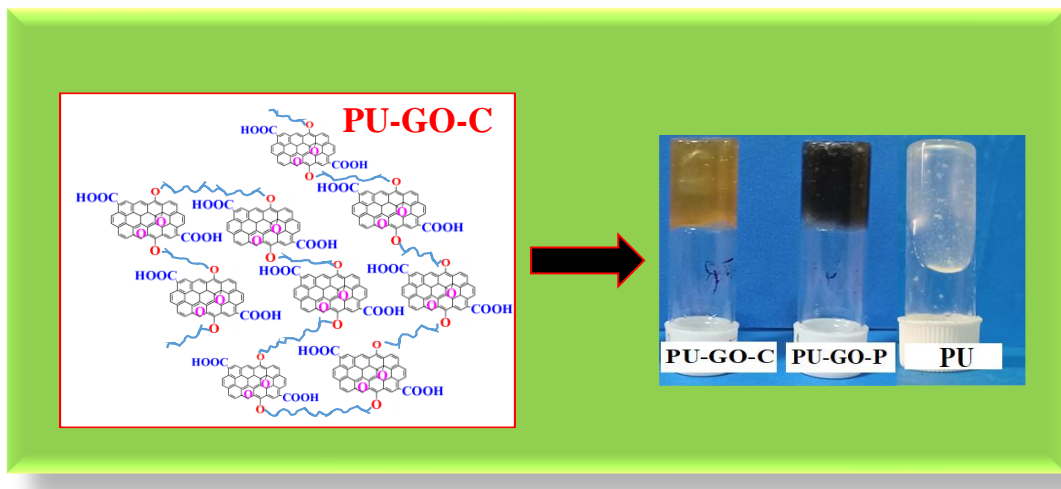# *The effect of chemical tagging of Graphene oxide in thermoplastic polyurethane on gelation behavior*

6.1 Introduction

Thermoplastic polyurethane (TPU) is an important class of polymeric materials which have high chemical and mechanical responses due to which it become novel materials for specialized application and attract the scientific community globally.[191-193] They possess good mechanical strength, wear and tear resistance and low temperature elasticity. The polyurethane multi-block copolymer consists of biphasic macrostructure containing hard and soft segment which are responsible for their thermoplastic and elastomeric behavior of polyurethanes, respectively.[194,195] These materials display both the characteristics of elastomer and plasticity and hence, it may be used as elastomeric thermoplast.[196,197] TPU consists of hard and soft segment; the hard segment is composed from the diisocyanates and soft segment from the long chain diols e.g. (polytetramethylene glycol (PTMG)) and diol/diamines are used as chain extender.[197] The hard segment is responsible for crystalline phase and rigidity in the polyurethanes and it controls the molecular self-assembly while the soft segments dictate its flexible behavior even at low temperature and the TPUs are referred to multi-block copolymers.[197,198] Polyurethanes are widely used materials in recent technology, like adhesive,[199,200] coating,[201] energy storage,[202] porous-foams, sealants, biomedical application,[203] tissue engineering, drug delivery vehicle and many more. After the successful synthesis of polymer nanocomposites, the knowledge of flow behavior and other properties (such as viscosity, storage modulus, loss modulus and complex viscosity, etc.) of gel polymer nanocomposites are still unexplored especially for their use in solar cell applications (gel electrolytes) required for the better use in research and devolvement and also future applications.

Rheology is a good technique to analyze the materials deformation and flow behavior of the materials in general. Rheology is based on three primary concepts: kinematics, conservation and

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constitutive relations. The kinematics is the science of motion and it explains the change in the shape of materials with time, and the term conservation deals with the forces stresses and the various energy interchange arising from the motion while the constitutive relations are special class of bodies such as viscous bodies and serve to link motion and forces the completing the description of the deformation.[204] The most of materials do not display the ideal flow behavior, hence the rheological study is essential for understanding the properties of the materials of common fluids, including polymers, paints, adhesives, printer inks, cosmetics and foods. The rheological study has great attention for the polymer processing industry, it gives the very important information about the flow behavior of polymer which help the polymer processing technique such as, compression molding, injection molding, extrusion etc. Our assumption is to develop chemically GO-tagged polymer gel which shows the better gelation kinetics and good rheological properties.

