The impact of graphene nanofiller loading on the morphology and rheology behaviour of highly rigid polyurethane copolymer

Muayad Albozahid, Salih Abbas Habeeb, Naaem A Ismael Alhilo and Alberto Saiani

1 Department of Materials Engineering, Faculty of Engineering, University of Kufa, Najaf, Iraq
2 Department of Polymers Engineering and Petrochemical Industries, Faculty of Materials Engineering, University of Babylon, Al-Hilla, Iraq
3 State Company for Rubber Industries and Tires, Al-Najaf, Iraq
4 School of Natural Sciences, Department of Materials, University of Manchester, M13 9PL Manchester, United Kingdom

E-mail: moayad.zahid@uokufa.edu.iq

Keywords: polyurethane copolymer, HRPUC, rheology properties, thermal conductivity, electrical conductivity, SEM, TEM morphology

Abstract

This work attempts to study the effects of the addition of graphene nanoplatelets (xGNP) on the rheology properties of new version of polyurethane copolymer with 1,5 pentane diol as chain extender, containing a high amount of hard blocks. Two-step polymerisation was employed to synthesise this kind of polymer. The thermal and electrical conductivity of this copolymer was also investigated. Meanwhile, the rheology response has been analysed by measuring the viscosity. It was found that the viscosity increases by 68% and 2 × 10^5% at loadings of 0.5 wt.% and 15 wt.% of xGNP, respectively, compared with that of neat polyurethane copolymer. This means that the melt viscoelastic behaviour of highly rigid polyurethane copolymer (HRPUC) is influenced by the presence of xGNP contents, transforming the behaviour of nanocomposite from liquid-like to solid-like. This result was attributed to the network formation and interaction between hard segments of the HRPUC structure and xGNP due to strong shear thinning behaviour. In addition, the thermal conductivity of HRPUC increases to 0.97 W m^-1 k^-1 (410%), electricity conductivity rose to 10^2 s m^-1 (1000%). SEM morphology images showed overall dispersion of xGNP in the HRPUC, implying a reduction in the interspacing of flakes with increasing xGNP concentration. Further investigation into HRPUC morphology and its nanocomposites was conducted using the TEM method, illustrating that the xGNP stacking resulted from poor ability to disperse at greater loadings of xGNP.

1. Introduction

Graphene is a single-atom layer of sp^2 bonded carbon atoms packed in a two-dimensional honeycomb lattice [1, 2]. The discovery of graphene [3] in the last decade brought about a revolution in both academia and industrial progress. Due to its unique mechanical, thermal and electrical properties, graphene usage has grown increasingly in different industrial applications [4, 5]. Polyurethanes (PUs) are essentially di-block copolymers consisting of the soft segments prepared from polyols, and hard segments formed from disocyanates and short polyols as chain extenders. Therefore, the microstructure and thus mechanical properties can mainly be changed by manipulating the chemical structure and ratio of these components. This process can significantly influence the degree of induced microphase separation that results from incompatibility between the hard and soft segments [6–9]. As is known, most polymers fundamentally suffer from weak resistance to mechanical loads in various conditions [10]. Hence, PU polymers belong to this group of polymers that are incapable of withstanding specific circumstances, especially at low amounts of hard microdomains [11, 12]. Among these PUs, HRPUC is alternatively one of the most important PUs due to its unique performance in a wide range of applications, such as anti-corrosion, strength and toughness requirements [13, 14]. However, its low thermal...
A new version of polyether-based polyurethane copolymer conductivity can be considered one of its biggest shortcomings and results in difficulty in terms of dissipating the heat that is generated in some service devices [15].

Despite these drawbacks, there is more than one method of improving the mechanical properties of PUs, for instance: firstly, changing the molecular structure of this polyurethane (PU) via justification of the building constituents (segmental chains), and secondly, implementing a reinforcement process by adding fillers such as graphene and its derivatives to PU matrices [16, 17]. In addition, carbon fillers contribute to improving other crucial properties such as thermal and electrical conductivity [16, 18]. xGNPs are desirable to work with according to their straightforward and low-cost production in comparison with single-layer graphene and carbon nanotubes (CNTs) [19].

The interaction between PU matrices and graphene can be an intrinsic challenge for many researchers [20, 21]. In particular, relatively high loadings of conductive fillers have been added to increase multifunctional properties such as electrical conductivity, in addition to mechanical performance [22, 23].

