Hybrid poly(ether ether ketone) composites reinforced with a combination of carbon fibres and graphene nanoplatelets

Dimitrios G. Papageorgiou*, Mufeng Liu, Zheling Li, Cristina Vallés, Robert J. Young, Ian A. Kinloch**

School of Materials and National Graphene Institute, University of Manchester, Oxford Road, M13 9PL, Manchester, United Kingdom

ARTICLE INFO

ABSTRACT

Poly(ether ether ketone) (PEEK), with its superb mechanical properties, excellent chemical resistance and high thermo-oxidative stability is one of the most important engineering thermoplastics for high-end applications. In this work, we investigate the elastic and viscoelastic properties along with the creep mitigation of two sets of samples: PEEK reinforced with graphene nanoplatelets (GNPs) and PEEK reinforced with a hybrid graphene/short carbon fibre (CF) filler. The melt viscosity of the PEEK nanocomposites was found to increase with increasing GNPs content; however, the viscosity of the hybrid CF-GNP samples with the highest filler content was equal to the one of the samples filled only with GNPs at low shear rates. This processability shows the advantage of GNPs over other nano and conventional fillers in the ability to use meaningful loadings. The introduction of GNPs improved significantly the stiffness and the storage modulus of the materials in both PEEK-GNP and PEEK-CF-GNP composites. Moreover, the presence of GNPs within the composites led to a restriction of the mobility of the macromolecular chains of PEEK, which resulted in enhanced creep properties at both room temperature and elevated temperatures. Overall, the nanocomposites produced displayed properties that make them attractive in applications where high stiffness and structural integrity at elevated temperatures are required.

1. Introduction

Polyarletherketones are considered very important engineering thermoplastics due to their combination of high strength and toughness, their high thermo-oxidative stability, excellent flame retardancy, their biocompatibility and their chemical and wear resistance [1]. Amongst polyarletherketones, poly(ether ether ketone) (PEEK) has emerged as one of the most important, high-performance engineering materials and has applications in demanding engineering components such as bearings and piston parts, in aerospace, automotive and chemical process industries, medical materials, etc [2]. The constant demand of advanced industries for even better-performing materials, has however led to the development of PEEK-based nanocomposites [3], where nanofillers such as carbon nanotubes [4–7] and (nano)fibers [8–12], silica [13], silicon carbide [14], tungsten disulphide [15], hydroxyapatite [16] and more recently, graphene [17–20] have been used as reinforcing agents in order to improve the mechanical, thermal and electrical properties of the matrix.

Graphene, since its first isolation [21] has attracted the attention of both industry and academia due to its extraordinary combination of properties, including its strength and stiffness, its high electron mobility at room temperature, its thermal conductivity and large surface area, amongst others [22–26]. As expected, this multifunctionality of graphene finds ideal use in the field of polymer nanocomposites, as the introduction of graphene-related materials (GRMs) has been proven to produce advanced, high-performing composites that can be used in a number of applications. Over the past years, the integration of GRMs in polymeric matrices has enabled the fabrication of polymer composites that are operational at high temperatures by enhancing their mechanical properties and creep resistance. The large interfacial area created between GRMs and the matrix, alters the network of polymer chains by preventing their extensive stretching and re-orientation during the creep tests that eventually leads to failure. Various kinds of nanofillers such as CNTs and nanoclays have also been used successfully in the past for the enhancement of the creep resistance of polymers [27–29]. A work from Zandiatashbar et al. [30] first reported the improved creep resistance of epoxy/graphene composites at different stresses and temperatures and importantly, revealed that the creep deformation was

---

* Corresponding author.
** Corresponding author.
E-mail addresses: dimitrios.papageorgiou@manchester.ac.uk (D.G. Papageorgiou), ian.kinloch@manchester.ac.uk (I.A. Kinloch).

significantly decreased compared to the epoxy/CNT composites, as a result of stronger bonds between graphene and epoxy. The same conclusion came out from the works of Tang and coworkers [31,32], where the creep deformation of polystyrene/graphene oxide composites was lower than that of carbon black and CNT-filled polystyrene. Even though a number of polymeric matrices reinforced by GRMs have been evaluated for their creep performance [20,33–38], there are no literature reports on the creep properties of PEEK-GRM composites.

In this work, we have introduced graphene nanoplatelets (GNPs) into PEEK by melt-mixing and observed their effect on the mechanical properties and creep mitigation under various experimental conditions. Moreover, as we investigated recently, a strategy that can enhance even further the properties of a composite material or counterbalance some of the disadvantages of a specific filler, is the production of hybrid composites, where two or more reinforcements are used in combination [39,40]. Therefore, we introduced GNPs in various loadings within PEEK/short carbon fibre (CF) composites, in order to observe any additive or synergistic effects on the mechanical properties of the hybrid materials. In the past, Diez-Pascual and coworkers introduced single walled carbon nanotubes (SWCNTs) in continuous PEEK-glass fibre laminates [41]. They observed significant improvements in the storage modulus and glass transition temperature of the nanocomposites, while the tensile properties improved moderately, as a result of the predominant strength of the continuous laminates. Recently, Su et al. [42] prepared carbon-nanotube/carbon-fibre/PEEK hybrid composites by spraying CNTs onto PEEK/CF prepregs. The final materials displayed enhanced interlaminar shear strength, flexural strength and modulus as a result of the mechanical interlocking effect of the CNTs. The same effect should be observed in our hybrid short carbon fibre/graphene nanoplatelet-based composites, that is expected to lead to enhanced mechanical and creep properties under various experimental conditions.

Herein, we have focused on the elastic and viscoelastic response of PEEK-GNPs and PEEK-CF-GNP composites evaluated by tensile testing and dynamic mechanical thermal analysis, which are measurements related to the microstructure of the composite materials. The rheology of the composite samples was also assessed as it is of great importance to evaluate how these fillers influence on the processing of PEEK materials. Creep, a property that can provide information on the durability of polymers for practical and engineering applications, has been evaluated both at 30 °C and at 240 °C. One of the major highlights (and novelties) of this work is the use of the hybrid GNP-CF fillers in the composites, which retained their processability in relation to their high filler content, while their mechanical behaviour in terms of modulus and creep performance were both enhanced. Moreover, in the current literature there are no other papers reporting on the preparation and improved physico-chemical properties of PEEK reinforced with a combination of short carbon fibres and graphene nanoplatelets.

2. Experimental

2.1. Materials

PEEK was supplied by Solvay under the commercial name KetaSpire KT-880 NT and had a specific gravity of 1.3 g/cc and a melt flow index of 36 g/10 min. The carbon-fibre-filled PEEK was also a part of the KetaSpire series of Solvay, under the commercial name KT-880-CF30. The carbon fibre content was 30 wt%. The specific gravity was 1.41 g/cc for KT-880-CF30, while the melt flow index was 11 g/10 min for KT-880-CF30. The graphene nanoplatelets (xGNPs-M25) were obtained by XG Sciences and according to the supplier, they exhibited a mean platelet diameter of 25 μm and a thickness of 6–8 nm. However, after careful evaluation of the lateral size of the specific batch of the nanoplatelets via SEM (Fig. S1-Supporting Information), the diameter was in the order of 7.66 ± 4.25 μm [43]. The significant difference in the two values may originate from the fact that there is a number of small

nanoplatelets (< 3 μm) that control the average size of the batch.