In this chapter, chemically-tagged graphene oxide thermoplastic polyurethane (GO/TPUs) nanocomposites have been synthesized using the in-situ polymerization process and compared the properties using physically tagged GO/TPUs nanocomposites, prepared using simple mixing process. The effect of chemical and physical tagging of graphene oxide in PUs has been explored through rheological studies.

6.2 Result and Discussion

6.2.1 Interaction of GO with Polymer Chain in terms of Gelation, Structural, Morphology and Thermal properties

The reaction scheme of the formation of chemically tagged GO-TPUs nanocomposite is shown in **Scheme 6**.1 where isocyanate end group prepolymer of TDI and PTMG react with graphene oxide to incorporate GO as a part of polymer chain. **Figure 6.1a** represent the schematic diagram of physically dispersed graphene oxide in thermoplastic polyurethane matrix *i.e.,* PU-GO-P as opposed to the chemically tagged graphene oxide with thermoplastics polyurethane matrix *i.e.,* PU-GO-C (**Figure 6.1b**). The corresponding photographic image of the gels in DMF (50 wt.%) of pure PU, PU-GO-P and PU-GO-C at 25 ^{0}C are shown in **Figure 6.1c** showing the flow behavior of pure PU gel while PU-GO-P and PU-GO-C exhibit strong gel in similar condition.
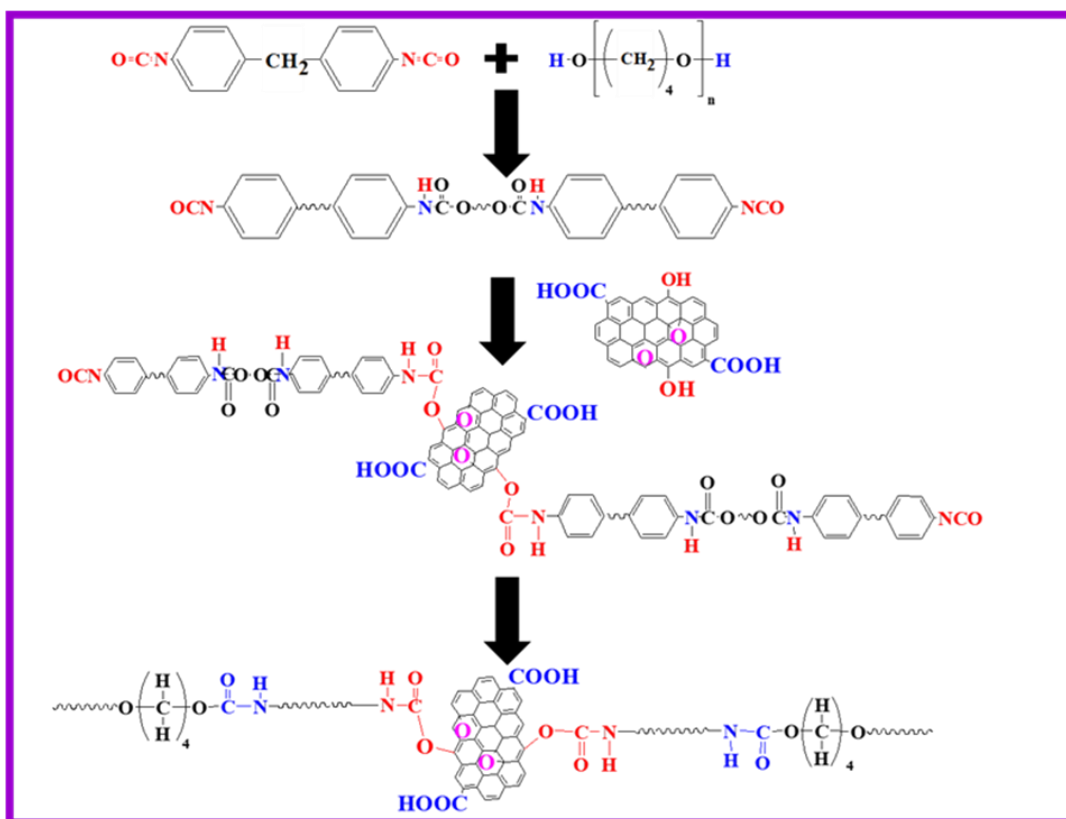
Scheme 6.1: Schematic diagram of the synthesis of PU-GO polymer hybrid (PU-GO-C).

