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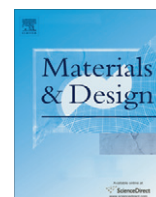
# Static and dynamic mechanical properties of poly(vinyl chloride) loaded with aluminum oxide nanopowder

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## ARTICLE INFO

## ABSTRACT

A series of nanocomposites from poly(vinyl chloride) loaded with different concentrations of $Al_2O_3$ nanopowder was prepared. The tensile mechanical properties of these composites were studied at different temperatures namely; stress–strain curves. The elastic modulus was calculated and found to decrease with increasing both filler loading and temperature. The strain at a certain stress at different temperatures was studied and the thermal activation energy for polymer chains was calculated. The complex viscosity as well as the storage modulus was found to decrease with increasing the filler loadings at different frequencies. The relaxation time of the polymer matrix was calculated and found to independent on the concentration of the filler but it decreased linearly with increasing frequency. The glass transition temperature was found to increase with increasing both filler loading and frequency.

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## 1. Introduction

Poly(vinyl chloride) PVC is one of the most important polymers used these days, since it has many applications in medical equipments, pipes as well as some machine elements [1]. Developments of the mechanical properties as well as other properties were achieved by adding inorganic filler phases throughout different processing techniques. Many studies reported the effect of different inorganic fillers in the nano-scale on the polymer host properties. PVC/inorganic nanocomposites based on silica [2], calcium carbonate [3], montmorillonite [4,5], and titania [6] and calcium carbonate [7,8] have been previously reported.

The study of the mechanical properties of polymer composites have made it desirable to choose these materials over traditional materials for numerous types of applications, such as binder constituents in explosives, load-bearing components, and jet engine modules. As the uses of polymer composites increase, an understanding of the mechanical behavior of these materials becomes vital for creating innovative and economical designs for various components. Polymer composites have more complicated properties as they display elastic and viscous responses at different strain rates and temperatures [9–11]. Young's modulus can be improved by adding inorganic fillers since it generally has a much higher stiffness than polymer matrices [12]. Stress transfer between the inorganic filler particles and the polymer matrix strongly affect the strength of the composite [13]. However, for poorly bonded micro-particles, strength reductions occur by adding particles [14].

Gibbs et al. [15] presented the general description of the nature of the glass transition temperature ($T_g$) of polymers. Different experimental techniques, including differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and dielectric measurements are used for the determination of $T_g$ [16–18]. The influence of various low dimensions particles, for example bismuth oxychloride and organic montmorillonite (MMT) on the glass transition temperature of PVC was reported [19,20]. Generally an increase of $T_g$ as a function of nanoparticles contained was found, however for the MMT an intercalation related decrease of $T_g$ was stated.

The aim of this work is to study the influence of $Al_2O_3$ nanoparticles with different ratios in PVC host on the tensile mechanical properties at different temperatures, rheological properties at different frequencies and DMTA properties.

## 2. Experimental

### 2.1. Materials

Poly(vinyl chloride) (PVC) used in this work was supplied from Sabic Company, Saudi Arabia. It was in the powder form (powder fraction of 90–120 μm, average size of 100 μm, density $\rho$ = 1.37 g/cm$^3$) was used as a polymeric matrix for preparation

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of composites. Aluminum oxide $Al_2O_3$ nanopowder filler with particle size diameter less than 50 nm was delivered from Aldrich.

## 2.2. Polymer composites preparation

The filler ($Al_2O_3$) were embedded into the polymer matrix with the needed proportions by mechanical mixing. Mechanical mixture of the PVC and filler powder was further homogenized by grinding in a porcelain mortar to a visually homogeneous state. For more well dispersion of the filler, the composite powder was ball-milled with two milling balls (stainless steel, 12 mm diameter) under 20 Hz vibration condition for 2 min at room temperature. Homogenized composite was placed into a hot steel mold heated up to 160 °C and then pressed (hot compacted) during 5 min at 20 MPa with subsequent cooling of the mold in the air flow up to room temperature.

## 2.3. Tensile tests

The tensile tests were carried out on dumbbell-shaped specimens. The measurements were done at different temperatures of 25, 40, 60 and 80 °C on a Dynamic Mechanical Analyzer DMA Q800 (TA Instruments LLC, Delaware, USA) instrument with film clamps at a force rate of 1.5 N/min according to ASTM D 412 [21].