The melt-mixing process took place in a high-temperature Thermo Fisher HAAKE Rheomix internal mixer, using 150 rpm for 20 min for each sample. The processing temperature was set at 360 °C. For the preparation of the dumbbell specimen for the tensile testing of the samples, neat PEEK and the PEEK-GNP samples (with the exception of the sample filled with 20 wt% GNPs) were injection moulded in a Haake Minijet Piston injection moulding system. The temperature of the mould was set at 245 °C and the temperature of the barrel was 370 °C. The injection pressure was 1200 bar for all samples. The rest of the dumbbells (including the PEEK-GNP sample filled with 20 wt% GNPs) were prepared by hot pressing the composite samples in a stainless-steel, dumbbell-shaped mould between two thermally insulating Kapton films due to their high viscosity and slightly higher melting point. The length of the carbon fibres after all the processing steps was estimated with an optical microscope and was found to be 152 ± 50 μm. The GNP contents used were 1, 5, 10 and 20 wt% in both sets of samples and the PEEK-filled materials will be named PEEK-GNPx throughout the manuscript, where x is the filler content in wt%. For the case of the hybrid samples, PEEK-CF30 was treated as matrix and GNPs were added during the melt mixing process, a fact that caused a proportional reduction in the overall CF content in the final composites, due to increasing GNP content. Four sets of samples were prepared for the carbon fibre-GNP reinforced composites, namely PEEK-CF29.7-GNP1, PEEK-CF28.5-GNP5, PEEK-CF27-GNP10 and PEEK-CF24-GNP20. The filler volume fraction was calculated from the relationship: $V_f = \frac{w_f/\rho_f}{w_f/\rho_f + w_m/\rho_m}$ where w_f is the weight fraction of the filler and ρ_f and ρ_m are the densities of the filler and the matrix, respectively. For the case of the hybrid samples, the density and the weight fraction of the CFs have been taken into account and the relationship has been adjusted. The conversion from weight fraction to volume fraction for all samples under study is presented in Table S1 – Supporting Information.

2.2. Characterization of the PEEK composites

Scanning electron microscopy (SEM) was performed on tensile-fractured samples using a FEI-Sirion FEG-SEM. A TA rheometer (HR-3) with parallel plate geometry (25 mm diameter) was used at a temperature of 360 °C to analyse the steady shear properties (flow properties) of neat PEEK and the prepared PEEK-GNP composites and PEEK-CF-GNP hybrid composites by recording the viscosity at increasing shear rates from 0.001 to 300 s^{-1}. A gap of 0.5 mm was used for all the tests. Tensile testing was performed using an Instron 3365 testing system with a load cell of 5 kN and the stress-strain curves were obtained under a tensile testing rate of 0.5 mm min^{-1}, in accordance with ASTM D638. At least five samples were tested for each filler content and the deformation was recorded using an extensometer mounted on the narrow section of the dumbbells. Prior to mechanical testing, a heat treatment procedure (200 °C for 3 h followed by 220 °C for 4 h) was performed, in order to ensure a similar degree of crystallinity of the matrix and the composites. All samples studied showed an average crystallinity of 25–30%, calculated from Differential Scanning Calorimetry. Dynamic Mechanical Thermal Analysis (DMTA) was undertaken from ambient temperature to 260 °C using a DMA Q800 analyzer (TA Instruments). A heating rate of 3 °C/min and a frequency of 10 Hz were applied under nitrogen flow. The creep and recovery tests of all samples were performed using the same DMA Q800 analyzer. The creep strain was recorded as a function of time (creep; 7500 s, recovery; 3600 s) under a low stress of 5 MPa at two different temperatures, namely 30 and 240 °C, in order to evaluate the creep behaviour at both glassy and rubbery states of the matrix. A dual cantilever bending mode was applied for the evaluation of both the dynamic mechanical and creep properties of the composites. Before each test, the samples were equilibrated for 4 min at each temperature.
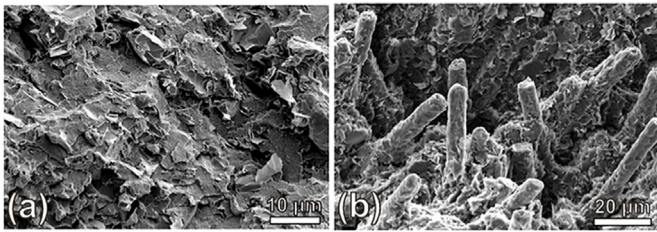
Fig. 1. Representative SEM images after tensile fracture of (a) PEEK-GNP10 and (b) PEEK-CF27-GNP10 samples.

3. Results and discussion

3.1. Scanning electron microscopy

Scanning electron microscopy was employed to investigate the fracture morphology of the samples after tensile testing at room temperature. From Fig. 1a, for the PEEK-GNP10 sample, it can be seen that the cross-sectional fractured surface of the composite was rough, with a number of flakes being pulled out of the matrix, as a result of the tensile testing procedure. As expected, the roughness of the fracture surfaces of the nanocomposites was increased with increasing filler content as a result of the high filler loadings and some unavoidable aggregation. A number of holes were observed that can be attributed to the GNP aggregates that acted as failure points during the elongation procedure, deteriorating the ultimate properties of the composites. The dispersion of the nanoplatelets was better at lower filler contents; however, the introduction of 20 wt% of GNPs led to significant aggregation (Fig. S2 (a-c)-Supporting Information), which is expected to reduce the strength of the composites. Regarding the hybrid PEEK-CF27-GNP10 sample presented in Fig. 1b and the rest of the hybrid composite samples in Figs. S1(d–f), it can be seen that a number of short carbon fibres were pulled out of the matrix. The length of the fibres was variable and they were randomly oriented. Again, a number of holes were observed as a result of fibres being pulled out and the unavoidable formation of GNP aggregates at such high contents. Moreover, it is important to note that all fibres were coated with a polymer/GNP mixture, possibly indicating improved interactions between the components of the hybrid composite (representative images shown in Fig. S3 (a-c)).

3.2. Rheological behaviour

The steady shear behaviour (flow properties) of the PEEK-GNP composites and PEEK-CF-GNP hybrid composites was studied to investigate how the incorporation of these reinforcing fillers influences the rheological properties and processing of PEEK. The variation of the viscosities of pure PEEK, PEEK-GNP and PEEK-CF-GNP composites was evaluated under increasing shear rates and the results are shown in Fig. 2.

A progressive increase of the viscosity of the neat PEEK with increasing loading of GNPs can be clearly seen from Fig. 2a. Whereas neat PEEK shows Newtonian behaviour at the range of shear rates studied, an increasing shear-thinning behaviour is observed with increasing GNP loading, related to the presence of a reinforcing network of GNPs in the polymer matrix, which breaks with increasing shear rates as previously observed and reported [44,45]. A maximum increase in viscosity of about four orders of magnitude was observed for 20 wt% loading of GNP, which is indicative of the difficulties in processing such stiff and high-temperature engineering materials. It is important though to point out that the processing characteristics and viscosity of PEEK filled with other nanomaterials such as carbon nanotubes at the same filler content would be significantly higher, making it very difficult to process the nanocomposites. Indeed, when the viscosity versus shear rate data of PEEK reinforced with multi-walled carbon nanotubes (MWCNTs) were plotted from Ref. [6] against our data, it can be seen that the viscosity of PEEK filled with 10 wt% of MWCNTs is more than two orders of magnitude higher than the PEEK-GNP10 sample. Moreover, even at the highest GNP content (20 wt%), the PEEK-GNP20 sample was much easier to process than PEEK-MWCNT10.