The test tube tilting method has been applied to measure the comparative rate of gelation. **Figure 6.2a** shows the gel kinetics (gelation rate) of pure PU and its two different nanocomposites gel in a wide range of temperature. Pure PU forms weak gel at low temperature and does not form gel beyond 10 °C while composite systems form strong gel up to 25 °C. The gelation rates are higher in case of composite gels and amongst the composites PU-GO-C exhibits significantly higher gelation rate than that of physical mixture (PU-GO-P). The much higher gelation rate of PU-GO-C lies in its chemically connected GO platelet-like structure which acts as better heterogeneous nucleation sites for gel formation. Further, the gelation rates gradually decrease with increasing temperature as usual while sharp reduction of gelation rate is observed in pure gel and PU-GO-P against quite higher gelation rate observed for PU-GO-C. However, chemically tagged GO with PU exhibit better gel formation as comparison to the physical mixture of PU and GO.
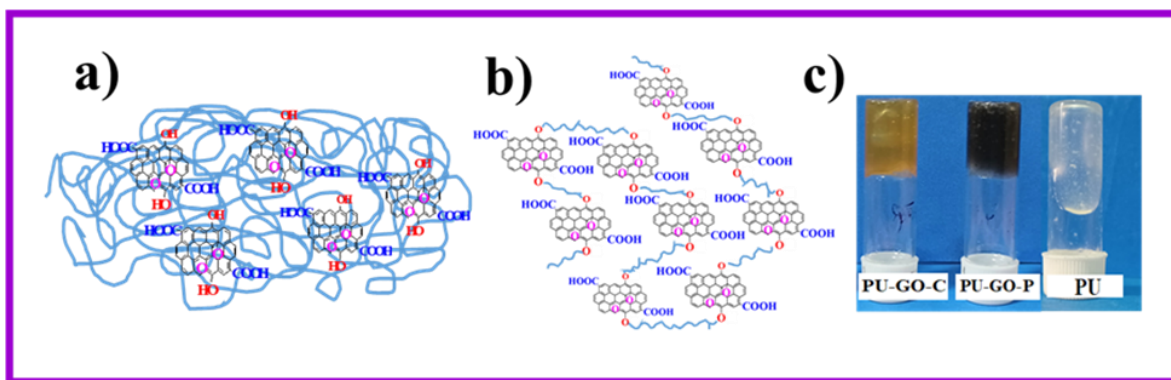

Figure 6.1: (a) Schematic diagram of physical mixing of GO in PU (PU-GO-P); **(b)** Schematic diagram of the chemical tagging of GO in PU chain (PU-GO-C); **(c)** Photographic images of pure PU, PU-GO-P and PU-GO-C gel at 25 °C.

To understand the solvent retention power of the gel, thermogravimetric measurements are done using PU and PU-GO-C nanocomposite gel as shown in **Figure 6.2b**. The solvent loss is defined as 5 % weight loss and pure PU gel start losing initial evaporation at 72 ^{0}C while PU-GO-C gel exhibits solvent loss at 84 ^{0}C. The higher solvent retention of nanocomposite gel is due to the presence of GO sheet in polymer matrix. The polymer degradation is observed in the temperature range of 300 - 450 ^{0}C. Two step degradation is prominent in pure PU (lower degradation at 321.8 ^{o}C for hard segment content and higher temperature at 396 ^{o}C is due to soft segment). First degradation in PU-GO-C is considerably suppressed as most of the urethane linkage is connected with graphene layer and thereby provide some thermal stability while the second degradation occurs at similar temperature of pure PU (396 ^{o}C). However, thermal stability of nanocomposite gel is much better than pure PU gel. The gel melting temperature/behavior are estimated by using differential scanning calorimetric (DSC) measurement as shown in **Figure 6.2c**.
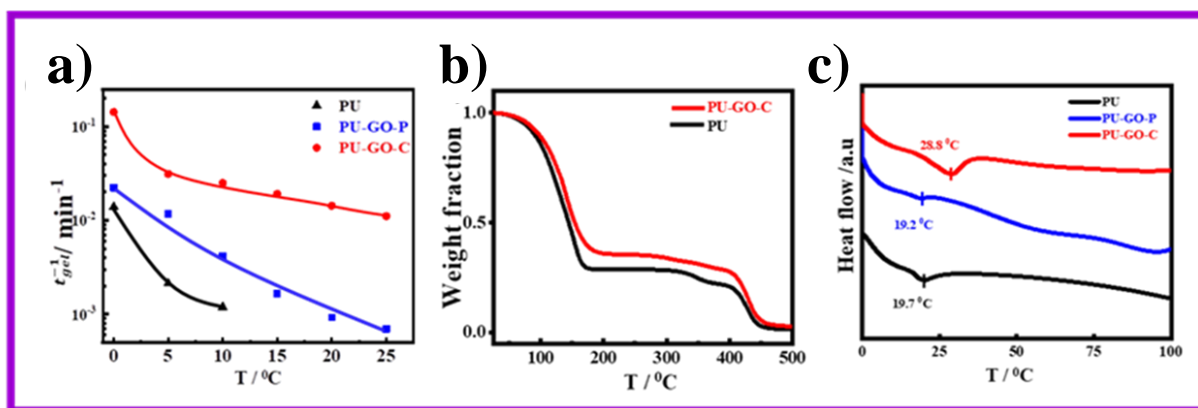

