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Research Article

Effect of graphene on the creep and stress relaxation behaviors of epoxy-nanocomposite in viscoplastic deformation regime

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ABSTRACT

In this study, the creep and stress relaxation behaviors of epoxy nanocomposites reinforced with functional graphene in the viscoplastic deformation regime were investigated. Determining these behaviors, which are important indicators of viscoelastic and viscoplastic behaviors, is critical for durability and reliability in the long-term behavior of polymer-based nanocomposites. The effect of graphene, which has been used in many research fields in recent years and has superior mechanical, thermal, and electrical properties, on these time-dependent behaviors has been experimentally determined. To ensure that the nanocomposites with a content of 0.1 wt% functional graphene remained in viscoplastic deformation, the creep measurement was experimentally measured at 200 MPa constant stress level, and stress relaxation tests were experimentally conducted at 35.5% constant strain level for the 7200s. The results were compared with pure epoxy and observed a 48.5% improvement in creep resistance and a 21.9% improvement in stress drop with 0.1% f-GNF reinforcement to epoxy in the viscoplastic area. In this study, different from the studies in the viscoelastic and yield region generally discussed in the literature, the creep and stress relaxation behaviors of nanocomposites in the viscoplastic area were determined and important results were revealed for the determination of comprehensive material behavior in the design of nanocomposite structures.

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INTRODUCTION

Graphene [1] has gained great attention in the scientific research world because of its unusual two-dimensional and single carbon atom weight structure since its discovery in 2004. Because of its excellent mechanical, thermal, electrical properties and high surface area per volume, graphene is used as a reinforcement material in polymer-based nanocomposites [2]. Epoxy is a widely used matrix material in polymer-nanocomposites, and various material properties of this thermoset resin have been enhanced by graphene reinforcement [3,4]. However, the inability to distribute graphene uniformly in the epoxy and produce a strong interfacial interaction between graphene and epoxy leads the material characteristics to deteriorate [5]. To overcome

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these problems, it is necessary to determine the most suitable material production method [6,7] and to functionalize graphene with various surfactants. Thus, the agglomeration problem can be minimized [3,8]

Polymer-nanocomposite materials show viscoelastic and viscoplastic behavior, and time-dependent characteristics such as stress relaxation and creep must be determined to determine a comprehensive material response. It is known that polymeric materials suffer from time-dependent plastic deformations such as creep and stress drops even at room temperature [9]. Considering this case, it is essential to consider the creep and relaxation behavior of polymer-nanocomposite materials in terms of durability and reliability in long-term applications [10].

Experimental studies on improving the creep resistance of polymeric materials with the reinforcement of different nanomaterials are presented [11–13]. When the creep and relaxation behaviors of epoxy-graphene nanocomposites are investigated, it is reported that the creep strain of the epoxy is reduced with graphene reinforcement. In the studies conducted, creep behaviors were investigated in the linear viscoelastic deformation regime representing 35% of the yield stress and around the yield region representing 70%, respectively [9,14,15]. There are limited studies in the literature on the stress-relaxation behavior of nanocomposites[16,17]. Colak et al, investigated the relaxation behavior of graphene-epoxy nanocomposites with the addition of 0.1 and 0.5 wt% f-GNF, and found an improvement in stress reduction compared to epoxy [15]. Hashemi et al, determined that the stress relaxation behavior of graphene-epoxy nanocomposites is interface-dependent [18]. According to our review, no study determines the creep and relaxation behaviors in the viscoplastic area of graphene-epoxy nanocomposites.

In experimental stress-strain behaviors of epoxy and epoxy-graphene nanocomposites, linear viscoelastic behavior, yielding, followed by strain softening and strain hardening is observed in material behavior, respectively [19–21]. In these studies, rate dependence is more pronounced in the viscoplastic area. Determining the creep and relaxation behavior in the viscoplastic areas where strain hardening starts is essential for all the material responses.