Interestingly, polyurethane has attracted tremendous attention among researchers as well as in industrial contexts. PU is commonly considered one of the most versatile plastic materials derived from different kinds of raw chemical such as MDI, which is responsible for the hard domain, and polyether or polyester polyol, which is responsible for the soft domain and gives the PUs extra flexibility for different applications [24–27]. In fact, phase separation between hard and soft segments as well as hydrogen bonding that exists between urethane bonds have a high impact on the final resultant mechanical properties of PU [28–30].

In this article, the authors focus mainly on the rheological properties and thermal and electrical conductivity improvements of new version of HRPUC/xGNP nanocomposites. In addition, the approach is to fabricate HRPUC with different exfoliated graphene nanoplatelets (xGNP) using a two-step polymerisation method via in situ polymerization and then to determine the effects on their properties and structures, including SEM and TEM characterisation.

2. Experimental method

2.1. Materials

A new version of polyether-based polyurethane copolymer (65 wt% of hard blocks) with an average molecular number of $M_n = 2000 \text{ g mol}^{-1}$ and functionality 2.0 was obtained from Sigma-Aldrich in the UK. The isocyanate, MDI, (4,4′ methylenebis phenyl isocyanate) and Chain Extender (1,5 Pentane Diol) were also purchased from Sigma-Aldrich UK. A Catalyst (DABCO-S) and the solvent N,N dimethylene-acetamide (DMAC) were also used as the solvent for solution-based HRPUC. The reinforcement filler used in this study was M-grade graphene nanoplatelets (xGNPs), purchased from Lansing, MI, USA (xgsciences.com), with an average thickness of 6–8 nm, which is about 18–24 layers of graphene according to the company data sheet, and a typical surface area of 120 to 150 m$^2$ g$^{-1}$.

2.2. Preparation of graphite nanoplatelets (xGNP-M15)

A particular amount of xGNP powder was weighed and mixed with DMAC solvent. This xGNP weight depended on the desired ratio for compounding with HRPUC. The next step was to sonicate the xGNP in a sonication bath machine for half an hour, utilising xGNP exfoliation to prevent aggregation tendencies during the compounding process with HRPUC. The xGNP was then kept in a storage container until it was added to the HRPUC solution during synthesis.

2.3. Synthesis of HRPUC

A new technique of two-step polymerisation approach was employed to synthesise the HRPUC polymer (65 wt% of hard blocks). A four-necked rounded flask was equipped with a nitrogen inlet as well as a reflux tube to prevent solvent evaporation. For the first and second steps, the reaction vessel was placed in an oil bath at a temperature of 80 °C, since the MDI chemical stoichiometry that was added to the vessel was equivalent to a 6:1 ratio. In the first step, the MDI amount which had been kept in the refrigerator at −20 °C was put in the reaction vessel and then in the oil bath under nitrogen gas. 5–10 min after the addition of MDI, the polyether polyol was added slowly drop-wise for 1 h and then the reactant components were left for two hours with mechanical stirring in order to obtain the pre-polymer (MDI bonded with polyol) with excess MDI. The pre-polymer was kept at 50 °C for the next step. The chain extender was inserted in the second step and both the catalyst (DABCO) and DMAC solvent were added according to stoichiometry. Continuous stirring was applied to this mixture with drop-wise addition of the prepolymer. After the drop-wise addition of the prepolymer, the reaction continued with stirring for at least two hours until completion. The final HRPUC solution was stored in particular containers to use in the fabrication of nanocomposites. Figure 1 shows the chemical structures of the synthesis process.
2.4. Preparation of HRPU/xGNP nanocomposites

Since xGNP solution was combined with the chain extender in the second stage with weight percentage (0.5, 2, 8 and 15 wt.%), this in situ polymerisation approach was used for the preparation of HRPU/xGNP nanocomposites. When synthesis was complete, the HRPU/xGNP solution was dried in a furnace at 80 °C for three days in preparation for the next step. Test samples of the HRPU/xGNP material were prepared by an injection-moulding process using a Haake Minijet II (Thermoscientific) with a barrel temperature of 200 °C, mould temperature 50 °C, injection pressure at 500–1200 bar for 10 s and holding pressure at 400–1000 bar for 5 s. The synthesis process is shown in figure 2.

Figure 1. Synthesis schematics for the two-step addition and polymerisation of HRPU.
2.5. Characterisation and measurements

2.5.1. ATR-FTIR
The ATR-FTIR instrument used in this study was a Thermo Nicolet 5700, furnished with a Smart Orbit ATR. The samples of xGNP were prepared through mixing with KBr salt with 0.5 mg filler weight of xGNP powder. The obtained spectrum of xGNP powder was collected via MNIC software with a resolution of 4 and number of scans of 32 at room temperature.