Figure 6.2: (a) Gelation kinetics of pure PU, PU-GO-P and tagged polymer nanocomposites (PU-GO-C); (b) Thermogravimetric curves of indicated gels showing relative rate of solvent evaporation; and (c) DSC thermograms of PU, PU-GO-P, and PU-GO-C gels showing the relative gel melting through vertical lines.

The gel melting temperature of pure PU and physical mixture (PU-GO-P) occurs at 19.7 and 19.2 ^{0}C, respectively, while significantly higher gel melting temperature is observed for PU-GO-C (28.8 ^{0}C) indicating the formation of strong gel when GO sheets are chemically connected with PU chains. The heat of fusion (ΔH) values, calculated from the area under the melting endotherm, are similar for pure PU and PU-GO-P (16.1 and 16.3 J/g, respectively) while higher ΔH is measured for PU-GO-C (17.3 J/g) indicating higher crystallinity in case of chemically tagged GO with polyurethane. However, thermal measurements indicate the formation of strong and stable gel formation when GO sheets are connected to polyurethane chains through covalent linkages. **Figure 6.3a** describes the UV-vis absorption spectra of pure PU, PU-GO-P and PU-GO-C dried gels. Pure PU dried gel shows the absorption peaks at 291 nm is due to n $\rightarrow \pi^*$ transition of polymer, whereas both physically and chemically tagged polymer nanocomposites dried gels exhibit red shifted absorption peaks observed at 319 and 323 nm, respectively, indicating greater interaction of GO platelets with PU chain.[154,205]
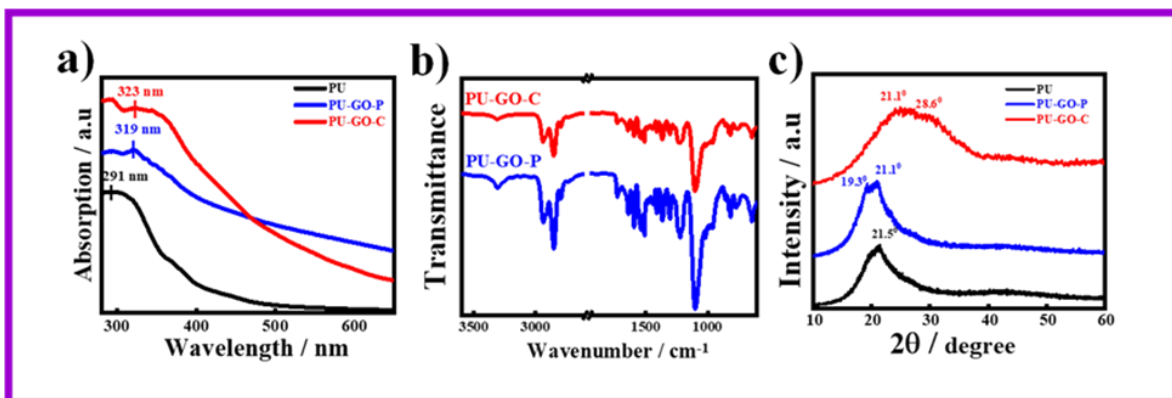

Figure 6.3: (a) UV-vis absorption spectra of PU, PU-GO-P and PU-GO-C nanocomposites dried gel; (b) FTIR spectra of chemically tagged and physical mixture of indicated nanocomposite dried gels; (c) XRD patterns of PU, PU-GO-P and PU-GO-C dried gels.