## 2.4. Rheological and dynamic mechanical

The mentioned DMA Q800 instrument was used through the rheological and dynamic mechanical studies. For these tests a film-clamp was used in dry mode. A slow heating rate of 1 °C/min was employed throughout to ensure that the sample was in thermal equilibrium with the instrument. The oscillating frequency was changed from 0.1 Hz to 200 Hz.

Rheological tests experiments were performed with the film under tension while the frequency is changed. A static pre-load force (0.01 N) was applied to the sample prior the dynamic oscillating force to prevent film buckling [22].

During measurement, the instrument was programed to maintain the static load at 125% of the force required to oscillate the sample. It is important that the film remained in its linear viscoelastic region during measurement (to ensure that the properties observed were independent of the deformation applied and truly reflected molecular motions), and so experiments were recorded maintaining constant strain. Generally, for thin polymer films, linear viscoelastic behavior can be assured with a strain less than 0.1%, and so this limit was used [22].

## 3. Results and discussions

### 3.1. Tensile properties

Figs. 1–5 present the stress–strain curves for PVC loaded with 0, 0.5, 1.0, 2.0 and 5.0 wt.% of aluminum oxide nanopowder different temperatures of 25, 40, 60 and 80 °C, respectively. The maximum stress reached in these figures is not the ultimate strength, but it is the maximum stress available for the instrument used. All composites at temperatures 25, 40 and 60 °C show straight lines relations between stress and strain in the studied range of stresses. This reflects the Hookean behavior of these composites at theses temperatures. One can differentiate between these figures at low strain using the inserts. At a temperature of 80 °C (which is close to the glass transition temperature of PVC), yielding of these materials takes place with yield stress values of 6.68, 7.77, 6.57, 5.89 and 6.49 MPa for samples loaded with 0, 0.5, 1.0, 2.0 and 5.0 wt.% of $Al_2O_3$, respectively.
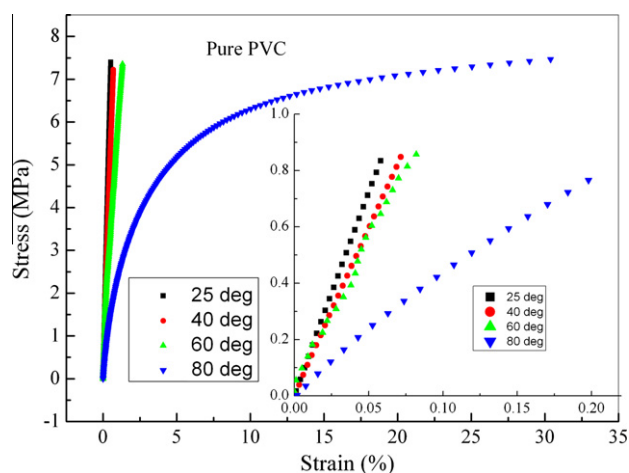