In this study, the creep and stress relaxation behavior of the graphene-epoxy nanocomposite in the viscoplastic deformation regime was experimentally determined at room temperature by adding 0.1wt% functionalized graphene (f-GNF) to the epoxy. The yield strength of epoxy-nanocomposite with a content of 0.1wt% functionalized graphene materials at a strain rate of 1.E-1 /s was determined as 150 MPa by Colak et al [15]. Creep test was performed at 200 MPa constant stress level and stress relaxation test at 35.5% constant strain level to ensure a viscoplastic deformation regime. These experimental results in the viscoplastic area were compared with the pure epoxy obtained by Bakbak et al [20]. When the results were examined, an improvement of 48.5% in the creep resistance and 21.9% in the stress drop of the nanocomposite material was determined compared to the epoxy. In particular, increasing the interfacial interaction with the functionalization of graphene and the material production method (three roll milling) was effective in these improvements. Functionalized graphene acted as a barrier by restricting the movements of the epoxy chains and had a positive effect on these time-dependent properties.

MATERIAL AND METHODS

Materials

This study used the Araldite LY 564/ Aradure 2954 epoxy combination as the matrix material. The reinforcement material is graphene, which is a product of the electric arc discharge method [22]. The functionalization procedure was carried out with Triton X-100 surface surfactant to improve the interaction of graphene with the matrix material and produce a more homogenous distribution. The functionalization processes of graphene are given in detail in the study by Colak et al. [15].

Sample production

Functionalized graphene-epoxy nanocomposites were produced by the three-roll milling (3RM) method, which aims for a more homogeneous distribution by creating high shear stresses on the material. At the production phase, epoxy and f-GNF are first mixed in a magnetic stirrer at 400 rpm for 15 min. The mixture is calendared with 3RM. To obtain the most optimal result, this process is repeated in five cycles [15]. After this process, the hardener is added to the f-GNF-epoxy mixture with a weight ratio of 100:35, as recommended by the manufacturer. The mixture is then stirred on a magnetic stirrer at 400 rpm for 5 min. To remove the gas bubbles in the mixture, the degassing process is performed for 60 min using a vacuum chamber. Finally, the mixture is poured into the mold and cured at 60°C for one h, then post-cured at 160°C for four h. The production stage of nanocomposite samples is presented in Figure 1.

Exact 80E, three roll milling device, is used for the homogeneous distribution of f-GNF into epoxy matrix. This equipment and the collection of materials in the calendared process are shown in Figure 2.

Experimental Results

In this study, the creep and relaxation behaviors of f-GNF-epoxy nanocomposite material in the viscoplastic area were investigated by two different tests. These are the creep test at constant stress level and stress relaxation tests at constant strain level under uniaxial compression loading. Tests are conducted on the cylindrical-shaped samples with a diameter of 12 mm and a length of 12 mm. The creep and stress relaxation tests of f-GNF-epoxy nanocomposites with a content of 0.1wt% f-GNF are performed using Instron 5982 (100 kN capacity) universal static test device