Amongst the nanocomposites, chemically tagged GO shows greater interaction as evident from large shift along with a very wide range of the absorption peak. FTIR spectra of pure PU, PU-GO-P and PU-GO-C dried gels are shown in **Figure 6.3b**. Pure PU shows the >NH stretching vibration at 3306 cm^{-1} while in both composite gels, the peaks are shifted towards higher wavenumber at 3309 and 3313 cm^{-1} for PU-GO-P and PU-GO-C gels, respectively, due to greater interaction of GO with polymer chains. The XRD diffraction patterns of pure PU and dried composite gels are shown in **Figure 6.3c**. Pure PU dried gel shows the characteristics peaks at $2\theta = 21.5^0$ indicating crystalline nature arising from the hard segment in PU matrix, while two peaks are observed at 2θ values of 19.3^0 and 21.1^0 due to physically incorporated GO in polymer matrix.[206,207] On the other hand, new hump at 28.8^0 is evident with considerably wider peak in PU-GO-C dried gel.
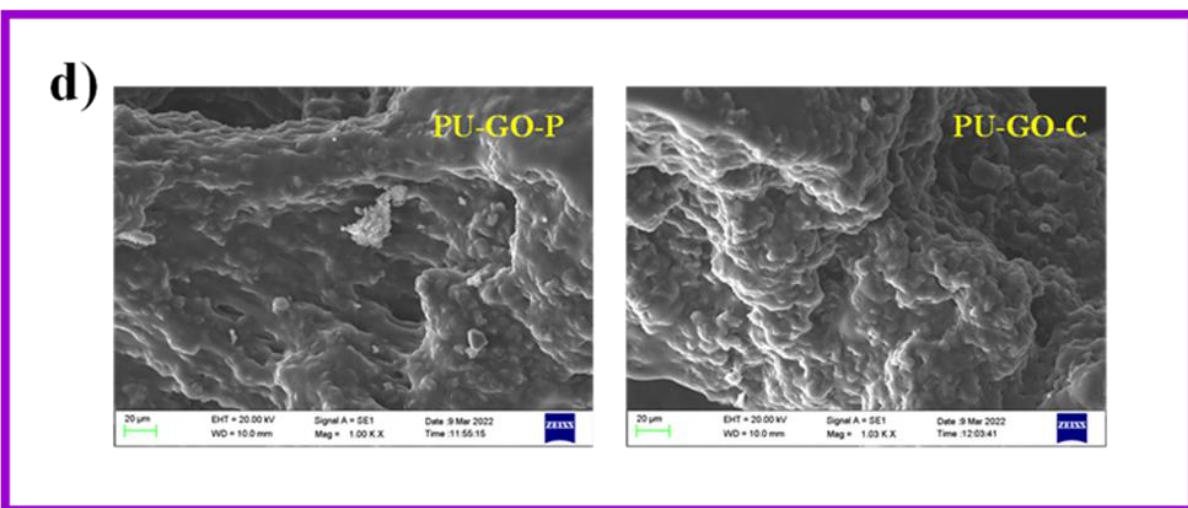

Figure 6.4: (d) SEM images of pure PUs and chemically tagged nanocomposite dried gel (PU-GO-C).

However, wider XRD peak along with greater shifting of peak positions in UV and FTIR patterns clearly indicate stronger interaction in chemically tagged PU-GO-C gel in comparison to the physical mixture. The SEM images of the physically and chemically tagged polymer nanocomposites dried gels are shown in **Figure 6.4a** and greater non-homogeneity of surface roughness is observed in chemically tagged gel.

6.3 Effect of Chemical Tagging on Rheological Behavior

The rheological measurements offer the knowledge of microstructural changes occurring within the polymer nanocomposites and in this case should show the distinct behavior while compared to physical mixture. with respect to angular frequency depending on the interaction between filler and polymer matrix. The storage modulus (G'), loss modulus (G") and complex viscosity (η^*) as a function of angular frequency have been performed using the gels as shown in **Figure 6.5a.** The storage moduli (G') show almost parallel to x-axis with increasing frequency for all the samples indicate the gel (three-dimensional network) nature while the gel strength increase in presence of GO sheets and significantly higher modulus is observed in case of PU-GO-C due to chemically attached GO sheet with polymer chain. The gel strengths (G') at 1 rad.s^{-1} are found to be 88, 560 and 12844 Pa for pure PU, PU-GO-P and PU-GO-C, respectively. On the other hand, loss moduli (G") increase gradually with increasing frequency for all the gels while the relative value of loss modulus follow the order PU-GO-C > PU-GO-P > PU throughout the whole range of frequency studied. This is to mention that the values of storage moduli are higher than the loss moduli for any particular gel, a characteristic of typical gel. The complex viscosity gradually decreases with increasing frequency for all three gels while the relative order of viscosity is maintained as PU-GO-C > PU-GO-P > PU. The chemical connectivity of graphene in PU-GO-C increases the