For the PEEK-CF-GNP hybrid composites (Fig. 2b), similar shear-thinning behaviour was observed. Once again, this observation is related to the formation of reinforcing networks in the polymer matrix, which break down at increasing shear rates. The viscosity of CF-reinforced PEEK (PEEK-CF30) at low shear rates did not increase much with the addition of GNPs. Even at the highest filler content, the addition of 20 wt% of GNPs to the CF-reinforced PEEK composite led to an increase of the viscosity at low shear rates of only one order of magnitude. It is interesting to note that similar viscosities were obtained for the PEEK-GNP20 composite and the PEEK-CF24-GNP20 hybrid composite, which suggests that the addition of GNPs to a highly-loaded PEEK-CF composite is helping improve the interface between polymer and carbon fibre, probably acting as a bridge between both entities. This result is expected to lead to enhanced levels of reinforcement (as will be shown in the following sections) without compromising the viscosity or the processing performance of the overall composite material (even for very high filler contents), which is of great importance for engineering applications. Compared to the viscosity of the PEEK-MWCNT10 sample from Ref. [6], the hybrids show once again significantly lower viscosity, indicating that processing should be easier. Infact, based on the results presented here, a material filled with more than 37 wt% (and up to 44 wt%) of hybrid CF-GNP filler displays a difference in viscosity of almost an order of magnitude, compared to 10 wt% of MWCNTs.
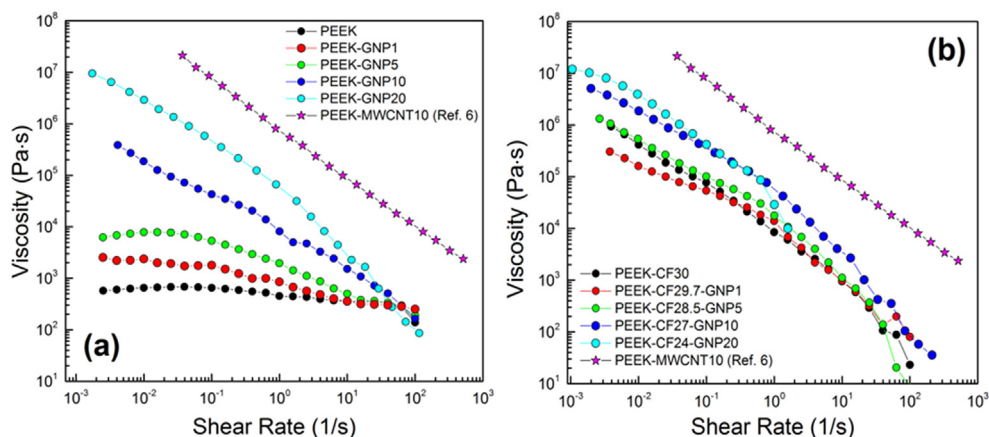

Fig. 2. Variation of the viscosity of (a) PEEK-GNP and (b) PEEK-CF-GNP composites with different loadings at increasing shear rates.
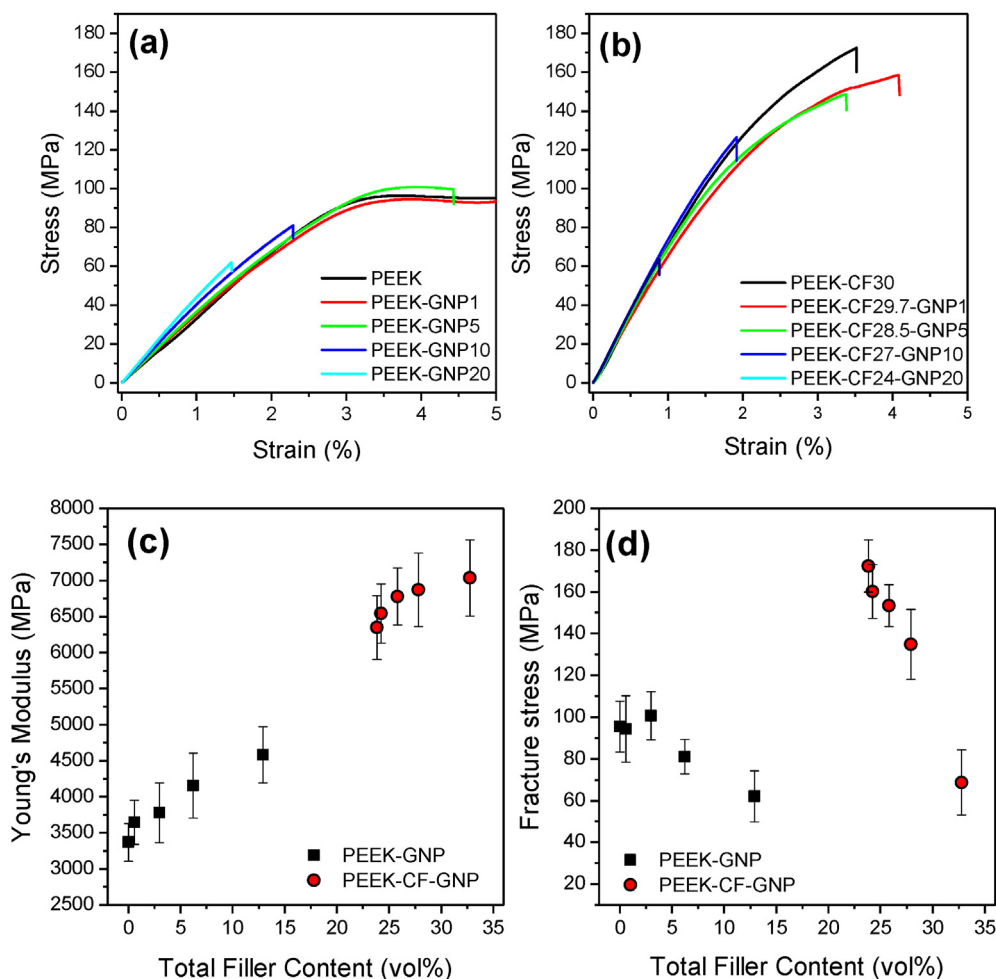
Fig. 3. Representative stress-strain curves for (a) PEEK-GNP and (b) PEEK-CF-GNP composites. Experimental results from Young's modulus (c) and fracture stress (d) for all samples under study.

3.3. Tensile testing

The mechanical properties of the composites were evaluated by tensile testing and representative stress-strain curves of the two sets of samples can be seen in Fig. 3(a and b). The results from mechanical testing can be seen in Fig. 3c, d. The presence of GNPs led to an increase of the tensile modulus of the composites, even though unfilled PEEK is already one of the stiffest engineering plastics. For the PEEK-GNP set of samples, an almost linear increase in the Young's modulus was observed with increasing filler content, indicating the reinforcement efficiency of the GNPs. For the hybrid samples on the other hand, the high filler contents led to a levelling off of the stiffness before reaching the highest total filler content, most probably due to aggregation through van der Waals forces and π-π interactions, typical of carbon fillers. The carbon-fibre-filled composites (PEEK-CF-GNP) gave higher modulus values than the PEEK-GNP samples as a result of the high inherent stiffness of CFs and the additive reinforcement from the simultaneous presence of CFs and GNPs [46,47].