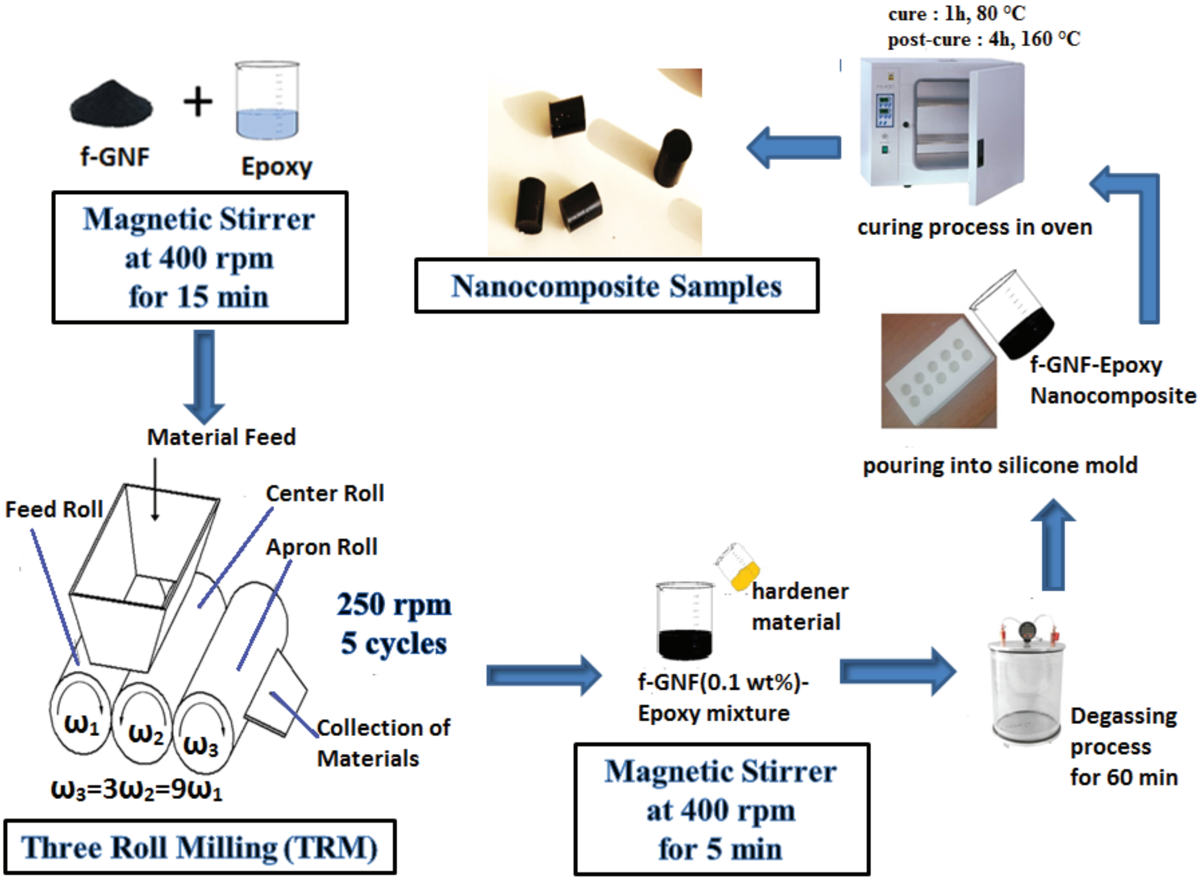

Figure 1. Schematics of nanocomposite manufacturing by using 3RM.