2.5.2. TGA
TGA experiments were carried out on a Q-500 from TA Instruments in a nitrogen atmosphere. Samples weighing about 5 mg were used to measure the thermal stability of PUC/OMMT nanocomposites with a heating rate of 10 °C min⁻¹ by heating up to 700 °C.

2.5.3. X-ray diffraction (XRD)
For the x-ray diffraction (XRD), an X’Pert x-ray diffractometer was used alongside a Cu Kα radiation source (λ = 1.542 Å) to first identify the xGNP structure in powder form. The crystallinity plane degree of semicrystalline PUC/xGNP nanocomposites was also performed for injection-moulded samples with a rectangular shape of 1 mm × 0.5 mm.

2.5.4. TEM microstructure
The morphological features of PUC/MMT were observed via transmission electron microscopy (TEM, via a Philips CM200, 200 kV, Japan). The PUC/OMMT samples were prepared for TEM measurement using a diamond-blade knife to cut sample slices of approximately 50–60 nm thickness from the core of the samples using an ultra-microtome machine (Leica EM UC6). This process was followed by using the square mesh copper TEM grids (300 Mesh) that supplied by Agar Scientific (UK) from the distilled water solution.

2.5.5. SEM morphology
The morphological features of HRPUC/xGNP nanocomposites were observed using Field-emission SEM (FESEM-CXL30). The cryogenically fractured surface of this nanocomposite was coated with a thin film of gold in order to make it conductive with the incident electron beam, thus producing a better SEM image. This process was conducted using a rotary-pumped coater (Q150R Plus from Quorum (UK)).

2.5.6. Thermal conductivity
Disc-like samples with a diameter of 50 mm and two different thicknesses (2 and 4 mm) were produced using a Fox 50 heat flow meter from LaserComp Inc. Two samples were prepared for each thickness with a diameter of 50 mm, and their thermal conductivity was calculated according to ASTM C518 and ISO 8301. The samples were placed between two plates in the test stack and the gradient of the temperature was 25 °C to 35 °C.
2.5.7. Electrical conductivity
In this study, the electrical conductivity was measured using a NumetriQ PSM1735 connected to an Impedance Analysis Interface (IAI). The NumetriQ PSM1735 displayed the data and supplied the voltage, whereas the IAI provided a wide range of shunts (1 mΩ–500 mΩ). Before the test, the HRPUC and their nanocomposite samples were cut to a rectangular cross-section bar (with an average length of 10 mm and width of 5 mm). These samples were carefully polished to eliminate errors caused by surface roughness. Afterwards, the smooth samples were coated using silver paint in order to minimise the contact resistance between the contact surface of the samples and the conductive wires. All prepared samples were then linked to the conductive wires using silver-filled epoxy adhesive. Subsequently, the samples were placed in an oven overnight at 60 °C to guarantee that the epoxy adhesive fully dried. A frequency range between 1 and 10⁶ Hz was applied at a voltage (rms) amplitude of 1.0 V for all tests. At least three samples were tested for each portion of HRPUC nanocomposites.

2.5.8. Melt rheology measurements
To evaluate the linear viscosity response of neat HRPUC and nanocomposites, a rheometer of HR-3 Discovery (Hybrid Rheometer) from TA Instruments was equipped with an aluminium parallel disc fixture (25 mm in diameter and with 1 mm gap) was employed. Rheological tests were performed at a temperature of 200 °C for HRPUC and HRPUC/xGNP nanocomposite samples. The oscillatory strain sweep was applied at 200 °C to find the steady-state region called the linear viscoelastic region (LVR). The storage and loss modulus behaviour were utilised to determine this LVR. Meanwhile, the selected strain (%) within the LVR was employed for frequency sweep (μ%) measurements to obtain the rheology responses such as the shear storage modulus, loss modulus and complex viscosity. This rheology test was conducted at an angular frequency range of 0.1 to 500 (rad s⁻¹). The final flow sweep was measured with a shear rate of (0.01–100 s⁻¹) for neat HRPUC and its nanocomposites.