Aggregation is known to affect significantly the enhancement of fracture stress in composites [23]. In this case, for both sets of samples, the strength generally decreased with the introduction of the GNPs. The only exception was a small increase in the fracture stress that was observed at PEEK-GNP samples with loadings up to 5 wt%, while at higher loadings, a decrease was also observed. This observation can provide an indirect indication regarding the different aggregation levels. For the PEEK-GNP set of samples, the strength of the composites decreased by ∼38% at the highest GNP content (∼14 vol%), while for the highest

CF-GNP content (∼34 vol%), strength was decreased by ∼150%. Therefore, as expected, aggregation was more pronounced in the hybrid samples and the ultimate effect of aggregation on the fracture stress of the composites was more distinct.

3.4. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis was also used in order to evaluate the reinforcing effect of the GNPs on the neat PEEK and the PEEK/CF samples. The storage modulus (E′) results seen in Fig. 4a-b clearly reveal that the presence of the nanoplatelets attributes an enhancement to the modulus values with increasing filler content for all samples studied. The adsorption of the GNPs onto the macromolecular chains of PEEK leads to a restriction of the movement of the chains and therefore, an improved storage modulus. It is interesting to notice that even though there was considerable aggregation at the highest GNP contents, the storage modulus presented an increase for those samples as well. The results from the values of storage modulus at room temperature for all samples under study can be seen in Fig. 4c. At ambient temperature and up to 130 °C, the differences between the samples are more pronounced than for higher temperatures, as a consequence of the samples being in a glassy state, while the increase of temperature leads to a reduction of E′ due to the softening of the polymer chains, resulting in higher energy dissipation. Overall, the composites filled with CFs and GNPs showed the highest modulus at room temperature, as a result of the additive reinforcing effects between the two stiff fillers and the higher stiffness of CFs. The results from DMTA are in good agreement
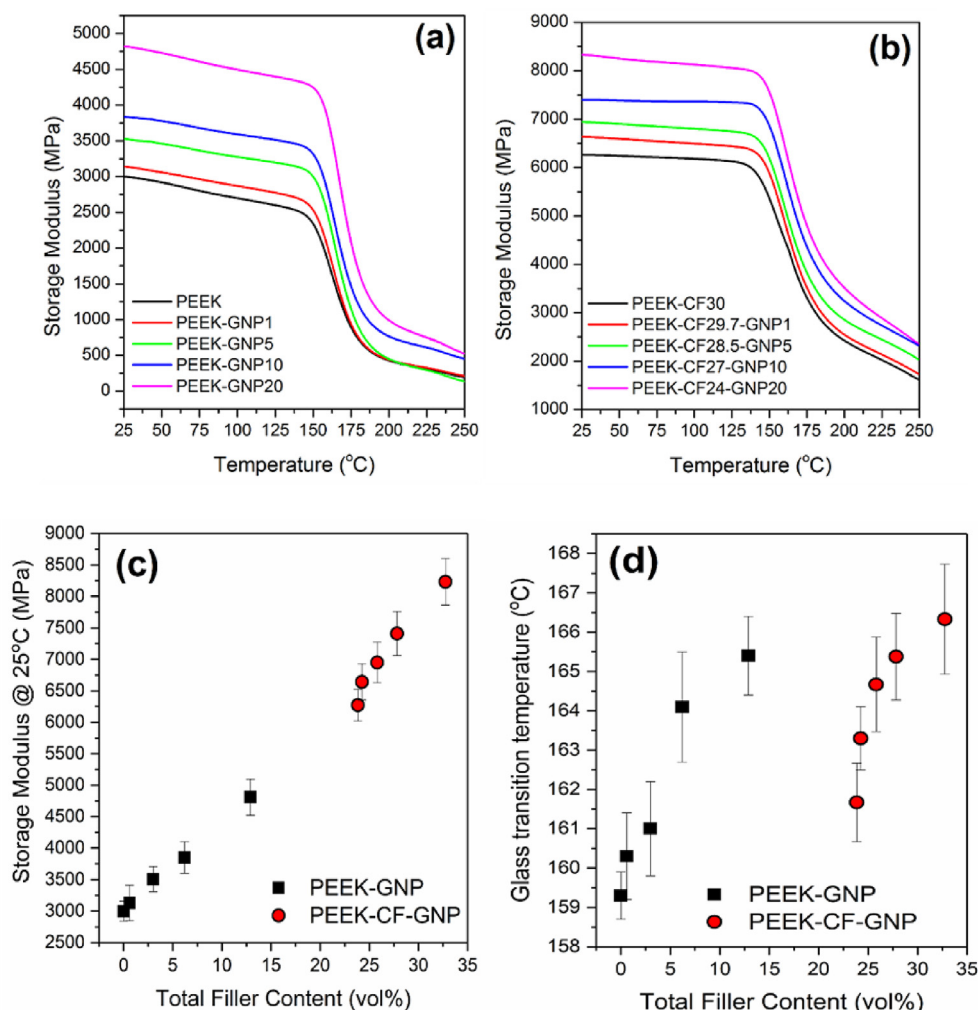
Fig. 4. Storage modulus values for (a) PEEK-GNP and (b) PEEK-CF-GNP composite samples; (c) storage modulus (E') at 25 °C and (d) glass temperatures for the composite samples.

with the ones obtained from tensile tests.

Regarding the glass temperatures (T_g), the results from the DMTA tests can be seen in Fig. 4d. The matrix displayed a T_g of around 159 °C, while there was a slight variation in the glass temperatures for the rest of the samples. It is obvious that the introduction of GNPs in the PEEK and the PEEK-CF systems led to an increase of the T_g, up to 6 °C for the PEEK-GNP samples, while the overall difference was in the order of 7 °C for the PEEK-CF-GNP samples (when compared with neat PEEK). This increase designates a restriction of the movement of the macromolecular chains of PEEK that contributes significantly to the stiffness of the materials as a result of enhanced interfacial interactions and conformational changes of the matrix in the vicinity of the nanoplatelets. The larger increase of the T_g in the case of the PEEK-CF-GNP sample is an indication that there is an enhanced immobilization of the PEEK chains when both CFs and GNPs are used as a hybrid filler due to higher jamming of the macromolecular chains and enhanced interaction density between PEEK and GNPs.

3.5. Creep and recovery

Creep properties can provide information on the structural behaviour of the materials under time-dependent deformation. During creep tests, in the case of polymers, the macromolecular chains are stretched and re-oriented under a constant load, resulting in dimensional mismatch and even failure of the materials. PEEK is known to display excellent creep resistance, especially at ambient temperatures [48] due to

a larger Kuhn length (~10.8 nm) [49] that makes the chain configuration between two entanglements stiffer than for flexible chains (molecular weight of entanglements for PEEK, M_e = 1490 [50]). The results from the creep and recovery tests of PEEK-GNP and PEEK-CF-GNP series of samples can be seen in Fig. 5a-d. The applied stress was 5 MPa, in order to ensure that the stress deformation of sample was within the elastic range. The increase of the GNP content in all sets of samples leads to a reduction of both the creep deformation and recovery, indicating an enhanced creep resistance of the composites after the addition of GNPs. The inelastic strain of PEEK-GNP samples is the highest amongst the two sets of samples, due to the lower stiffness of the materials (in comparison with PEEK-CF-GNP), observed from both tensile and DMTA tests. From Fig. 5(b, d) it can be realised that the increase in temperature leads to an increase of the creep strain as a result of the softening of the polymer matrix at elevated temperature [51]. Moreover, the different slope of the curves during the creep part after the temperature increase is the outcome of the enhanced configurational mobility of polymer chains, as the thermodynamic barrier is overcome through the transformation of enthalpic gain to entropic gain. Therefore, the tie-point stiffness is reduced and the slippage of the chains past each other is facilitated [31,52].