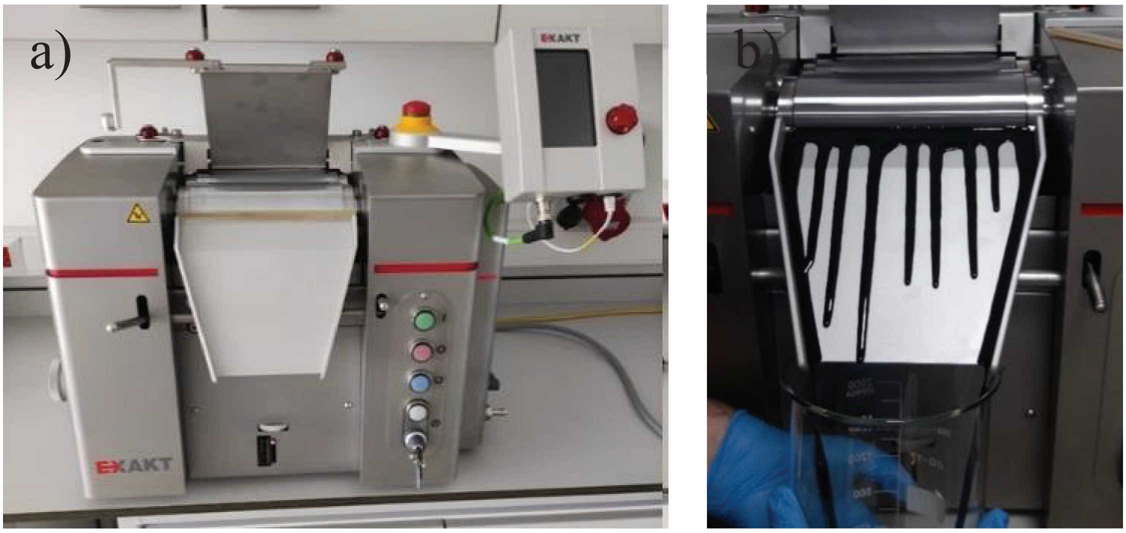

Figure 2. Three roll milling equipment (Exact 80E) and image from manufacturing.

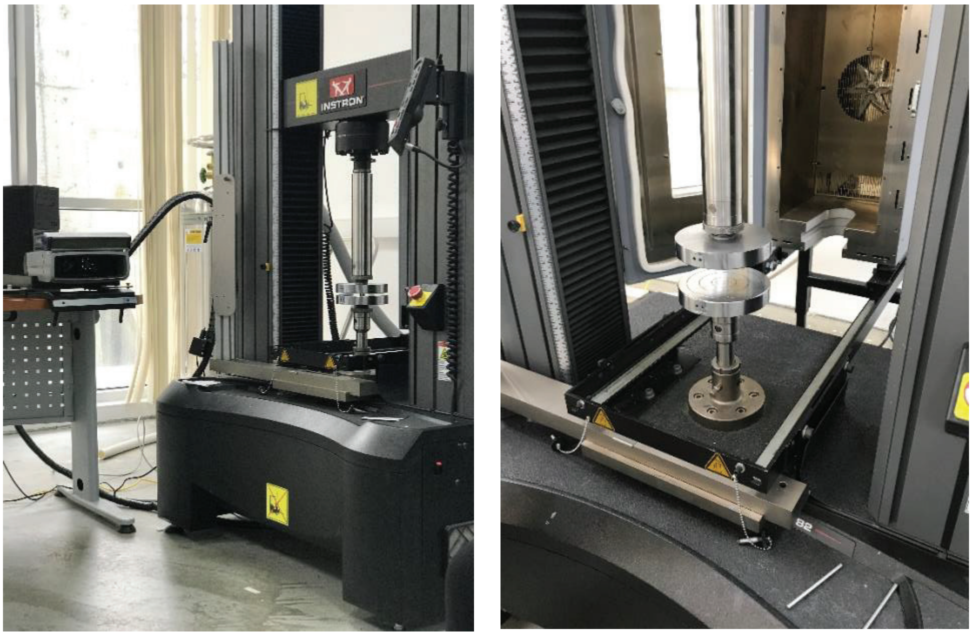

Figure 3. Universal static test device equipment used for experimental characterization.

at a strain rate of 1.E-1 /s and at room temperature. Test equipment is shown in Figure 3.

In the stress-controlled Creep tests, the amount of force corresponding to constant stress levels was calculated by the device software and kept constant during the experiment, and the movement of "the crosshead of the device" was recorded depending on time, and thus the creep strain is measured. In experimental studies investigating the effect of f-GNF reinforcement on the creep strain and stress drop behavior of epoxy in viscoplastic deformation regime, both creep and stress relaxation tests were repeated three times and average results were reported. Repeatability was ensured in the tests. The obtained test results are compared with pure epoxy from Bakbak et al [20].

Creep Test

Creep tests are performed to determine time-dependent plastic deformations under constant stress. In this study, the creep behavior of the f-GNF-epoxy nanocomposite with a content of 0.1 wt% f-GNF in the viscoplastic area is detected. The yield strength of the material was determined as 153 MPa [15]. Considering the yield strength, tests were carried out at a constant stress level of 200 MPa for two h (to ensure a viscoplastic deformation regime) to investigate the creep behavior of nanocomposites in the viscoplastic area. The creep response of the f-GNF-epoxy nanocomposite material was compared to that of pure epoxy reported by Bakbak et al. [20]. The true stress-true strain behavior from the test results is shown in Figure 4 and a comparison of the creep strain results as a function of time is depicted in Figure 5.

