragments of macromolecules. A decrease in the effective cross section of the resin material when replacing part of its volume with filler particles limits in some way freedom of movement, which may be one of the reasons for increasing the effective modulus of the composite, however, it is not the only and, presumably, not the main one. The second possible reason is a decrease in the tangential (along
the interphase boundary) mobility of fragments of macromolecules that provide plastic deformation of the matrix. We believe that the same reasons are also responsible for the decrease in the intensity of tension and creep relaxation processes observed in composites as compared to pure resin.

Creep like PEA without filler and with the addition of sand at the investigated strains in the whole time interval sufficiently well (R²> 0,99) is described by a logarithmic function (Fig. 2) of the form

$$\varepsilon = a \ln t + \delta$$  \hspace{1cm} (1)

where $\varepsilon$ is the deformation (deflection), mm, $t$ – time (sec); $a$ and $\delta$ – constants.

The regression equations and the values of the approximation reliability criterion are given in Table 1. Parameter $b$ in formula (1) characterizes the intensity of the creep process (slope of the straight line in Fig. 2). Table 2 shows that, firstly, its value increases with increasing stress, and, secondly, it is almost an order of magnitude lower for the composite compared to pure PEA (Fig. 3). Therefore, the introduction of a filler significantly reduces the creep rate, while the nature of the time dependence (logarithmic) practically does not change.

The behavior of the parameter $\delta$ was not actually observed.

| $\sigma$, MPa | Equation               | $R^2$ |
|--------------|------------------------|-------|
| PEA          | $y = 0.1874 \ln(x) + 0.1118$ | 0.9952 |
|              | $y = 0.7094 \ln(x) - 0.9904$ | 0.9904 |
|              | $y = 0.9992 \ln(x) - 0.5493$ | 0.9096 |
| PEA + sand   | $y = 0.0179 \ln(x) + 0.1177$ | 0.9956 |
|              | $y = 0.0428 \ln(x) + 0.1708$ | 0.9925 |
|              | $y = 0.1088 \ln(x) + 0.156$ | 0.9859 |

Figure 2. Creep of PEA at a stress of 10 MPa. Axis of time on a logarithmic scale.
The dependence of the parameter characterizing the intensity of the process from the stress: creep (a, left) and tension relaxation (b, right); the upper lines are PEA without filler, the lower lines are a composite with a fine sand fraction.

Tension relaxation in PEA, both without filler and with sand additives, at the studied tensions over the entire time interval is described quite well ($R^2 > 0.98$) by a logarithmic function (Fig. 4) of the form

$$\Delta \sigma = \beta - b \ln t,$$

where $\Delta \sigma$ – tension change, MPa; $t$ – time (sec); $\beta$ and $b$ – constants.

The regression equations and the values of the approximation reliability criterion are given in Table 2.

**Table 2. Parameters of stress relaxation in PEA and composite.**

| $\sigma$, MPa | Equation | $R^2$ |
|---------------|----------|-------|
| **PEA**       |          |       |
| 10            | $y = 954.5 - 67.38 \ln(x)$ | 0.9691 |
| 20            | $y = 1972.9 - 138.7 \ln(x)$ | 0.9937 |
| 30            | $y = 3010.2 - 244.9 \ln(x)$ | 0.9642 |
| **PEA + sand**|          |       |
| 10            | $y = 808.65 - 29.58 \ln(x)$ | 0.9917 |
| 20            | $y = -91.13 \ln(x) + 1673.3$ | 0.9976 |
| 30            | $y = 2891.9 - 180.9 \ln(x)$ | 0.9827 |

Parameter $b$ characterizes the intensity of the relaxation process (slope of the straight line in Fig. 4). From table 2 it is seen that, firstly, its value increases with increasing stress, and, secondly, it is less for the composite compared to pure PEA (Fig. 3). Consequently, the introduction of a filler decreases...
the relaxation rate, although weaker than the creep rate. The nature of the time dependence (logarithmic) also practically does not change.

The value of parameter $\beta$ is close to the value of the initial stress.

It should be noted, however, that at sufficiently high stress, in some cases, a significant deviation from the logarithmic law can be observed (Fig. 4 b).