3. Results and discussion

3.1. Characterisation of graphene nanoplatelets (xGNP)
Figure 5 displays the different features relevant to quantify xGNP characterisation. Firstly, figure 3(a) shows the thermal stability of xGNP ranging from 0 °C–1000 °C. The overall degradation temperature of xGNP particles shows lower thermal stability compared to the reference of graphite. Figure 3(b) displays the infrared spectrum which reveals the surface chemistry of xGNP. A variety of peaks can be observed for xGNP with the presence of hydroxyl groups (−OH) and C−C band stretching at ca. 3435 cm⁻¹ and at ca. 2370 cm⁻¹, respectively. In addition, the stretching vibration of the OH group at 1631 cm⁻¹ was ascribed to OH bending vibration [31]. Furthermore, it was crucial to obtain the characterisation of the morphology of xGNP in order to obtain an in-depth morphology of xGNP. The TEM morphology of xGNP was used to show the individual layers of highly exfoliated xGNP, which is displayed in figure 3(c). Additionally, figure 3(d) shows the TEM diffraction mode of a single layer of xGNP. Meanwhile, the XRD pattern of the xGNP is illustrated in figure 4, indicating the intense diffraction peaks of crystalline regions at 26.52° and 54.64°. These peaks show the basal planes of xGNP corresponding to the reflections of (002) plane and (004) plane, measuring the d-spacing of 1.73 nm and 0.95 nm, respectively [32, 33] according to Bragg’s equation. A slight shift in the 2θ values for xGNP structure was observed, demonstrating the increase in inter-gallery spacing due to the exfoliation process. This xGNP structure was clearly reported by Jin Lin et al showing diffraction peaks of highly exfoliated graphite nanoplatelets (xGNP) [34]. Figure 3 shows the SEM morphology variation of exfoliated xGNP during the sonication process, which is considered to play a role in good dispersion during the mixing process [35]. The tendency of xGNP to aggregate is one of the main reasons for a reduction in the final performance of produced nanocomposites due to an increase in thickness [36]. The thickness of a single xGNP sheet is ~8–10 nm and diameter is ~15 μm, in agreement with estimates found in the literature [37, 38]. It has been suggested that a remarkable restacking of xGNP may occur because of the Van der Waals attraction between xGNP layers [39].

3.2. SEM micrographs of HRPUC/xGNP nanocomposites
The morphology of cryogenically fractured surfaces of pure HRPUC and their composites containing xGNP is shown in figure 6. The SEM images reveal the filler’s dispersion as well as its distribution within the HRPUC matrices. As is known from the work of previous authors, during the process of mixing graphene with polyurethane, several aggregates of xGNP flakes occur due to Van der Waal forces [32]. Thereby, homogeneity dispersion of xGNP nanoparticles was difficult to achieve, showing of rough surfaces of HROPUC/xGNP samples. The SEM morphology exhibited shiny regions, indicating the clearly agglomerated xGNP, particularly at higher loadings of 8 wt.% and 15 wt.%. The green arrows and red circles on the SEM images illustrate the location of agglomerated xGNP. Such observations were proved in a study by Sheng-Tsung Hsiao [40].
Figure 3. (a) Thermal stability of xGNP; (b) FT-IR spectrum of xGNP; (c) TEM image of xGNP; and (d) diffraction pattern of xGNP.

Figure 4. XRD of xGNP flakes with respect to graphite, showing the crystalline regions.
instance, hard segments of PUC tend to interact with nanofillers rather than soft segments and thus produced more distinctive regions of phase separated PU [41].

3.3. TEM of HRPUC/xGNP nanocomposites
The dispersion of xGNP within HRPUC was examined using in-depth TEM morphology. After fabrication of the nanocomposite samples by injection moulding, several parts of these samples were taken to prepare a very thin layer and were placed on a copper grid to be tested. The detailed pictures of HRPUC/xGNP samples clearly show that the dark spots illustrate the graphene nanoplatelets or even the strong interaction with urethane chains [31]. However, as depicted in figure 7, it was more difficult to obtain a very clear image due to the strong aggregation of xGNP within the PUC, particularly at high loadings. The cryo-fractured nanocomposite samples obtained from SEM were correlated with thin film to show the aggregation of xGNP flakes in both directions, despite the difficulty in recognising a single graphene layer [42].