**Fig. 1.** Stress–strain curves for unloaded PVC at different temperatures.
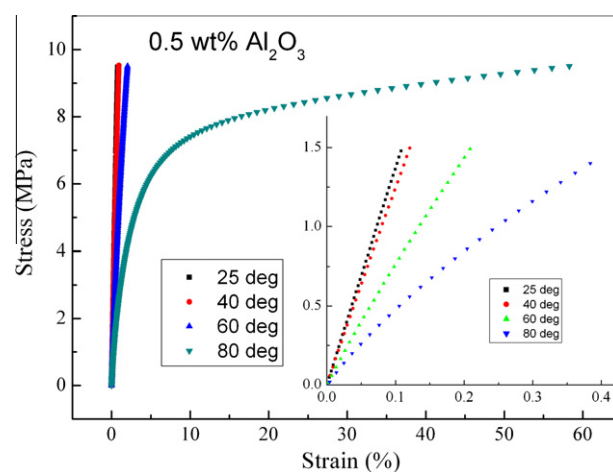


**Fig. 2.** Stress–strain curves for PVC loaded with 0.5 wt.% of $Al_2O_3$ nanopowder at different temperatures.
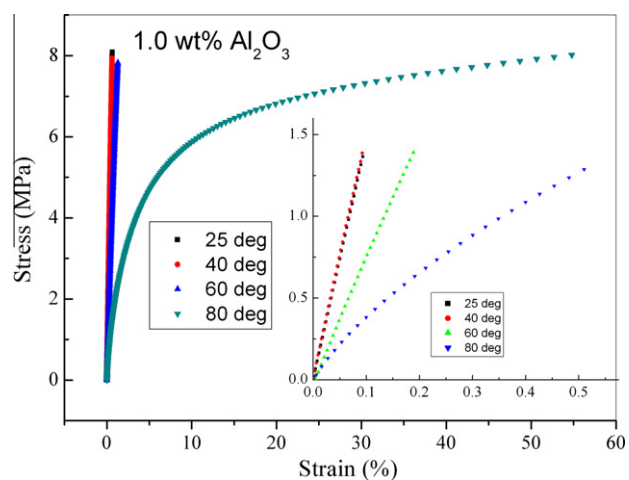


**Fig. 3.** Stress–strain curves for PVC loaded with 1.0 wt.% of $Al_2O_3$ nanopowder at different temperatures.

The inserts of the figures are used to calculate the elastic modulus E of these composites for the different samples and at
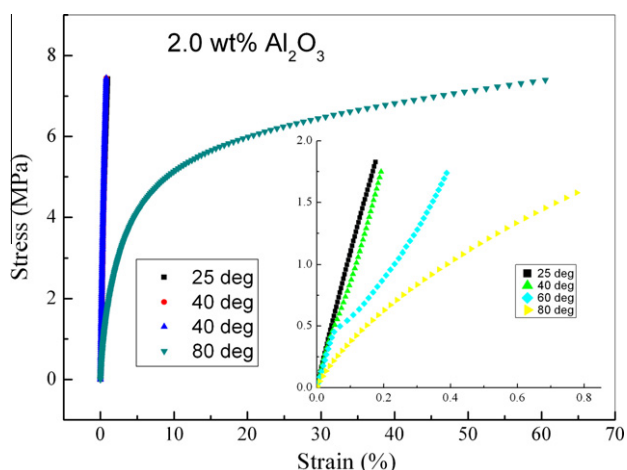
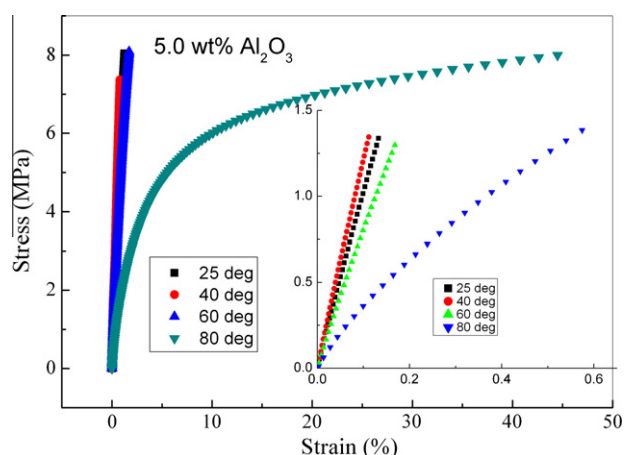**Fig. 4.** Stress–strain curves for PVC loaded with 2.0 wt.% of Al$_2$O$_3$ nanopowder at different temperatures.



**Fig. 6.** The strain at an applied stress of 6.5 MPa as a function of temperature for the different concentrations of Al$_2$O$_3$ nanopowder.



**Fig. 5.** Stress–strain curves for PVC loaded with 5.0 wt.% of Al$_2$O$_3$ nanopowder at different temperatures.



**Fig. 7.** The complex viscosity as a function of frequency for the different concentrations of Al$_2$O$_3$ nanopowder.

**Table 1**
The calculated values of the elastic modulus $E$ at different temperatures, $\alpha$, $\gamma$ and the thermal activation energy $w$.