In experiments with cycling during unloading, processes and relaxation of tension and creep occur simultaneously in the sample, but at the initial stage (high stresses), stress relaxation occurs predominantly, and at the final stage (low stresses), creep takes precedence. In fig. Figure 5 shows the time dependence of the stress for the upper part of the unloading of the sample in the first cycle for one of the PEA samples. The stress scale in this figure is built on a logarithmic scale, while the experimental points fit well on a common straight line.

In experiments with cycling during unloading, processes and relaxation of stress and creep occur simultaneously in the sample, but at the initial stage (high stresses), stress relaxation occurs predominantly, and at the final stage (low stresses), creep takes precedence. Figure 5 shows the time dependence of the stress for the upper part of the unloading of the sample in the first cycle for one of the PEA samples. The stress scale in this figure is built on a logarithmic scale, while the experimental points fit well on a common straight line.

\[ \sigma = \sigma_0 \exp\left(-t/\tau\right), \quad (3) \]

where $\sigma_0$ and $\tau$ – constants.

**Figure 5.** The time dependence of the stress in the upper part of the unloading curve during cycling.

This form usually has a time dependence of the parameters of the relaxation process with relaxation time $\tau$. However, in our case, the physical meaning of the parameter $\tau$ needs additional understanding.

It was shown in the following works [6,7] that a logarithmic law of type (1) or (2) for the time dependence of mechanical relaxation processes is also characteristic of cured synthetic resins (polyester and epoxy) and composites based on them with different fillers. The exponential law corresponding to relaxation processes with one relaxation time is not observed for these materials. It follows that the logarithmic law in these materials, including those studied in this work, is most likely associated with the multiplicity of molecular processes occurring in them.

### 4. Conclusion

1. The mechanical tests of cured polyester acrylate resin and composites based on it with silica sand as a filler were carried out.
2. It was shown that the intensity of stress and creep relaxation in the composite is much weaker than in pure resin.
3. It was shown that PEA and composites based on it are characterized by a logarithmic time dependence of stress relaxation and creep, which is also characteristic of other materials based on synthetic resins.
4. Based on the similarity of time dependences, it was concluded that the atomic-molecular mechanisms of stress relaxation and creep are of the same nature.
5. It is shown that during a cyclic change in the compressive load, stress relaxation processes prevail at the beginning of unloading, and creep processes prevail at the end of it.
6. It is concluded that the main laws of behavior of the relaxation properties of PEA-based composites, like other composites based on synthetic resins, are mainly due to the properties of the binder.

Acknowledgements
The work was carried out as part of the project 18-48-130013 p.a "Comprehensive study of physicochemical processes in composite materials based on epoxy resins and other synthetic polymers, promising for use in construction".