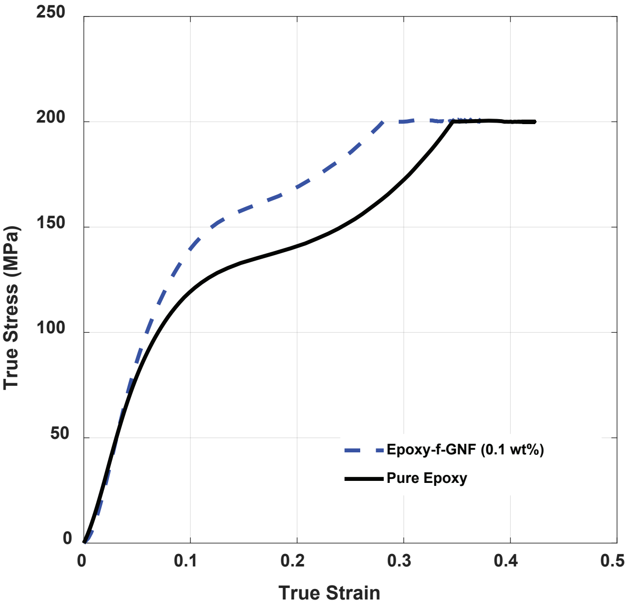

Figure 4. True stress–true strain curve for creep test conducted at 200 MPa stress level. Experimental data for pure epoxy is taken from Bakbak et al. [20].

As can be seen from Figures 4 and 5, the nanocomposite's creep strain is lower than epoxy. This situation is expected because, when we look at the literature [10,23,24], it is understood that the reinforcement element improves the creep resistance. This improvement in the creep resistance of the nanocomposite material is due to the reduction in both the viscoelastic and viscoplastic components of the total creep strain. Increased creep resistance with the

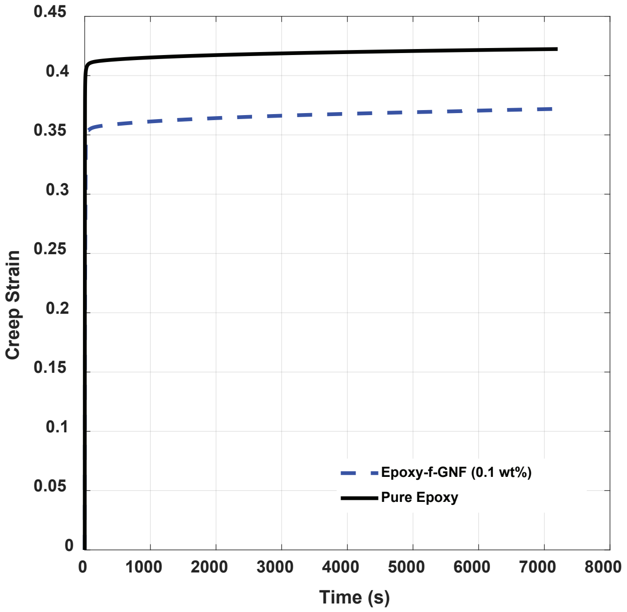

Figure 5. Comparison of the time-dependent change of creep strain in the viscoplastic area. Experimental data for pure epoxy is taken from Bakbak et al. [20].