In order to obtain quantitative results on the effect of GNPs on the creep properties of PEEK and the hybrid samples under different temperatures, the ratio of difference in the magnitudes of creep strains between the matrix and the GNP-reinforced composites was calculated from the following relationship, which can be considered as a measure
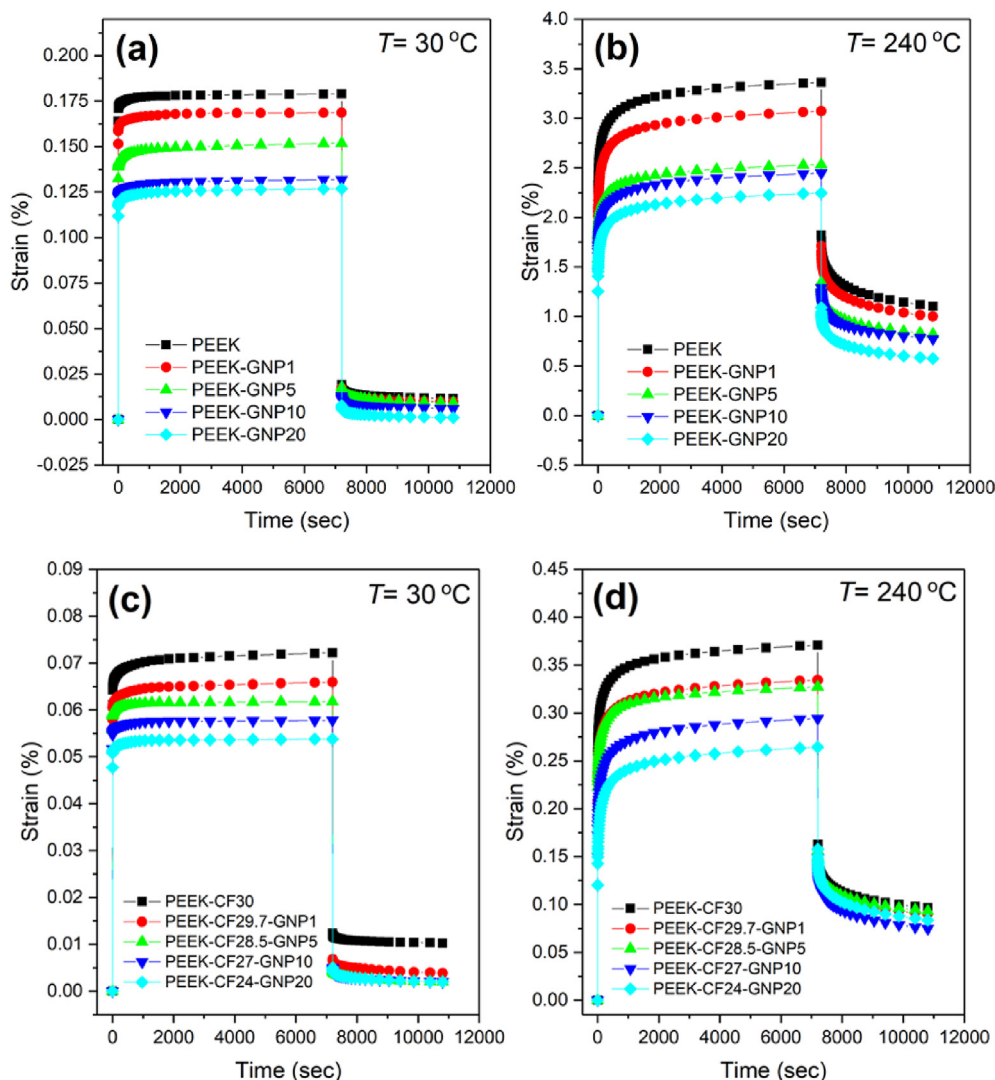
Fig. 5. Creep and recovery data as a function of time at 30 °C and 240 °C for PEEK-GNP (a, b) and PEEK-CF-GNP (c, d) set of samples.

of the creep reinforcing efficiency [53]:

$$\psi(\%) = \frac{\varepsilon_{PEEK} - \varepsilon_{PEEK-GNP}}{\varepsilon_{PEEK}} \times 100$$

In the case of the hybrid samples, the neat PEEK sample was once again considered as the matrix, in order to export conclusions on the combined effect of both CFs and GNPs on the reinforcing efficiency (ψ). From Fig. 6 (a, c) it can be seen once again that the graphene nano-platelets are efficient in the reduction of creep as a result of the formation of a network of cross-linking elements that interconnect the macromolecular chains, increasing this way the cross-linking density and obstructing a disentanglement of the chains under stress and localized re-orientation. However, the combination of the two fillers in the hybrid samples (Fig. 6 b, d) leads to significantly larger improvements in the reinforcing efficiency, as the fillers act additively towards the increase of the crosslinking density and reduction of creep. Moreover, the good performance of the composites at both low and high temperatures indicates that the matrix-filler interface and the ability of the GNPs to obstruct the re-orientation of the chains is not significantly weakened from the increase of temperature. If we examine the results individually, we can realise that for both the PEEK-GNP and PEEK-CF-GNP samples, the ψ values are quite close at low and high temperatures for both sets of samples, indicating the structural stability of the PEEK/GNP and PEEK/CF/GNP interface, even at high temperatures. For the

PEEK-CF-GNP samples, the creep reinforcing efficiency ψ was higher than PEEK-GNP at both low and high temperatures, as a result of a more effective stress transfer through the PEEK-CF-GNP interface [54]. This is in agreement with a previous study from our group, when a hybrid glass fibre-GNP filler transferred stress more effectively than neat GNPs [40]. At higher temperatures, however, this effect seems to be more pronounced than lower temperatures, due to the increased immobility of the amorphous region compared to neat PEEK (at 240 °C) as a result of the presence of both CFs and GNPs that act as blocking sites and the high aspect ratio of both fillers.