| Concentration of Al$_2$O$_3$ | $E$ (GPa) | | | | $\alpha$ | $\gamma$ | $w$ (eV) |
|---|---|---|---|---|---|---|---|
| | 25 °C | 40 °C | 60 °C | 80 °C | | | |
| 0 | 1.44 | 1.187 | 0.953 | 0.365 | 0.0135 | 0.208 | 0.062 |
| 0.5 | 1.381 | 1.251 | 0.738 | 0.373 | 0.098 | 0.146 | 0.087 |
| 1 | 1.572 | 1.315 | 0.746 | 0.272 | 0.0091 | 0.136 | 0.048 |
| 2 | 1.108 | 0.871 | 0.447 | 0.268 | 0.009 | 0.213 | 0.052 |
| 5 | 1.24 | 1.033 | 0.797 | 0.246 | 0.0145 | 0.237 | 0.058 |

different temperatures. These values of $E$ are listed in Table 1. The general behavior of E is found to decrease with increasing the filler. At low concentrations of Al$_2$O$_3$ nanopowder, it acts as inactive filler distributed in the PVC matrix. At higher concentrations, beside its inactivity, it may make scission of PVC chains. Al$_2$O$_3$ nanopowder can be considered as a solid phase surrounded by a soft phase of PVC without interfacial interactions between them or between the nanoparticles themselves. This may be the reason behind the decrease in the elastic modulus.

The strain at an applied stress of 6.5 MPa for all the studied samples at different temperatures is presented in Fig. 6. A high
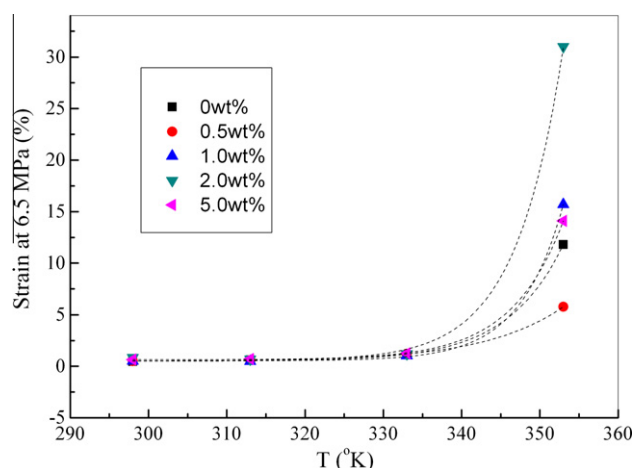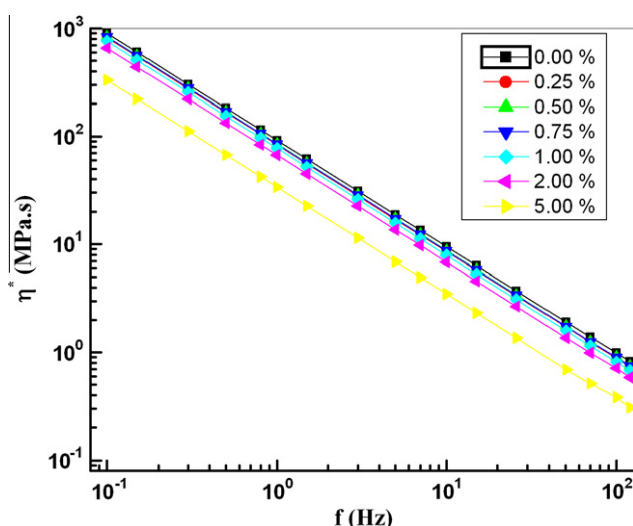
difference in the strain at this applied stress is observed well at a temperature of 80 °C. The behavior of this strain is fitted very well with an exponential function of the form

$$\varepsilon_T = \varepsilon_o + \varepsilon' \exp\left(\frac{kT}{w}\right) \tag{1}$$

where $\varepsilon_T$ and $\varepsilon_o$ are the strains at temperatures $T$ and $T_o$, respectively, $\varepsilon'$ is a fitting parameter, $k$ is the Boltzmann constant and $w$ is a constant and has the dimensions of energy and may refers to the thermal energy acquired by the polymer chains upon heating. The values of $w$ are listed in Table 1.