addition of nanofillers such as graphene or carbon nanotubes can be attributed to several factors. In work by Zhang et al. [23], it is demonstrated that single-walled carbon nanotube additives effectively limit the load-induced reorientation of epoxy chains and result in a significant slowing of the creep response. The nanofillers act as sites, blocking the movement of the epoxy chains, hence, they restrict the viscous flow of the amorphous epoxy. Also, the large interfacial area which contributes to significant interface adhesion between the nanofillers and the epoxy matrix improves the load transfer. Ensuring a good load transfer between the epoxy matrix and nanofiller will give rise to good creep resistance of the nanocomposite [23,24]. Another reason for the improvement in viscoelastic properties such as creep resistance is considered to be due to the increase in cross-link density with the addition of functionalized graphene (f-GNF) to the epoxy. Cross-linked density is an important factor affecting the mechanical and thermal properties of epoxy-nanocomposites [25,26]. While high cross-linked density obtained by adding reinforcement to the polymer provides an increase in these properties, improvements are not sufficient at low cross-linked density. The reason for this is the low interfacial interaction and strength between nanofillers and the matrix [27]. To overcome this case, the functionalization process of the reinforcement element becomes important [15]. In the work of Yu et al., functionalized graphene oxide (GO) was used as a reinforcement and the cross-linked density of the nanocomposite was calculated. A higher cross-linked density was obtained compared to pure epoxy, and the improvement in the properties of the nanocomposite was attributed to the higher cross-linked density [27]. As a result, it is also considered that the increase in cross-linked density affects the improvement of creep resistance by reducing and preventing the movements of epoxy chains. Here, the nanofiller restricts these movements by stretching the segments of the epoxy chains. Jian et al. also explained that the low creep strain of CNT-epoxy nanocomposite is achieved with this state of CNT during the deformation process [28].

The creep test results performed in the viscoplastic area are given in detail in Table 1. The change in creep strain with the addition of 0.1 wt% f-GNF to the epoxy is shown in Figure 6.

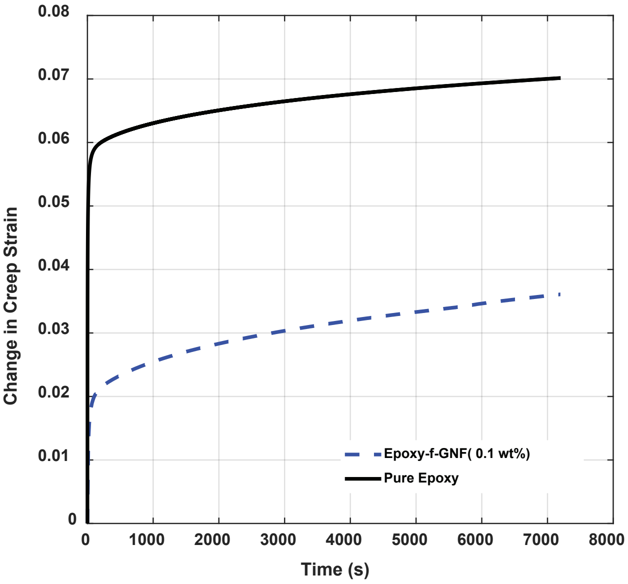

Figure 6. Comparison of the change in creep strain of pure epoxy [20] and f-GNF-epoxy nanocomposite materials in the viscoplastic deformation regime.

Table 1. Creep data obtained under the constant stress of 200 MPa

Constant Stress (MPa)	Material	Creep Strain (t =1 s)	Creep Strain (t =7200 s)	Change in creep strain	Decrease in creep strain (%)	Improvement in creep stain compared to pure epoxy (%)
200	Pure Epoxy [20]	0.35223	0.42238	0.07	20	48.5
200	Epoxy-f-GNF (0.1 wt%)	0.33584	0.37192	0.036	10.74	

When Table 1 and Figure 6 are examined in detail, it is observed that the creep strain decreases with f-GNF reinforcement. As a result of the two h creep test, the increase in creep strain was 20% in epoxy and 10.74% in nanocomposite material. Compared to epoxy, this decrease in creep strain, ie improvement in creep resistance, is 46%. It is observed that f-GNF has a considerable impact on creep behavior and boosts creep resistance in the viscoplastic zone of the material by preventing epoxy chain movements.