A number of models have been proposed for the evaluation and simulation of the creep and recovery behaviour of polymeric materials. The most popular of these models are the Burger's model and the Weibull distribution function. The individual parameters that can be obtained from each model provide information on the creep deformation and recovery mechanisms of the materials. Representative fittings of the creep and recovery experiments, measured at 30 °C for the PEEK-GNP set of samples, are presented in Fig. 7, while the rest of the samples are presented in Figs. S3–S5. Additionally, the results from the fitting procedure are presented in Tables S2–S5. It can be seen that the theoretical results are in good agreement with the experimental ones and some important conclusions can be exported, which support our previous results from rheology, tensile testing and DMTA. For example, from the application of Burger's model it can be realised that the
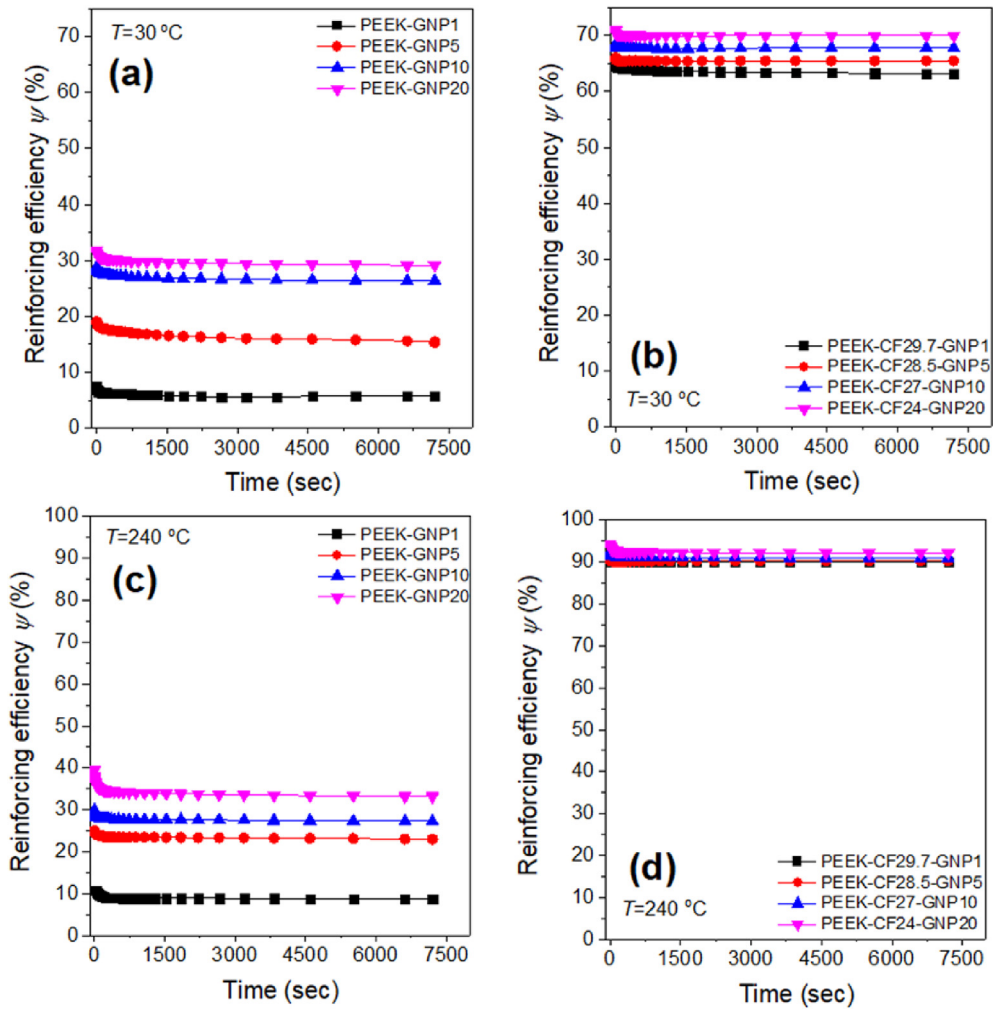
Fig. 6. Reinforcing efficiency of GNPs for PEEK: (a) at 30 °C, (c) at 240 °C and PEEK-CF-GNP: (b) at 30 °C and (d) at 240 °C.
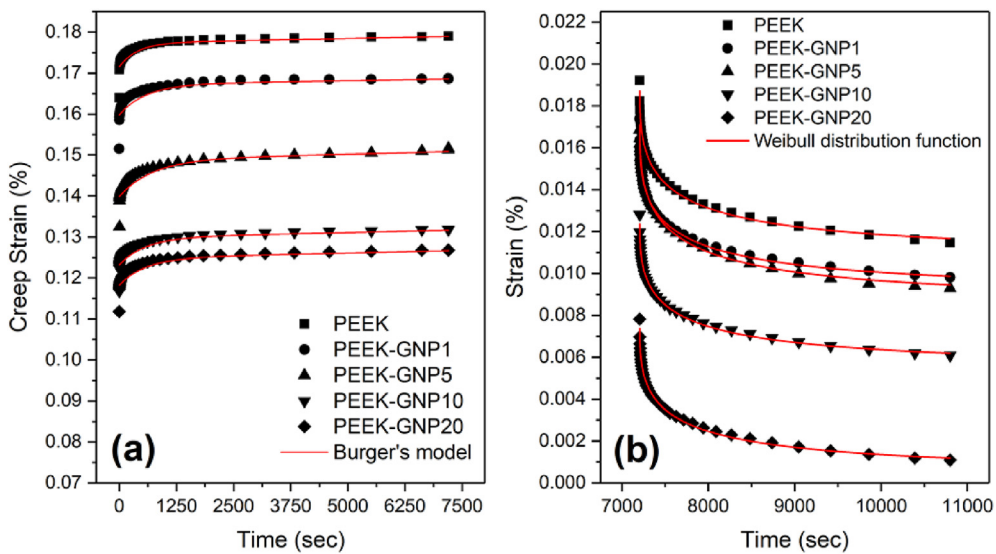

Fig. 7. Modelling results of creep and recovery for the PEEK-GNP set of samples, measured at 30 °C; (a) fitting of the creep phase with the Burgers' model, (b) fitting of the recovery phase with Weibull distribution function.

modulus of the Maxwell spring (E_M) increases with increasing filler content. Moreover, the retardant elasticity (E_K) that is related to the stiffness of the amorphous macromolecular chains increases as a result of the reinforcement of the GNPs and the hybrid filler on the Kelvin-Voigt unit [55]. The viscosity parameter (η_K), also increased with increasing filler loadings, in agreement with the results from rheology presented earlier. Furthermore, from the use of the Weibull distribution function for the fitting of the recovery data, both the viscoelastic strain recovery (ε_{KV}) and the permanent strain (ε_∞) decrease with increasing filler contents, revealing the enhanced recovery performance of the composites. For a more detailed discussion on the creep modelling results, the readers are referred to the respective part in the Supporting Information of the paper.

4. Conclusions

The effect of the presence of GNPs and the simultaneous presence of CFs and GNPs on the viscoelastic properties and creep mitigation of a PEEK matrix was investigated. In terms of their rheological properties, the viscosity of the hybrid samples increased at similar levels to the PEEK-GNP samples, indicating similar processability but significantly improved properties, compared to neat PEEK or even PEEK-CF30. Compared to the viscosity of PEEK reinforced with MWCNTs, based on the data from Ref. [6], the GNP-filled composites displayed considerably lower values, at significantly higher filler contents, indicating the ease of processing. The presence of GNPs also enhanced the stiffness of the matrix, while the combination of the fillers led to additive reinforcement in terms of both the Young's modulus and storage modulus of the hybrid composites. The high aspect ratio of the GNPs led to a confinement of the macromolecular chains of PEEK, restricted the mobility of all samples and enabled better stress transfer efficiency. These factors, along with the high stiffness of the materials led to an enhancement of the creep properties of the composites. It was shown that the GNPs increased the cross-link density and obstructed a disentanglement of the PEEK chains at both low and high temperatures. The hybrid CF-GNP reinforced composites displayed better creep properties at both temperatures, since the presence of both CFs and GNPs that act as blocking sites and the high aspect ratio of both fillers constrained the mobility of the amorphous region and prevented a re-orientation of the macromolecular chains of PEEK. Creep modelling was performed by applying the Burger's model for the evaluation of the creep behaviour and Weibull's distribution function for the evaluation of the recovery behaviour of the experimental data. The parameters obtained from the fitting procedure confirmed that the instantaneous and retardant modulus increased, while the viscoelastic strain recovery and the permanent strain decreased with increasing GNP loading for both sets of samples. Overall, the GNPs were efficient in reinforcing PEEK, either as a single filler or by acting additively with CFs in a hybrid system and the PEEK composites presented here, display improved elastic, viscoelastic and creep properties that should be attractive for advanced engineering applications.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compscitech.2019.03.006.