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viscosity as compared to physical mixture even though the viscosity of polyurethane in presence of GO (physical mixture) is higher than that of pure PU due to change in microenvironment in presence of GO platelets.
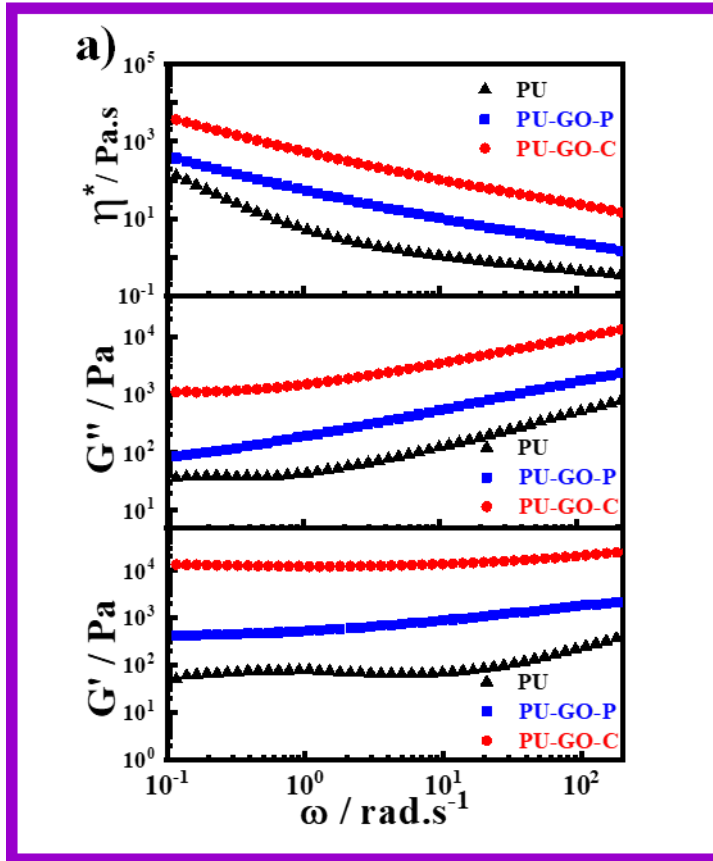

Figure 6.5: (a) Frequency sweep measurement of polymer nanocomposites gels in terms of storage modulus, loss modulus and complex viscosity as a function of angular frequency measured at 25 ºC.

6.4 Viscous Flow Behavior

Figure 6.6a describes the viscosity flow behavior of PU, PU-GO-P, and PU-GO-C gels at 25 ^{0}C for wide range of shear rate. Pure PU exhibit a small zero shear viscosity indicating liquid like