Stress Relaxation Test

Stress Relaxation tests are performed to determine the stress changes in the material under constant strain. In this study, the stress relaxation behavior of epoxy nanocomposites with a content of 0.1wt% f-GNF in the viscoplastic area was investigated at 35.5% constant strain level for 7200s. The stress relaxation response of the f-GNF-epoxy nanocomposite is compared to that of pure epoxy reported by Bakbak et al [20]. A comparison of the true stress-true strain behavior is depicted in Figure 7. The stress drop response as a function of time from the relaxation test is shown in Figure 8.

As seen in Figure 7, improvements in material properties are observed with the addition of f-GNF to epoxy. Likewise, in Figure 8, it is observed that the stress drops decrease with the addition of f-GNF. The improvement in the stress drop in the viscoplastic deformation regime of the nanocomposite material is more pronounced than in the viscoelastic deformation regime where the time dependence is lower [15]. Here, graphene plays a role in increasing the strength of the material by restricting the movements of the epoxy chains. The results of the stress relaxation test performed in the viscoplastic area are given in detail in Table 2. The change in stress behavior with the addition of f-GNF to the epoxy is presented in Figure 9.

It is seen in detail from the data in Table 2 and the changes in Figure 9 that the stress drop is improved by f-GNF reinforcement. The stress relaxation test revealed that epoxy had a stress drop of 29.5%, whereas f-GNF-Epoxy nanocomposite material had a stress drop of 22%. With the addition of 0.1% f-GNF to the epoxy, the improvement in the stress relaxation behavior in the viscoplastic deformation regime is approximately 25%. Functional graphene

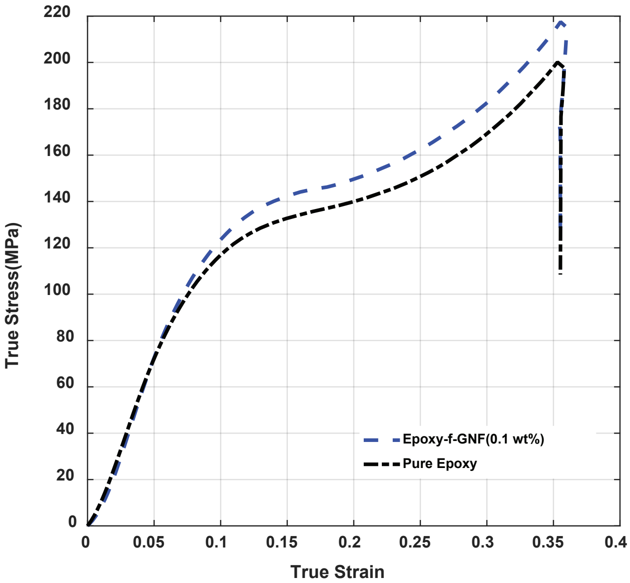

Figure 7. True stress–true strain curve for stress relaxation test performed at 35.5% strain level.

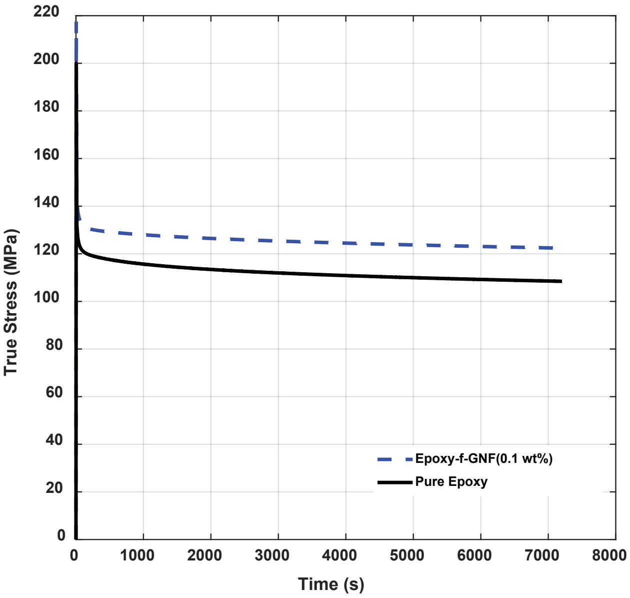

Figure 8. Comparison of the time-dependent change of stress-drop in the viscoplastic area.