### 3.2. Rheological properties

The complex viscosity for all studied composites as a function of frequency is shown in Fig. 7. Apparently, Al$_2$O$_3$ nanopowder has a bounded effect on the rheological behavior of the composites, even at low loadings. The complex viscosity decreases, in general, with increasing Al$_2$O$_3$ content in the entire frequency range. In the studied frequency range the impact of Al$_2$O$_3$ nanopowder on the
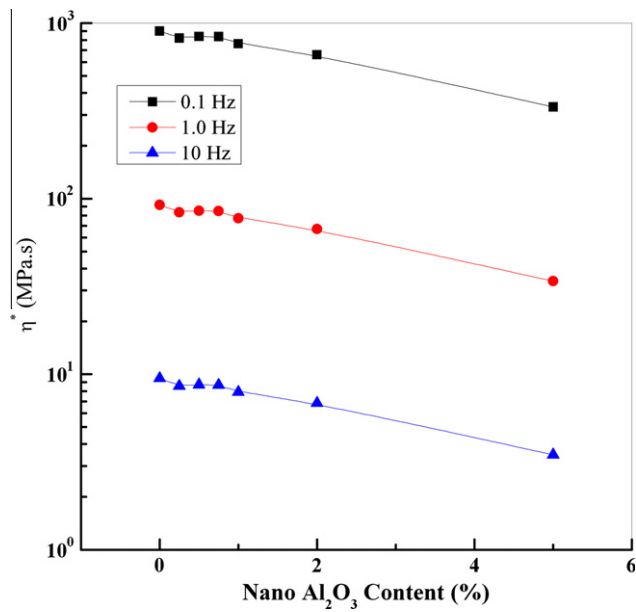
**Fig. 8.** The complex viscosity as a function of the concentrations of $Al_2O_3$ nanopowder at different frequencies.



**Fig. 9.** The storage modulus as a function of frequency for the different concentrations of $Al_2O_3$ nanopowder.
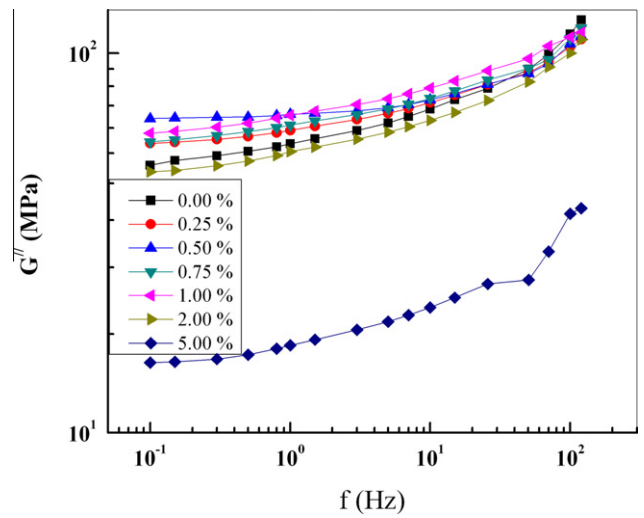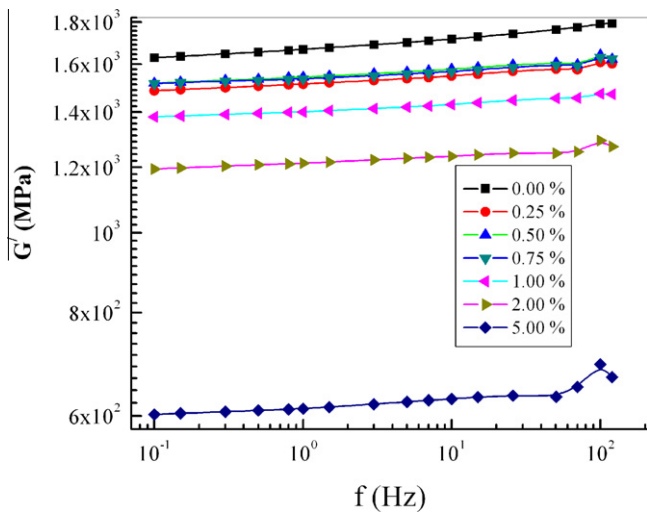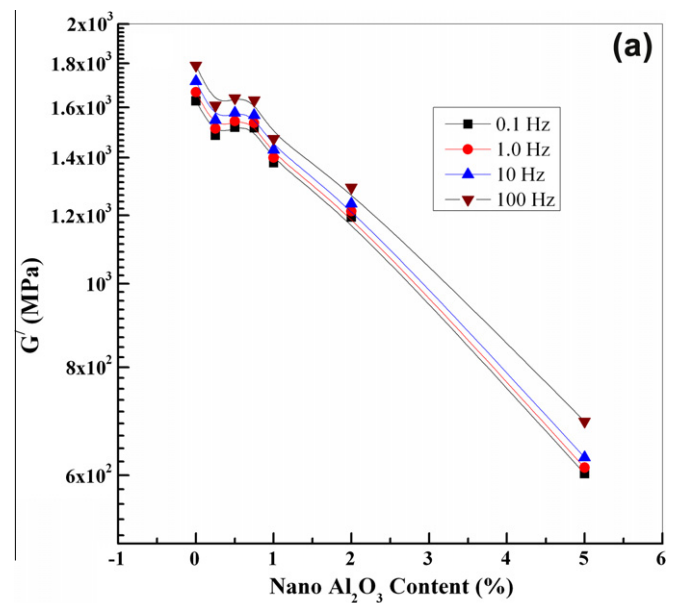


