



A study on the role of silica nanoparticles on the viscoelastic behavior of polyethylene

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ABSTRACT

In the current research the role of silica nanoparticles on the viscoelastic behavior of polyethylene (PE) has been investigated. To do so PE reinforced with different content of silica nanoparticles (i.e. 0, 1, 3, 5 and 10 Wt%) have been produced using extrusion and injection molding methods. In order to investigate the viscoelastic properties, Dynamic mechanical thermal analysis (DMTA) has been performed. The results showed that at constant frequency (1 HZ) the storage modulus of all materials including PE and its nanocomposites decreased as temperature increased from -150 up to 120 °C. For example the storage modulus of neat PE and PE reinforced with 5Wt% SiO₂ decreased from 2900 and 3400 MPa to 80 and 250 MPa respectively. Also the value of loss modulus increased as the polyethylene and its nanocomposites approached from low temperatures to the glass transition temperature. The loss modulus of PE and its nanocomposite has not any significant difference at low frequency. But this difference becomes more as frequency increases gradually. For example the difference between loss modulus of pure PE and PE/1Wt% SiO₂ at 50 HZ and 250 HZ are about 8 and 15 MPa respectively. The highest amount of tan δ is for the pure polyethylene sample, and with the addition of SiO₂ nanoparticles, the decreasing trend of tan δ observed. The lower values of tan δ indicating a reduction in the damping effect in composite samples compared to pure polyethylene.

Keywords: Polyethylene, Silica nanoparticles, Viscoelastic behavior.

1. Introduction

In the case of elastic behavior, the shape of a solid is changed due to an external stress and whenever the applied stress is removed, the object returns to its original state. Hooke's law is an ideal linear relationship for elastic bodies in which the stress is proportional to strain. Similarly, in Newtonian fluids, the shear stress is proportional to the shear rate, which is also called viscous behavior. An ideal form for viscous fluids is Newton's law in which stress is proportional to strain and changes with

time. Many materials exhibit both viscous and elastic behavior the so called viscoelastic materials. on the other hand viscoelasticity is the property of a group of materials that exhibit a behavior between elastic and viscous, and these properties appear when an external force is applied to them. In viscoelastic materials, the viscous part wastes energy, but the elastic part of the material stores energy in itself and releases it immediately as soon as it is unstressed [1].

Polymers, for example polyethylene, are

viscoelastic materials. This means that they have both elastic and viscous properties. In a long time or at high temperatures, they behave like a viscous liquid, and in a short time or at low temperatures, they behave like an elastic solid. When an external force is applied to the elastic material, it releases the stress and returns to its original form. But if the material is viscous, the strain created in the material is irreversible and the energy is dissipated in other forms such as heat [2]. One of the ways to determine the viscoelastic properties of a material is the mechanical dynamic analysis (DMA). It is performed by applying an oscillating force to the material results a sinusoidal strain. By measuring the amplitude of the strain fluctuation at the peak of the sinusoidal wave and the phase delay between the sinusoidal curves of stress and strain, the magnitudes of elastic and viscous modulus and glass transition temperature can be calculated. This temperature is the temperature below which the segment of polymer chains have not enough energy to vibrate or move and the polymer behaves like a brittle material. Above this temperature, the material softens and becomes more viscous. Physical and mechanical properties such as specific volume, modulus, tensile strength and hardness of the polymer show drastic changes at this temperature [3]. For example, if a polymer is heated until passes the glass transition temperature and becomes rubbery, its modulus suddenly drops tens of times. The variation of modulus with temperature can be detected by the DMA test. This modulus is not the same as conventional shear modulus, and is a complex modulus (G^*), mixed with a storage modulus (G') related to elastic behavior and a dissipation or loss modulus (G'') related to viscous behavior ($G^*=G'+iG''$). The ratio of these two parameters the so called $\tan\delta$ and refers to the damping behavior of the polymer. In fact δ is the phase difference between stress and strain, and whatever the material has more elastic property, δ becomes smaller and G' plays a greater role. The higher δ means the viscous behavior overcomes on the elastic one [4].

Qajar and his colleagues [5] investigated the effect of dispersion of carbon nanotubes as reinforcements on the viscoelastic properties of polymer nanocomposite. Their results showed that the viscous behavior depends strongly on agglomeration and dispersion of Reinforcement. Yang-Tse and Cheng [6-8] investigated the nano hardness of elastic and viscoelastic solids under

different loading [9]. They provided a sound basis for using the relationship for determining properties of viscoelastic solids using indentation techniques. Ashrafi and his colleagues [10, 11] investigated the contact issues between nano indenters and thin polymer layers using viscoelastic contact mechanics theories. Their results showed that by appropriate formulation of the viscoelastic constitutive equations, the problem can be solved numerically using the Matrix Inversion Method. Celentano et al. [12] published a paper on the characterization of the viscoelastic mechanical response of short-fiber reinforced thermoplastic tubes. The mechanical behavior of the composite lamina is characterized by means of monotonic and loading/unloading tensile tests at different deformation rates for specimens extracted in the axial and circumferential directions of the tube. Based on the experimental results, a three-dimensional Maxwell model with eight parameters, five to describe the elastic anisotropy response and three to describe the incompressible-isotropic viscoplastic response, is proposed. Nikhah et al.[13] reported the influence of applied tensile stretching rate and temperature on amorphous polyethylene/graphene (PE/Gr) and polyethylene/amino functionalized graphene (PE/aFG) interfaces via molecular dynamics (MD) simulations. The simulations results indicated that the interfacial adhesion during stretching process was increased with increasing the stretching rate (V) while decreased with increasing the temperature (T). viscoelastic properties of branched polyethylene investigated by Kil-Park et al. [14]. They reported that the viscoelastic properties of the branched polyethylene were very complicated due to the combined effect of the molecular weight difference and the degree of chain branching as well as the branching structure.