Table 2. Stress relaxation data obtained under 35.5% constant strain

Constant Strain (%)	Material	Initial stress [MPa]	Last stress [MPa]	Stress Drop [MPa]	Stress Drop (%)	Improvement in stress drop compared to epoxy (%)
35.5	Pure Epoxy [20]	153.68	108.44	45.2	29.5	21.9
35.5	Epoxy-f-GNF (0.1 wt%)	157.3	122	35.3	22	

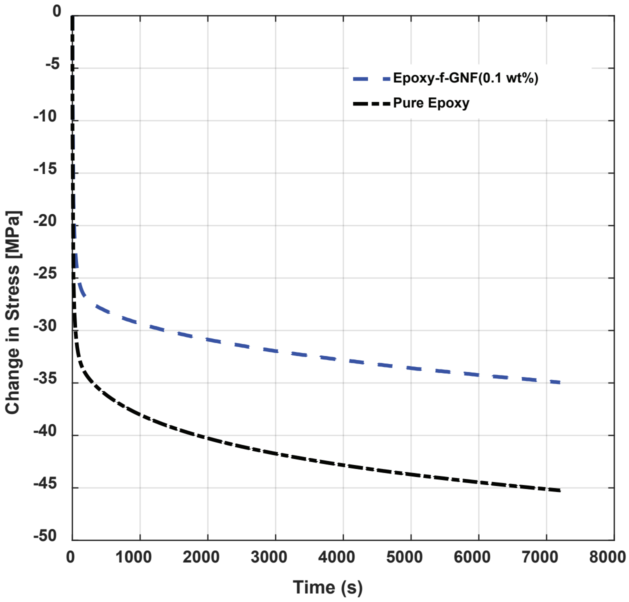

Figure 9. Comparison of the change in stress of pure epoxy [20] and f- GNF-epoxy nanocomposite materials in the viscoplastic deformation regime.

had a significant effect on the relaxation behavior as in the creep strain, and a strong interfacial interaction between f-GNF and the matrix material decreased the stress drop in the viscoplastic area of the material.

CONCLUSIONS

In this study, the effect of functionalized graphene on the creep and stress relaxation behavior of epoxy nanocomposites under uniaxial compression loading at room temperature was investigated experimentally. f-GNF epoxy nanocomposites were produced by using three roll milling as the main strategy to achieve a homogeneous dispersion and prevent agglomeration. Following the manufacturing, creep and stress relaxation behaviors of f-GNF reinforced epoxy-nanocomposite in viscoplastic deformation regime were investigated. This time-dependent behavior of the nanocomposite material was compared with that of pure epoxy. With the addition of f-GNF to epoxy, a decrease in creep strain was observed and a 48.5% improvement in creep resistance was detected compared to pure epoxy. Similarly, a reduction in the stress drops of f-GNF-epoxy nanocomposites was achieved and an improvement of 21.9% was observed compared to pure epoxy. Observed creep behavior can be divided into two main stages: the primary creep and secondary creep which is the steady-state case. Functionalization of graphene to increase interfacial interaction and uniform distribution of f-GNF in epoxy depending on the production method limited the movement of epoxy chains in the viscoplastic area. In our previous work [15], the functionalization procedure of pure graphene performed to increase the interfacial interaction between graphene and matrix material was confirmed by structural characterization results such as Raman spectroscopy and Fourier transform infrared spectroscopy (FT-IR). Depending on the functionalization of graphene and production method of nanocomposite, the improvements in the viscoelastic and viscoplastic properties obtained were attributed to the uniform distribution of the graphene in matrix material. The results were also demonstrated by the SEM images in the previous work [15]. The strong bond between epoxy and graphene significantly affected on the reduction of creep strain and stress drop in the viscoplastic deformation regime.

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AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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