**Fig. 10.** The loss modulus as a function of frequency for the different concentrations of $Al_2O_3$ nanopowder.



**Fig. 11.** The storage modulus (a) and the loss modulus (b) as a function of the concentrations of $Al_2O_3$ nanopowder at different frequencies.

rheological properties is definitely weak, which suggests that the nanopowder do not significantly influence the short-range dynamics of the polymer chains. Generally, $Al_2O_3$ nanopowder has a slight effect on the local motion at short ranges [23]. The decrease in the complex viscosity with increasing frequency indicates a non-Newtonian behavior over the frequency range investigated. The shear thinning behavior observed in the $Al_2O_3$/PVC nanocomposites may be attributed to the orientation of the rigid molecular chains in the nanocomposites during the applied force.

The variation of $\eta^*$ for $Al_2O_3$/PVC nanocomposites with the $Al_2O_3$ content at different frequencies is shown in Fig. 8. It can be seen that $\eta^*$ of the nanocomposites decreases with increasing $Al_2O_3$ content over the frequency ranges investigated. This decrease in $\eta^*$ with increasing $Al_2O_3$ content may be attributed to the decrease in physical interactions between PVC chains. The decrease in $\eta^*$ of $Al_2O_3$/PVC nanocomposites with the addition of
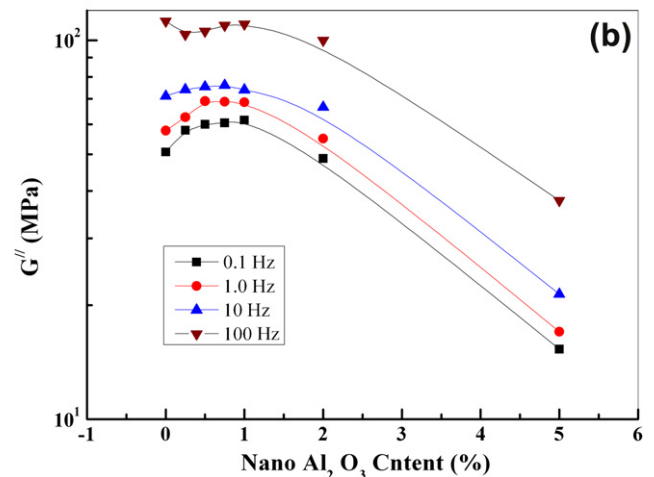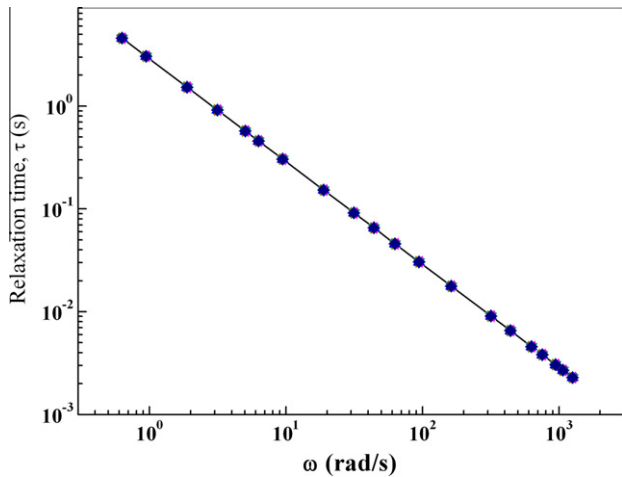
**Fig. 12.** The relaxation time as a function of the angular frequency for the different concentrations of Al$_2$O$_3$ nanopowder.
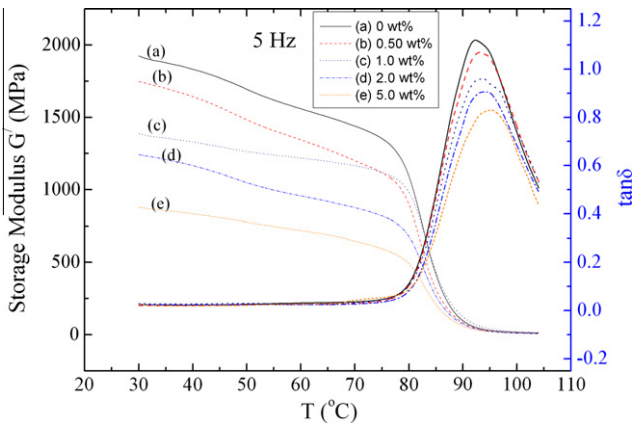