3.4. Rheology measurements of HRPUC/xGNP nanocomposites
Figure 8 displays the relationship of visco-elastic performance as a function of strain sweep to reveal information about internal structural changes. These rheological properties include storage modulus ($G'$), loss modulus ($G''$), and complex viscosity ($\eta^*$). The main purpose of measuring different visco-elastic properties with constant frequency and the range of strain percentage is to find the clear plateau of the linear viscosity region (LVR) of pure HRPUC and its nanocomposites. The point at which the region changes from a linear to a non-linear viscoelastic region is known as the critical strain ($\gamma_C$) value. This behaviour was based on previous studies relevant to nanoparticle reinforced polymers [43–45]. The extracted data of rheology measurements demonstrate the state of the internal network produced by manufactured HRPUC/xGNP nanocomposites. The important role of rheology measurements is to quantify the capability of well-dispersed xGNP into HRPUC via good interfacial interaction and thus enhance the resistance to applied shear forces in the melt state.

The excellent adhesion and interface are produced by the existence of the multifunctional groups on the xGNP surfaces. Furthermore, the existence of hydrogen bonding in the HRPUC chains gives good behaviour in melt rheology performance [46]. As illustrated in figure 8, the increment values in rheology response with
respect to all melt rheological properties ($G'$, $G''$, and $\eta^*$) with the strain ranging from 0.1%–1000% were significantly increased to several folds with increasing xGNP concentration. As showed, LVR tends to decrease for composite samples with a great amount of xGNP, owing to the poor inter-connection between PUC chains and xGNP even at low strain [47]. It is well known that the rheological behaviour are very associated to the dispersion of polymer/nanocomposites and the $G''$ is less sensitive with the filler addition than the value of $G'$ and complex viscosity, $\eta^*$. However, the improvement in rheology properties is attributed to the ability of xGNP as known fillers with high surface area to increase the interfacial adhesion with HRPUC chains and thus prohibit the HRPUC chain mobility at melt state [48].

Overall, the $G'$ value tends to display higher levels of enhancement compared to $G''$, which emphasises the probability of solid-like behaviour rather than liquid-like behaviour of resultant materials [43]. This trend also shows constancy with the value of complex viscosity. As mentioned before, the optimum value for strain sweep was chosen to conduct the next step in the rheology test (at constant strain sweep) with frequency variations. Herein, the value of 0.1% was found to be the best value at which to undertake further investigations with the melt rheology test.

Additionally, frequency measurements ($\omega$) were carried out in the frequency range from 0 rad s$^{-1}$ to 500 rad s$^{-1}$ at a temperature of $\sim$200 °C, which is slightly above the melting point of HRPUC. This temperature was kept for all samples containing xGNP particles. However, the remarkable percolation threshold of the network structure of xGNP-reinforced polyurethane can give a good prediction for the 3D network architecture [41]. This variation in rheology was observed using this investigation focusing on measurement of storage.
modulus, loss modulus and complex viscosity ($\eta^*$). As depicted in figure 9, as the weight fraction of xGNP within HRPUc increased, the storage modulus increased compared to pure HRPUc, showing a clear increment with frequency variation. In fact, HRPUc was found to have amorphous soft segments and partially crystalline hard segments, suggesting several changes during calculation of the viscoelastic properties [20]. Meanwhile, in low frequency areas, an apparently higher magnitude of viscosity performance relevant to all measurements ($G'$, $G''$ and $\eta^*$) was indicated for the PUC/xGNP nanocomposites [49].
A significant increase in melt rheology was clearly seen for both \(G'\) and \(G''\) in the range of frequency sweep of HRPUC/xGNP, especially at low xGNP content, owing to a pseudo-solid network that formed due to well-dispersed xGNP distribution and filler-filler interaction \([50]\). In fact, the complex viscosity plots showed a slight change at low loading of xGNP, and then showed no change with angular frequency increasing. However, the high concentration of xGNP impeded in HRPUC showed a steep increase in complex viscosity then rapidly decreased with respect to increase in angular frequency, owing to the break-down of the network structure of HRPUC/xGNP due to its aggregation tendency. These values agree with those found in the literature \([50–54]\).

The indication for the region in which the HRPUC/xGNP nanocomposites transition from liquid-like behaviour to solid-like behaviour corresponds to the low addition of xGNP nano-fillers \([55]\). The high-aspect-ratio fillers with optimised compatibility with polymer chains were responsible for enhanced rheology properties of HRPUC/xGNP nanocomposites. Consequently, strong shear-thinning behaviour can be proven by the reduction of \((\eta^\ast)\) for low content of HRPUC/xGNP nanocomposites \([54, 56]\).

This reduction in the prominent complex viscosity value at greater amounts of xGNP compared to little variation or even plateau for lower xGNP content reflects the probability of destroying the formed solid 3D network, owing to the assumption of weaker shear thinning induced by poor dispersibility of nanofillers \([55]\). Thus, the structure of the xGNP might play an important role in the filler–polyurethane network \([57]\).