behavior while continuous decrease of the viscosities is noticed both for PU-GO-P and PU-GO-C gels. This is to mention that the viscosity of chemically tagged GO with PU exhibits significantly higher viscosity as compared to physical mixture throughout the whole range of shear rate studies. The shear thinning behavior is observed for pure PU weak gel (liquid-like behavior) with Newtonian plateau, while for PU-GO-P and PU-GO-C polymer nanocomposite gels this plateau disappear due to the presence of GO sheet in the physical mixture (PU-GO-P) and significant shear thinning is noticed in PU-GO-C gel arising from the non-ideal behavior when GO sheet is chemically attached with PU chain. Hence, the chemical attachments of GO in polymer matrix enhanced the viscosity of the nanocomposite gels as compared to pure PU gel.
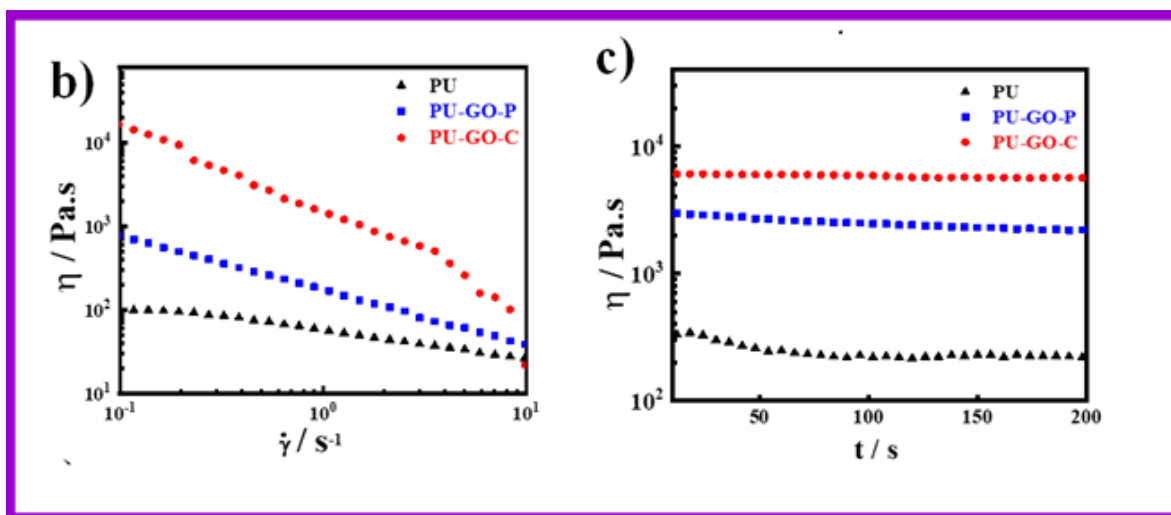

Figure 6.6: (a) viscosity flow curve behavior of PU, PU-GO-P and PU-GO-C nanocomposite gels as a function of shear rate; and (b) Constant shear measurement ($\dot{\gamma} = 1$ s^{-1}) of nanocomposite gels as function of time.

The steady shear viscosity as a function of time for all the gels (pure PU, PU-GO-P and PU-GO-C) are shown in **Figure 6.6b** ($\dot{\gamma} = 1$ s^{-1}). The initial viscosity for pure PU, PU-GO-P and PU-GO-C gels are found to be 3.6×10^2, 3.1×10^3 and 6.17×10^3 Pa. s, respectively. Slight reduction of viscosity is noticed at longer time scale in case of pure PU gel, arises from the weak nature of the gel (disordered structure appears from shearing effect). Physical mixture shows very slight reduction while the chemically tagged GO with PU (PU-GO-C) exhibits steady shear without any reduction indicating its strong structure at a particular shear rate ($\dot{\gamma} = 1$ s^{-1}). The absolute value of the steady shear viscosity of PU-GO-C is significantly higher as compared to pure PU gel primarily due to the tagging of graphene oxide in the polymer chain.

6.5 Stress Relaxation Behavior

The stress relaxation behavior of pure PU and GO tagged polymer nanocomposites gels are shown in **Figure 6.7,** which describe the relaxation modulus G(t) as a function of time (t) under an applied constant shear strain of 10%. The relaxation modulus G(t) is related to relaxation time, equilibrium modulus (G_∞) and time (t) at constant temperature of the polymer gels is estimated using the following equation.

$$\text{G(t)} = G_\infty \left[1 + (t/\tau_0)^{-m}\right] \qquad \text{…………………………. (6.4)}$$

where, G(t) is the relaxation modulus, G_∞ is the equilibrium modulus, t is the time and τ_0 is the relaxation time and m is exponent depend on the material. The parameter m of the materials is promotional to the cross linked density of the materials or in other words complexity in the system developed by the presence of additives or modified chemical nature of the system.[208] The