**Fig. 13.** The Storage modulus and the loss factor as a function of temperature for the different concentrations of Al$_2$O$_3$ nanopowder at a constant frequency of 5 Hz.
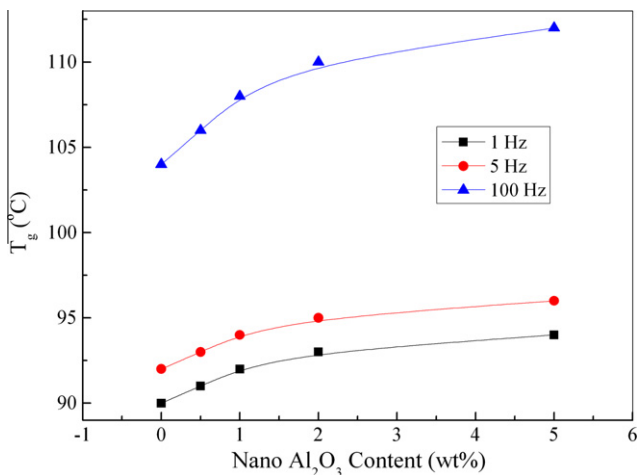


**Fig. 14.** The glass transition temperature as a function of the concentrations of Al$_2$O$_3$ nanopowder at different frequencies.

Al$_2$O$_3$ was closely related to the decrees in the storage modulus, which will be described in the following section. The complex viscosity can be expressed by a power law $\eta^* \alpha \omega^{-\beta}$. The value of $\beta$ is constant and equal 0.98 for all Al$_2$O$_3$ contents.

The storage modulus $G'$ and loss modulus $G''$ for Al$_2$O$_3$/PVC nanocomposites as a function of frequency are shown in Figs. 9 and 10. The values of $G'$ and $G''$ are slightly increased with increasing frequency while a decrease is observed with increasing Al$_2$O$_3$ content. This rheological response is similar to the relaxation behavior of the typical filled-polymer composite systems [24]. It is known that the polymer chains are fully relaxed and exhibit characteristic homopolymer-like terminal flow behavior, resulting in that the flow curves of polymers being expressed by the power law $G' \alpha \omega^2$ and $G'' \alpha \omega$ [25–27]. Krisnamoorti and Giannelis [27], reported that the slopes of $G'(\omega)$ and $G''(\omega)$ for polymer/layered silicate nanocomposite were much smaller than 2 and 1, respectively, which are the values expected for linear homodispersed polymer melts. They suggested that large deviations in the presence of a small quantity of layered silicate might be due to the formation of a network structure in the molten state.

The dependence of $G'(\omega)$ and $G''(\omega)$ for Al$_2$O$_3$/PVC nanocomposites can be expressed by power laws of the forms $G'(\omega) \alpha \omega^{\alpha}$ and $G''(\omega) \alpha \omega^{\gamma}$ with the values of $\alpha$ and $\gamma$ are presented in Table 1. These values indicate the nonterminal behavior with the power-law dependence for $G'$ and $G''$ of the Al$_2$O$_3$/PVC nanocomposites.

Similar nonterminal rheological behavior has been observed in ordered block copolymers and smectic liquid-crystalline small molecules [28–30]. The slope of $G'$ versus frequency is approximately unchanged (and also of $G''$) which indicates that the nanopowder filler Al$_2$O$_3$ is an inert one and decreases the interaction between host polymer chains.