References

[1] R.J. Young, P.A. Lovell, Introduction to Polymers, CRC press, 2011.
[2] S.M. Kurtz, J.N. Devine, PEEK biomaterials in trauma, orthopedic, and spinal implants, Biomaterials 28 (32) (2007) 4845–4869.
[3] A.M. Díez-Pascual, M. Naffakh, C. Marco, G. Ellis, M.A. Gómez-Fatou, High-performance nanocomposites based on polyetherketones, Prog. Mater. Sci. 57 (7) (2012) 1106–1190.
[4] B.A. Newcomb, H.G. Chae, L. Thomson, J. Luo, J.-B. Baek, S. Kumar, Reinforcement efficiency of carbon nanotubes and their effect on crystal-crystal slip in poly (ether ketone)/carbon nanotube composite fibers, Compos. Sci. Technol. 147 (2017) 116–125.
[5] A.M. Díez-Pascual, M. Naffakh, M.A. Gómez, C. Marco, G. Ellis, M.T. Martínez, A. Ansón, J.M. González-Domínguez, Y. Martínez-Rubi, B. Simard, Development and characterization of PEEK/carbon nanotube composites, Carbon 47 (13) (2009) 3079–3090.
[6] D. Bangarusampath, H. Ruckdäschel, V. Altstädt, J.K. Sandler, D. Garray, M.S. Shaffer, Rheology and properties of melt-processed poly (ether ether ketone)/multi-wall carbon nanotube composites, Polymer 50 (24) (2009) 5803–5811.
[7] F. Deng, T. Ogasawara, N. Takeda, Tensile properties at different temperature and observation of micro deformation of carbon nanotubes–poly(ether ether ketone) composites, Compos. Sci. Technol. 67 (14) (2007) 2959–2964.
[8] J. Sandler, P. Werner, M.S. Shaffer, V. Demchuk, V. Altstädt, A.H. Windle, Carbon-nanofibre-reinforced poly (ether ether ketone) composites, Compos. Appl. Sci. Manuf. 33 (8) (2002) 1033–1039.
[9] C. Rong, G. Ma, S. Zhang, L. Song, Z. Chen, G. Wang, P. Ajayan, Effect of carbon nanotubes on the mechanical properties and crystallization behavior of poly (ether ether ketone), Compos. Sci. Technol. 70 (2) (2010) 380–386.
[10] S.-L. Gao, J.-K. Kim, Cooling rate influences in carbon fibre/PEEK composites. Part 1. Crystallinity and interface adhesion, Compos. Appl. Sci. Manuf. 31 (6) (2000) 517–530.
[11] J. Sarasua, P. Remiro, J. Pouyet, The mechanical behaviour of PEEK short fibre composites, J. Mater. Sci. 30 (13) (1995) 3501–3508.
[12] A. Bismarck, M. Hofmeier, G. Dörner, Effect of hot water immersion on the performance of carbon reinforced unidirectional poly(ether ether ketone) (PEEK) composites: stress rupture under end-loaded bending, Compos. Appl. Sci. Manuf. 38 (2) (2007) 407–426.
[13] Y.-H. Lai, M. Kuo, J. Huang, M. Chen, On the PEEK composites reinforced by surface-modified nano-silica, Mater. Sci. Eng., A 458 (1–2) (2007) 158–169.
[14] A.K. Kadiyala, J. Bijwe, P. Kalappa, Investigations on influence of nano and micron sized particles of SiC on performance properties of PEEK coatings, Surf. Coat. Technol. 334 (2018) 124–133.
[15] N. Wang, Z. Yang, K. Thummavichai, F. Xu, C. Hu, H. Chen, Y. Xia, Y. Zhu, Novel graphitic carbon coated IF-WS 2 reinforced poly (ether ether ketone) nanocomposites, RSC Adv. 7 (56) (2017) 35265–35273.
[16] M.A. Bakar, P. Cheang, K. Khor, Mechanical properties of injection molded hydroxyapatite-polyetheretherketone biocomposites, Compos. Sci. Technol. 63 (3–4) (2003) 421–425.
[17] J. Chen, K. Wang, Y. Zhao, Enhanced interfacial interactions of carbon fiber reinforced PEEK composites by regulating PEI and graphene oxide complex sizing at the interface, Compos. Sci. Technol. 154 (2018) 175–186.
[18] M. Kalin, M. Zalaznik, S. Novak, Wear and friction behaviour of poly-ether-ether-ketone (PEEK) filled with graphene, WS2 and CNT nanoparticles, Wear 332 (2015) 855–862.
[19] J.A. King, J.M. Tomasi, D.R. Klimek-McDonald, I. Miskioglu, G.M. Odegard, T.R. King, J.W. Sutherland, Effects of carbon fillers on the conductivity and tensile properties of polyetheretherketone composites, Polym. Compos. 39 (S2) (2018) 807–816.
[20] G. He, F. Gong, J. Liu, L. Pan, J. Zhang, S. Liu, Improved mechanical properties of highly explosive-filled polymer composites through graphene nanoplatelets, Polym. Compos. 39 (11) (2018) 3924–3934.
[21] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Electric field effect in atomically thin carbon films, Science 306 (5696) (2004) 666–669.
[22] A.K. Geim, K.S. Novoselov, The rise of graphene, Nat. Mater. 6 (3) (2007) 183.
[23] D.G. Papageorgiou, I.A. Kinloch, R.J. Young, Graphene/elastomer nanocomposites, Carbon 95 (2015) 460–484.
[24] D.G. Papageorgiou, I.A. Kinloch, R.J. Young, Mechanical properties of graphene and graphene-based nanocomposites, Prog. Mater. Sci. 90 (2017) 75–127.
[25] A.C. Neto, F. Guinea, N.M. Peres, K.S. Novoselov, A.K. Geim, The electronic properties of graphene, Rev. Mod. Phys. 81 (1) (2009) 109.
[26] A.A. Balandin, Thermal properties of graphene and nanostructured carbon materials, Nat. Mater. 10 (8) (2011) 569.
[27] Z. Yao, D. Wu, C. Chen, M. Zhang, Creep behavior of polyurethane nanocomposites with carbon nanotubes, Compos. Appl. Sci. Manuf. 50 (2013) 65–72.
[28] S. Siengchin, J. Karger-Kocsis, Structure and creep response of toughened and nanoreinforced polyamides produced via the latex route: effect of nanofiller type, Compos. Sci. Technol. 69 (5) (2009) 677–683.
[29] J.-L. Yang, Z. Zhang, A.K. Schlarb, K. Friedrich, On the characterization of tensile creep resistance of polyamide 66 nanocomposites. Part I. Experimental results and general discussions, Polymer 47 (8) (2006) 2791–2801.
[30] A. Zandiatashbar, C.R. Picu, N. Koratkar, Control of epoxy creep using graphene, Small 8 (11) (2012) 1676–1682.
[31] L.-C. Tang, X. Wang, L.-X. Gong, K. Peng, L. Zhao, Q. Chen, L.-B. Wu, J.-X. Jiang, G.-Q. Lai, Creep and recovery of polystyrene composites filled with graphene

additives, Compos. Sci. Technol. 91 (2014) 63–70.