The rheology can be measured with correspondence to shear rate to explore viscosity variation and evidence for the resultant HRPUC/xGNP microstructure, as shown in figure 10. The rise in viscosity value with further xGNP can indicate pseudo-plastic behaviour in nanocomposite systems. This pseudo-plastic behaviour indicates that xGNP agglomeration is responsible for such behaviour, since xGNP layers act as weak physical cross-linking points, comparable with entanglement between hard and soft segments. The aggregated xGNP leads to the break-up of the network of xGNP with respect to shear rate increase \([58]\). Meanwhile, the rheological behaviour of the HRPUC/xGNP is converted from a quasi-Newtonian fluid to a strongly non-Newtonian fluid, resulting from xGNP addition. Such a reduction was also reported by Olivia Menes \([57]\), which resulted from the aggregation of xGNP at higher loadings. Apparently, the overall Newtonian plateau is rapidly shifted to a lower shear rate as the xGNP is increased, indicating a rapid deterioration in the 2D network in spite of shear-thinning behaviour \([18]\).

![Figure 9. Frequency sweep measurements conducted within LVR (\(\gamma = 0.2\%\)) at 200 °C show the values of shear storage modulus, \(G'\), shear loss modulus, \(G''\) and complex viscosity, \(\eta^\ast\) against frequency for HRPUC-65 HS and PUC-xGNP nanocomposites.](image-url)
3.5. Thermal conductivity and electrical conductivity measurements

Thermal conductivity of pure HRPUC with respect to HRPUC/xGNP was measured and plotted as shown in figure 11(a). The conductivity of pure HRPUC is approximately 0.17 W mK$^{-1}$, which then increased for nanocomposites reaching 0.23, 0.24, 0.65 and 0.97 W mK$^{-1}$ for xGNP-filled HRPUC polymer, respectively. The greater thermal conductivity of xGNP particles \cite{59} is related to better phonon scattering particularly in the plane of the xGNP. This enhancement in thermal conductivity properties is mainly connected to homogeneous dispersion of xGNP within PUC during synthesis. The results obtained emphasise that the thermal conductivity of the neat HRPUC and its nanocomposite increase with increasing xGNP, which implies that the contact between xGNP and HRPUC is rather good. This could produce interfacial thermal flow at the interface between xGNP and HRPUC. J K Zhao et al \cite{15} found that a good increment in thermal conductivity of polyurethane was reinforced by CNT due to the capability of CNT to facilitate phonon conduction and consequently better thermal transport. However, the improved interfacial adhesion between the matrix and the nanofiller would increase the thermal conduction of the pure polymer \cite{36,45,59}. In figure (b), the electrical conductivity was tested to reveal improvements in this property. Meanwhile, the electrical percolation was evaluated to convert the HRPUC from isolated to conductive polymer. In our case, the electrical conduction was observed at a loading equal to 3% (between 2% and 8%). An overall increment in electrical conductivity was seen, as depicted in figure 12. The slope line corresponds to frequency, which implies the non-conductivity of this composite. Furthermore, this behaviour was seen to change after the percentage of 8% since the trend was likely to plateau and increase at high frequency. This result demonstrates that the formation of conductive network is strongly

![Figure 10. Complex viscosity, $\eta^*$, of neat HRPUC and HRPUC with xGNP at frequency sweep measurements conducted at 200 °C.](image)

![Figure 11. Thermal and electrical conductivity of neat HRPUC and HRPUC with xGNP at different loading ratios.](image)
influenced by particle concentration, which plays a crucial role to form a conductive pathways [60]. Table 1 is available online at stacks.iop.org/MRX/7/125304/mmedia shows a comparison of the current study with previous studies, indicating the effect of different carbon fillers on thermal and electrical properties [61–64].

4. Conclusions

Highly rigid polyurethane copolymer (HRPUC) was a new kind of polyurethane series that required improvement for various applications such as electromagnetic shielding and electronic devices. Thus, graphene nanoplatelets (xGNP) were added to respond to these requirements of HRPUC in various applications. This study focused on rheological properties due to the rigidity of HRPUC. However, the results of morphology images showed the microstructure and conformation of resultant HRPUC/xGNP nanocomposites. In fact, a significant enhancement in rheological performance was seen and a conversion from liquid-like material to solid-like material occurred as xGNP increased. Meanwhile, the xGNP had a positive impact on the final electrical and thermal conductivity. The advantage of adding xGNP was observed in the viscoelastic properties of HRPUC, followed by improvements in thermal and electrical conductivity.