relaxation modulus of pure PU gel decreases rapid with time indicating very weak nature of the gel which relaxes quickly.
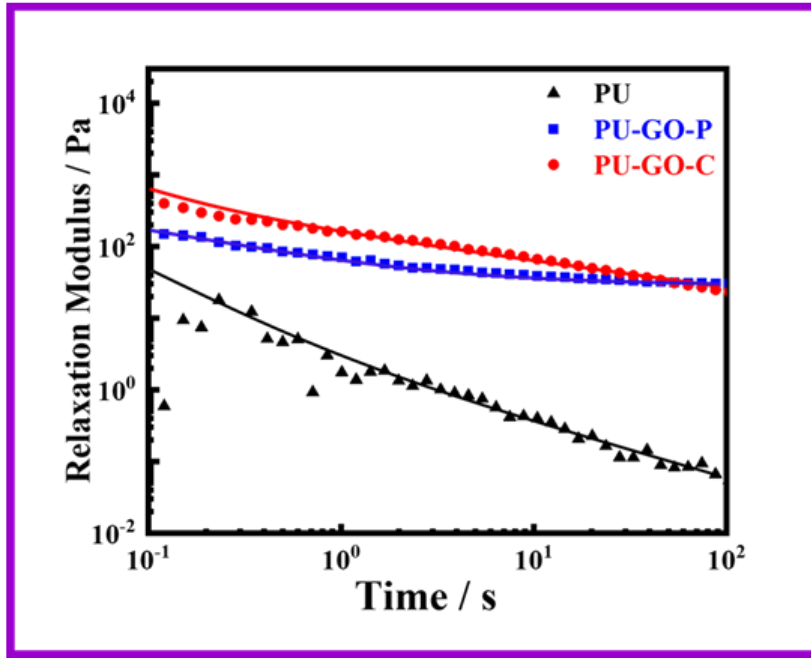

Figure 6.7: Stress relaxation behavior of pure PU, PU-GO-P, and PU-GO-C gels at 25 ^{0}C.

Table 6.1. Various parameters as obtained from the fitting of the curve as per the Chasset and Thrion equation.

System	G_∞ (Pa)	τ_0 (ks)	m
PU	0.15	4.70	0.21
PU-GO-P	1.87	5.14	0.26
PU-GO-C	2.94	5.46	0.27

On the other hand, the chemically tagged GO (PU-GO-C) exhibits steady relaxation modulus (only slight reduction with time) indicating elastic gel formation when GO is tagged with PU chains. Physical mixture also shows moderately low reduction of relaxation modulus with time though the absolute value of the modulus is higher in PU-GO-C as compared to PU-GO-P. Hence, the relaxation modulus, viscoelastic properties and relaxation behavior of the chemically tagged GO polyurethane polymer are significantly higher as compared to pure PU and physically mixed GO with polymer matrix gels. In order to understand the applicability of the Chasset and Thrion equation in pure PU gel and chemically and physically GO-tagged nanocomposite gels was subjected to curve fitting as per equation 4, and the representative fitting results are shown in **Figure 6.7**. Apparently, the better fitment of experimental data with Chasset-Thrion equation is obtained in all prepared gels system studied and for the comparison purposes G_∞, τ_0 and m ware determined for each prepared gel from the fitted data, which are shown in **Table 6.1**. The characteristics relaxation time τ_0 are worth mentioning here and the trends in τ_0 is consistent with perceived role of the dangling chains. The value of m is linearly dependent on the cross-linked density of the gels; however, the value of m increases with increases the cross-link density. Dzierzra et.al ware determined the relaxation time for polyurethane polymer with various degree of cross-linked density and they observed the relaxation time value ($\tau_0 = 0.0168$-50.8 ks) increase with increases the cross-link density. The pure PU gels have low relaxation time value 4.70 ks whereas, the presence of GO- sheet in polymer matrix the cross-linked density of the prepared nanocomposite gel was enhanced resulting the nanocomposite gels τ_0 values are increases to be 5.14 ks and 5.46 for the PU-GO-P and PU-GO-C respectively. The larger relaxation value of cross-linked polymer nanocomposite gels is due to the presence of the GO-sheet in polymer matrix and

the interaction between polymer matrix chains enhanced hence, required larger relaxation time for the polymer chains relaxation.

6.6 Conclusion

The graphene oxide is successfully tagged with polyurethane chains through three stages of polymerization technique and prepared the gels in organic solvent and studied the effect of chemical tagging on gelation behavior. Dramatic enhancement of gelation rate is observed when graphene is chemically tagged with polymer. Pure PU forms a weak gel while graphene tagged PU formulate a strong gel as evident from high gel melting and better solvent retention properties. Graphene oxide interact nicely with polyurethane chains as evident from the UV and FTIR peak shifting as compared to physical mixture of the two components. The structure formation and homogeneity of morphology alter considerably when GO is chemically tagged with PU chains. The details rheological studies have been measured to understand the effect of chemical tagging of GO in polyurethane. The gel strength significantly increases in chemical tagging of GO in PU while viscosity enhances considerably as compared to pure PU and physical mixture gel. The stress relaxation modulus as a function of time has been measured to understand the elastic effect caused by the chemical tagging of GO with PU. The limitation of the experimental work is to fabricate and measure the device performance in inert atmosphere.