References
[1] Erofeev, V, Bobryshev, A, Shafigullin, L, Zubarev, P, Lakhno, A, Darovskikh, I and Tretiakov, I 2016 Building Heat-insulating Materials Based on the Products of the Transesterification of Polyethylene Terephthalate and Dibutyltin Dilaurate Procedia Engineering 165 1455-1459 doi: 10.1016/j.proeng.2016.11.879
[2] Erofeev, V, Smirnov, V and Myshkin, A 2019 The study of polyester-acrylate composite’s stability in the humid maritime operating conditions Materials Today: Proceedings 19 2255–2257 https://doi.org/10.1016/j.matpr.2019.07.547
[3] Erofeev, V, Smirnov, V and Myshkin, A 2019 The study of species composition of the mycoflora, selected surface samples poliferation composites in humid maritime climate IOP Conference Series: Materials Science and Engineering 698 https://doi.org/10.1088/1757-899X/698/2/0220828
[4] Erofeev, V T 2016 Frame Construction Composites for Buildings and Structures in Aggressive Environments Procedia Engineering 165 1444-1447 doi: 10.1016/j.proeng.2016.11.877
[5] Myshkin, A V and Erofeev, V T 2013 Structure optimization of polyesteracrylate composites Regional architecture and construction 3 56–61
[6] Ivlev, V I, Sigachyov, A F, Fomin, N E and Yudin, V A 2017 Relaxation in resins with low-frequency mechanical cycling Materials Physics and Mechanics 32 207-212
[7] Ivlev, V I, Sigachyov, A F and Yudin, V A 2019 Stress relaxation and creep of a composite material based on epoxy resin filled with the hemp boon Materials Physics and Mechanics 42 484–490
[8] Pargi, M N F, Teh, P L, Hussiensyah, S, Yeoh, C K and Ghani, S A 2015 Recycled-copper-filled epoxy composites: the effect of mixed particle size J Mech Mater 10 3 https://doi.org/10.1186/s40712-015-0030-2
[9] Qiu, Y, Wu, D, Xie, W, Wang, Z and Peng, S 2018 Thermoplastic polyester elastomer composites containing two types of filler particles with different dimensions: Structure design and mechanical property control Composite Structures 197(1) 21-27 https://doi.org/10.1016/j.compstruct.2018.05.035
[10] Atuanya, C U, Government, M R, Nwobi-Okojie, C C and Onukwuli, O D 2014 Predicting the mechanical properties of date palm wood fibre-recycled low density polyethylene composite using artificial neural network Int J Mech Mater Eng 9 7 https://doi.org/10.1186/s40712-014-0007-6
[11] Willis, M R and Masters, I 2003 The effect of filler loading and process route on the three-point bend performance of waste based composites Composite Structures 62(3–4) 475-479 https://doi.org/10.1016/j.compstruct.2003.09.021
[12] Kinvi-Dossou, G, Matadi, Boundimba, R, Bonfoh, N, Garzon-Hernandez, S, Garcia-Gonzalez, D, Gerard, P and Arias, A 2019 Innovative acrylic thermoplastic composites versus conventional composites: Improving the impact performances Composite Structures 217 1-13 https://doi.org/10.1016/j.compstruct.2019.02.090
[13] Dinmohammadi H R, Davoodi A, Farzi G A and Korojy B 2014 Water-based acrylic copolymer as an environment-friendly corrosion inhibitor onto carbon steel in 1 M H2SO4 in static and dynamic conditions Int J Mech Mater Eng 9 24 https://doi.org/10.1186/s40712-014-0024-5

[14] Bulut H A and Şahin R 2019 A study on mechanical properties of polymer concrete containing electronic plastic waste Composite Structures 178 50-62 https://doi.org/10.1016/j.compositesb.2017.06.058

[15] Zhang S Y and Kitching R 1987 Experimental relaxation behaviour of chopped-strand mat glass fibre reinforced polyester beams in three point bending Composite Structures 7(1) 59-76 https://doi.org/10.1016/0263-8223(87)90060-2

[16] Palanivelu S, Paepegem W V, Degrieck J, Vantomme J, Kakogiannis D, Ackeren J V, Hemelrijck D V and Wastiels J 2011 Crushing and energy absorption performance of different geometrical shapes of small-scale glass/polyester composite tubes under quasi-static loading conditions Composite Structures 93(2) 992-1007

[17] Dhakal H N, Zhang Z Y, Bennett N and Reis P N B 2012 Low-velocity impact response of non-woven hemp fibre reinforced unsaturated polyester composites: Influence of impactor geometry and impact velocity Composite Structures 94(9) 2756-2763

[18] Gomes C E M, Sousa A K D, Araujo M E S O, Ferreira S B and Fontanini P 2019 Mechanical and Microstructural Properties of Redispersible Polymer-Gypsum Composites Mat. Res. 22(3) https://doi.org/10.1590/1980-5373-mr-2018-0119

[19] Santos C M, Silva B C, Backes E H, Montagna L S, Pessan L A and Passador F R 2018 Effect of LLDPE on Aging Resistance and Thermal, Mechanical, Morphological Properties of UHMWPE/LLDPE Blends Mat. Res. 21(5) https://doi.org/10.1590/1980-5373-mr-2018-0320

[20] Cunha C B, Lopes P P, Mayer F D and Hoffmann R 2018 Assessment of Chemical and Mechanical Properties of Polymers Aiming to Replace the Stainless Steel in Distillation Column Mat. Res. 21(3) https://doi.org/10.1590/1980-5373-mr-2017-0679