Acknowledgments

The author is grateful to the department of science and engineering in the University of Manchester. Another thank to materials department at university of Kufa, faculty of Engineering, to their unlimited support to fulfill this study.

Funding

This research received no specific grant from any funding agency or company.

Conflict of interest

None

ORCID iDs

Muayad Albozahid © https://orcid.org/0000-0002-1480-3432
Salih Abbas Habeeb © https://orcid.org/0000-0003-4687-1744
References

[1] Meyer J C, Geim A K, Katsnelson M I, Novoselov K S, Booth T J and Roth S 2007 The structure of suspended graphene sheets Nature 446 60–3

[2] Georgakilas V et al 2012 Functionabilization of graphene: covalent and non-covalent approaches, derivatives and applications Chem. Rev. 112 6156–214

[3] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films. Science 306 666–669

[4] Lawal A T 2019 Graphene-based nano composites and their applications. A review Biosens. Bioelectron. 141 111384

[5] Soldano C, Mahmood A and Dujardin E 2010 Production, properties and potential of graphene Carbon 48 2127–50

[6] Kolapo Adekwe O O 2016 Handbook of Thermoplastics (Boca Raton, FL: CRC Press)

[7] D’Hollander S, Van Assche G, Van Mele B and Du Prez F 2009 Novel synthetic strategy toward shape memory polyurethanes with a well-defined switching temperature Polymer 50 4447–54

[8] Rebeca Hernandez J W, Padasaligkar A, Choi T, Angelo E, Lin J S, Xu L-G, Siedlecki C A and Runt J 2008 A comparison of phase organization of model segments polyurethanes with different intersegmental compatibilities Macromolecules 41 9767–76

[9] Yan Huan J L, Wang J, Wu F and Yang X 2017 Physical Properties and morphology of crosslinked polyurethane synthesized from para-phenylene disocyanate and polyether polyol J. Appl. Polym. Sci. 134 45241

[10] Bartczak Z, Argon A S, Cohen R E and Weinberg M 1999 Toughness mechanism in semi-crystalline polymer blends: II. High-density polyethylene toughened with calcium carbonate filler particles Polymer 40 2347–65

[11] Yousefi N et al 2013 Highly aligned, ultralarge-size reduced graphene oxide/polyurethane nanocomposites: mechanical properties and moisture permeability Composites Part A: Applied Science and Manufacturing 49 42–50

[12] Kim H, Miura T and Maconko C W 2010 Graphene/polyurethane nanocomposites for improved gas barrier and electrical conductivity Chem. Mater. 22 3441–50

[13] Pedrazzoli D and Manas-Zloczower I 2016 Understanding phase separation and morphology in thermoplastic polyurethanes in situ Nanotechnology 27 165103

[14] Prisacariu C 2011 Polyurethane Elastomers: From Morphology to Mechanical Aspects (Berlin: Springer)

[15] Zhao J-C et al 2011 Thermal conductive and electrical properties of polyurethane/hyperbranched poly(urea-urethane)-grafted multi-walled carbon nanotube nanocomposites Composites Part B: Engineering 42 2111–6

[16] Ramin Shamsi M M and Koohsa M 2016 Synthesis of CNT-polyurethane nanocomposites using ester-based polyols with different molecular structure: mechanical, thermal, and electrical properties J. Appl. Polym. Sci. 154 44567

[17] Akimoto Y O, Beg M D H, Ghazali S, Islam M R, Jayarajnam N and Yuvaraj A Rev. Sci. Instrum. 6 114453–82

[18] Yan D, Xu L, Chen C, Tang J, Li X and Li Z 2012 Enhanced mechanical and thermal properties of rigid polyurethane foam compositions containing graphene nanosheets and carbon nanotubes Polym. Int. 61 1107–14

[19] Li Band Zhong W-H 2011 Review on polymer/graphite nanoplatelet nanocomposites J. Mater. Sci. 46 5395–614

[20] Chen J et al 2015 Carbon nanotube network structure induced strain sensitivity and shape memory behavior changes of thermoplastic Mater. Des. 69 105–13

[21] Cai D, Yusho K and Song M 2009 The mechanical properties and morphology of a graphite oxide nanoplatelets/polyurethane composite Nanotechnology 20 085712