The variations of the storage modulus and loss modulus for Al$_2$O$_3$/PVC nanocomposites with the Al$_2$O$_3$ content at different frequencies of 0.1, 1.0, 10 and 100 Hz are shown in Fig. 11. It can be seen that the incorporation of small quantity of Al$_2$O$_3$ up to 1.0 wt.% into PVC matrix slightly increases the values of $G''$ for the Al$_2$O$_3$/PVC nanocomposites over the frequency range investigated, except at a frequency of 100 Hz. This phenomenon may be attributed to some rearrangement of polymer chains. Beyond this concentration, significant decrease is observed for both $G'$ and $G''$ for all investigated frequencies in accordance with the decrease in the complex viscosity described before as well as the tensile elastic modulus $E$. This may be attributed to the formation of the viscous surface layers around the dispersed nanofiller powder leading to an increase in the free volume in this nanocomposite system, making it easier for flow to occur [31].

The relaxation time $\tau$ under dynamic shear in the polymeric systems that involved the pseudostructures can be calculated from the following equation [28].

$$J' = \frac{G'}{(|\eta^*|\omega)^2} = \frac{\tau}{|\eta^*|} \tag{2}$$

where $J'$ and $\omega$ are the compliance and the angular frequency, respectively. It is expected that the presence of some molecular order or the physical structure leads to a much longer relaxation time [31]. As shown in Fig. 12, the relaxation time Al$_2$O$_3$/PVC nanocomposites decreases with increasing frequency according to an equation of the form

$$\log(\tau) = a - b\log(\omega) \tag{3}$$

where $a$ is a constant and $b$ is the slope of the log–log plot between $\tau$ and $\omega$ and equal unity. Interestingly, it is observed that the incorporation of Al$_2$O$_3$ into PVC host polymer does not affect the relaxation time at all.

### 3.3. Dynamic mechanical properties

Fig. 13 plots the storage modulus $G'$ and the loss factor tan $\delta$ of Al$_2$O$_3$/PVC nanocomposites, obtained by DMA measurement, as a function of temperature at a constant frequency of 5 Hz. The loss

factor is very sensitive to the structural transformation of the materials, and can be calculated from the ratio of the loss modulus to the storage modulus ($G''/G'$). Below the glass transition temperature, $T_g$, the $Al_2O_3$/PVC nanocomposites exhibit a high storage modulus. The storage moduli of the $Al_2O_3$/PVC nanocomposites at about 40 °C are decreased by introducing $Al_2O_3$ as described before. Adding $Al_2O_3$ nanoparticles to the PVC matrix shifts the tan $\delta$ peak values of these composites to high temperature regions. Since the storage modulus decreases with increasing $Al_2O_3$ content due to the absence of interfacial interactions between the filler and PVC chains, so the increase in $T_g$ indicates that the nanofiller particles are well dispersed and a mechanical restriction on the mobility of the PVC chains. Increasing the $Al_2O_3$ content does not change the breadth of the tan $\delta$ peak which relates to the relaxation of the polymer chain which confirms the constant relaxation time achieved before.

Fig. 14 plots the relationship between the glass transition temperature of $Al_2O_3$/PVC nanocomposites and $Al_2O_3$ at different frequencies. All the $T_g$ values of $Al_2O_3$/PVC composites increased with the $Al_2O_3$ content. The solid phase $Al_2O_3$ nanoparticles act as obstacles for the polymer soft phase chains and restrict their mobility. Since the glass transition is inherently kinetic, it is strongly influenced by the rate or frequency of mechanical energy input. The substantial molecular relaxation involving cooperative segmental motion of the polymer chains occurs in the region of $T_g$. The rate of this segmental motion depends on temperature, so that if the test frequency is increased, the relaxations associated with the glass transition have difficulty in keeping up with the mechanical strain input, and the polymer appears to be more rigid. The segmental motion associated with $T_g$ then can occur only at a higher temperature. Thus $T_g$ increases with frequency as illustrated in Fig. 14.

## 4. Conclusions

Loading of PVC with nanopowder $Al_2O_3$ with concentrations up to 5.0 wt.% decreases the elastic modulus, complex viscosity and storage modulus. Increasing the test temperature decreases the elastic modulus as well as the yielding stress, while the strain at a stress of 6.5 MPa is increased. The complex viscosity, storage modulus, loss modulus and the glass transition temperature increase with increasing driving frequency. The relaxation time of polymer chains is independent on the nanofiller concentration while it decreases with frequency. The glass transition temperature increases with increasing both nanofiller concentrations and frequency.

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