[32] X. Wang, L.-X. Gong, L.-C. Tang, K. Peng, Y.-B. Pei, L. Zhao, L.-B. Wu, J.-X. Jiang, Temperature dependence of creep and recovery behaviors of polymer composites filled with chemically reduced graphene oxide, Compos. Appl. Sci. Manuf. 69 (2015) 288–298.

[33] A. Marotta, G.C. Lama, V. Ambrogi, P. Cerruti, M. Giamberini, G. Gentile, Shape memory behavior of liquid-crystalline elastomer/graphene oxide nanocomposites, Compos. Sci. Technol. 159 (2018) 251–258.

[34] S. Dul, A. Pegoretti, L. Fambri, Effects of the nanofillers on physical properties of acrylonitrile-butadiene-styrene nanocomposites: comparison of graphene nanoplatelets and multiwall carbon nanotubes, Nanomaterials 8 (9) (2018) 674.

[35] C. Lin, G. He, J. Liu, L. Pan, S. Liu, J. Li, S. Guo, Construction and non-linear viscoelastic properties of nano-structure polymer bonded explosives filled with graphene, Compos. Sci. Technol. 160 (2018) 152–160.

[36] J. Shang, Y. Chen, Y. Zhou, L. Liu, G. Wang, X. Li, J. Kuang, Q. Liu, Z. Dai, H. Miao, L. Zhi, Z. Zhang, Effect of folded and crumpled morphologies of graphene oxide platelets on the mechanical performances of polymer nanocomposites, Polymer 68 (2015) 131–139.

[37] L. Liu, Y. Gao, Q. Liu, J. Kuang, D. Zhou, S. Ju, B. Han, Z. Zhang, High mechanical performance of layered graphene oxide/poly(vinyl alcohol) nanocomposite films, Small 9 (14) (2013) 2466–2472.

[38] J. Bustillos, D. Montero, P. Nautiyal, A. Loganathan, B. Boesl, A. Agarwal, Integration of graphene in poly(lactic) acid by 3D printing to develop creep and wear-resistant hierarchical nanocomposites, Polym. Compos. 39 (11) (2018) 3877–3888.

[39] D.G. Papageorgiou, Z. Terzopoulou, A. Fina, F. Cuttica, G.Z. Papageorgiou, D.N. Bikiaris, K. Chrissafis, R.J. Young, I.A. Kinloch, Enhanced thermal and fire retardancy properties of polypropylene reinforced with a hybrid graphene/glass-fibre filler, Compos. Sci. Technol. 156 (2018) 95–102.

[40] D.G. Papageorgiou, I.A. Kinloch, R.J. Young, Hybrid multifunctional graphene/glass-fibre polypropylene composites, Compos. Sci. Technol. 137 (2016) 44–51.

[41] A.M. Díez-Pascual, B. Ashrafi, M. Naffakh, J.M. González-Domínguez, A. Johnston, B. Simard, M.T. Martínez, M.A. Gómez-Fatou, Influence of carbon nanotubes on the thermal, electrical and mechanical properties of poly(ether ether ketone)/glass fiber laminates, Carbon 49 (8) (2011) 2817–2833.

[42] Y. Su, S. Zhang, X. Zhang, Z. Zhao, D. Jing, Preparation and properties of carbon nanotubes/carbon fiber/poly (ether ether ketone) multiscale composites, Compos.

[43] R.J. Young, M. Liu, I.A. Kinloch, S. Li, X. Zhao, C. Vallés, D.G. Papageorgiou, The mechanics of reinforcement of polymers by graphene nanoplatelets, Compos. Sci. Technol. 154 (2018) 110–116.

[44] E. Tarani, D.G. Papageorgiou, C. Valles, A. Wurm, Z. Terzopoulou, D.N. Bikiaris, C. Schick, K. Chrissafis, G. Vourlias, Insights into crystallization and melting of high density polyethylene/graphene nanocomposites studied by fast scanning calorimetry, Polym. Test. 67 (2018) 349–358.

[45] C. Vallés, A.M. Abdelkader, R.J. Young, I.A. Kinloch, The effect of flake diameter on the reinforcement of few-layer graphene–PMMA composites, Compos. Sci. Technol. 111 (2015) 17–22.

[46] Y. Huang, R. Young, Effect of fibre microstructure upon the modulus of PAN-and pitch-based carbon fibres, Carbon 33 (2) (1995) 97–107.

[47] O. Frank, G. Tsoukleri, I. Riaz, K. Papagelis, J. Parthenios, A.C. Ferrari, A.K. Geim, K.S. Novoselov, C. Galiotis, Development of a universal stress sensor for graphene and carbon fibres, Nat. Commun. 2 (2011) 255.

[48] R.D. Maksimov, J. Kubat, Time and temperature dependent deformation of poly (ether ether ketone) (PEEK), Mech. Compos. Mater. 33 (6) (1997) 517–525.

[49] M.T. Bishop, F.E. Karasz, P.S. Russo, K.H. Langley, Solubility and properties of a poly(aryl ether ketone) in strong acids, Macromolecules 18 (1) (1985) 86–93.

[50] L.J. Fetters, D.J. Lohse, D. Richter, T.A. Witten, A. Zirkel, Connection between polymer molecular weight, density, chain dimensions, and melt viscoelastic properties, Macromolecules 27 (17) (1994) 4639–4647.

[51] W. Zhang, A. Joshi, Z. Wang, R.S. Kane, N. Koratkar, Creep mitigation in composites using carbon nanotube additives, Nanotechnology 18 (18) (2007).

[52] M. Ganss, B.K. Satapathy, M. Thunga, R. Weidisch, P. Pötschke, A. Janke, Temperature dependence of creep behavior of PP–MWNT nanocomposites, Macromol. Rapid Commun. 28 (16) (2007) 1624–1633.

[53] S. Kumar Ghosh, R.K. Prusty, D.K. Rathore, B.C. Ray, Creep behaviour of graphite oxide nanoplates embedded glass fiber/epoxy composites: emphasizing the role of temperature and stress, Compos. Appl. Sci. Manuf. 102 (2017) 166–177.

[54] A. Anand, P. Banerjee, D. Sahoo, D.K. Rathore, R.K. Prusty, B.C. Ray, Effects of temperature and load on the creep performance of CNT reinforced laminated glass fiber/epoxy composites, Int. J. Mech. Sci. 150 (2019) 539–547.

[55] Y. Jia, K. Peng, X.-l. Gong, Z. Zhang, Creep and recovery of polypropylene/carbon nanotube composites, Int. J. Plast. 27 (8) (2011) 1239–1251.