[22] Lee Y R, Baghu A V, Jeong H M and Kim B K 2009 Properties of waterborne polyurethane functionalized graphene sheet nanocomposites prepared by an in situ method Macromol. Chem. Phys. 210 1247–54

[23] Ding J N, Fan Y, Zhao C X, Liu Y R, Yu C T and Yuan N Y 2011 Electrical conductivity of waterborne polyurethane/graphene composites prepared by solution mixing J. Compos. Mater. 46 747–52

[24] Khudyakov Igor V, Zopf R, David and Turro Nicholas J. 2009 Polyurethane nanocomposites Des. Monomers Polym. 12 279–90

[25] Woods G 1990 The ICI Polymers Book 2nd edn. (New York: Wiley)

[26] Marcelo Antunes Á C, Realinho V, Arencón D and Velasco J I 2014 Compression properties and cellular structure of polyurethane nanocomposites prepared by solution mixing Des. Monomers Polym. 15 360–7

[27] Maroof S et al 2014 Functionalization of graphene nanosheets and carbon nanotubes Polym. Int. 63 214–21

[28] Bera M and Maji P K 2017 Effect of structural disparity of graphene-based materials on thermomechanical and surface properties of thermoplastic polyurethane nanocomposites Polymer 58 48–57

[29] Gencer G C, Giorcelli M, Frache A and Badini C 2017 Thermal behavior of thermoplastic polyurethane nanocomposites containing graphene nanoplatelets J. Appl. Polym. Sci. (https://doi.org/10.1002/app.48414)

[30] Drzal HL and T L 2012 Nanolaminated polyethylene nanocomposites with Enhanced Mechanical and Thermal Properties. Technical Proc. of the 2006 NSTI Nanotechnology Conf. and Trade Show 2006

[31] Park J’ K, Lee Y, Drzal L T and Cho D 2016 Flexural properties, interlaminar shear strength and morphology of phenolic matrix composites reinforced with xGnP-coated carbon fibers Carbon Letters 17 33–8

[32] Liu H et al 2016 Organic vapor sensing behaviors of conductive thermoplastic polyurethane–graphene nanocomposites J. Mater. Chem. C 4 4549–69
[40] Hsiao S T et al 2015 Effect of covalent modification of graphene nanosheets on the electrical property and electromagnetic interference shielding performance of a water-borne polyurethane composite ACS Applied Materials & Interfaces 7 2817–26
[41] Sahebi Jouflibi I, Karnak M and Nazokdast H 2017 Nanoparticle effects of thermoplastic polyurethane on kinetics of microphase separation, with or without preshear Polym. Compos. 39 4551–9
[42] Piana F and Pionteck J 2019 Exploitation of the hard/soft segments ratio in thermoplastic polyurethane (TPU) for the tuning of electrical and mechanical properties of expanded graphite (EG) based composites SN Applied Sciences 1
[43] Bai J J et al 2019 Preparation and rheology of isocyanate functionalized graphene oxide/thermoplastic polyurethane elastomer nanocomposites Journal of Macromolecular Science, Part B 58 425–41
[44] Karolina Gaska R K, Xu X, Gubanski S, Müller C, Pandit S, Mokkapati V R S S, Mijakovic I, Rybak A, Siwek A and Svensson M 2019 Highly structured graphene polyethylene nanocomposites AIP Conf. Proc. 2065 030061
[45] Gaska K, Kadar R, Rybak A, Siwek A and Gubanski S 2017 Gas barrier, thermal, mechanical and rheological properties of highly aligned graphene-LDPE nanocomposites Polymers. 9 1–14
[46] Sajedi S H M T 2016 Fumed silica/polyurethane nanocomposites: effect of silica concentration and its surface modification on rheology and mechanical properties Iran. Polym. J. 25 697–710
[47] Batista N L et al 2018 Mass-produced graphene—HDPE nanocomposites: thermal, rheological, electrical, and mechanical properties Polymer Engineering & Science. 59 675–82
[48] Ma H L, Zhang H B, Li X, Zhi X, Liao Y F and Yu Z Z 2014 The effect of surface chemistry of graphene on cellular structures and electrical properties of polycarbonate nanocomposite foams Ind. Eng. Chem. Res. 53 4697–703
[49] Huang A, Wang H, Ellingham T, Peng X and Turling L S 2019 An improved technique for dispersion of natural graphite particles in thermoplastic polyurethane by sub-critical gas-assisted processing Compos. Sci. Technol. 182 107783
[50] Eriksson M, Hamers J, Peijs T and Goossens H 2019 The in...