To the best of our knowledge the role of nano silica on viscoelastic properties of polyethylene has not been under more attention particularly at different temperatures and frequencies, and in the current research it is tried to fill the literature gap in this issue.

2. Experimental procedure

2.1. Materials

In the current research silica nanoparticles with average size of about 8-16 nm and density 2.1 g/cm³ have been used. The transmission electron microscopy (TEM) image of the nanoparticles can

also be seen in Figure 1. As seen the morphology of nano silica is almost spherical and the distribution of its size is uniform. In order to prevent agglomeration, these particles have been modified with silane as a surface agent. Polyethylene (PE) with the trade name HD 7255 is prepared from Maroon petrochemical Complex, Iran. Melt flow rate (190 °C/2.16kg) and density of the used PE are 4 (g/10min) and 0.954 (g/cm³) respectively.

2.2. Sample preparation

In order to make polyethylene nanocomposites a double screw extruder was performed in the temperature range of 200-230 °C. Afterward the standard samples were produced using injection molding. PE nanocomposites reinforced with different percentages of silica nanoparticles (i.e. 0, 1, 3, 5 and 10) were produced by Monomat model injection machine (Germany) in a temperature range of 220 to 230 °C. The composition and short name of all produced samples are summarized in

Table I.

2.3. Dynamic mechanical thermal analysis (DMTA)

The purpose of dynamic mechanical thermal analysis is to investigate the viscoelastic behavior of materials and determine some properties such as storage and loss moduli and glass transition temperature. In order to perform this test, the samples were tested using the DMA1 (Mettler-Toledo) star system model, manufactured by Switzerland. This test has been done in a temperature range of -150 to 120 °C and a certain frequency (1 HZ), as well as in a constant temperature (ambient temperature) and a variable frequency of 1 to 300 Hz. The used samples were tested with dimensions of approximately 20 mm in length, 9.16 mm in width, and 2.3 mm in thickness.

3. Results and discussion

Figures 2 and 3 show the variation of storage modulus (E') and loss modulus (E'') for pure

Table 1- The composition and short name of all produced samples

Short name	A	B	C	D	E
%SiO ₂	0	1	3	5	10

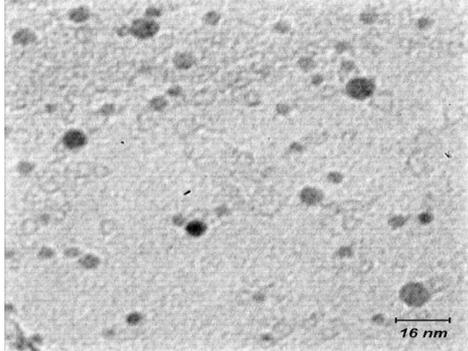


Fig. 1- TEM micrograph of silica nanoparticles

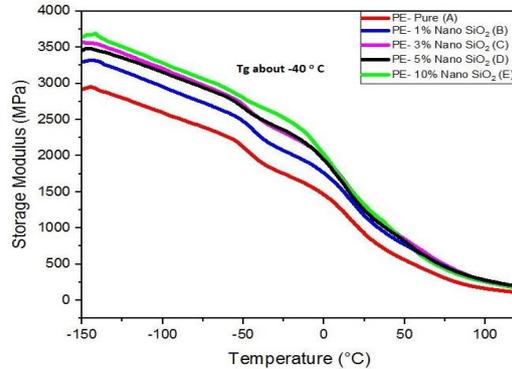


Fig. 2- Variation of storage modulus in the range of -150 up to 120 °C, at constant frequency (1 HZ)

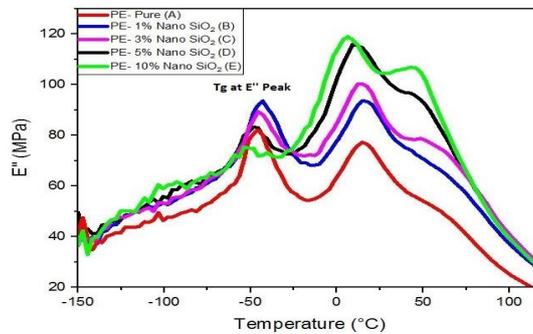


Fig. 1- Variation of loss modulus in the range of -150 up to 120 °C at frequency of 1 HZ.

polyethylene (sample A) and polyethylene reinforced with different content of SiO₂ (Samples B, C, D and E) on temperature at constant frequency (1HZ). As seen the storage modulus of all materials including PE and its nanocomposites decreases as temperature increases. The reason of this variation can be attributed to the fact that the storage modulus plays as a criterion for measuring the store of energy during deformation. Upon heating the storage modulus decreases because the molecular bounds will be weakened as temperature increases [15, 16]. As a matter of fact less force is required for slipping/stretching/compression the chains. The addition of SiO₂ nanoparticles to the PE causes to increase the storage modulus due to the effect of reducing the mobility of PE chains. Indeed an increase in storage modulus indicates the improvement of the stiffness of the polymer material in the presence of SiO₂ nanoparticles. As can be seen in Figure (2), at low temperatures (below the glass transition temperature, about -40 °C), the storage modulus of the nanocomposite is higher than that of pure PE and it is clear that the highest storage modulus belongs to sample E. The reason refers to the fact that Young's modulus of SiO₂ nanoparticles is much higher than PE and since it has a high thermal resistance, it keeps the storage modulus of composites high enough even at higher temperature. On the other hand the presence of SiO₂ nanoparticles prevents the decrease of polymer modulus. This is because an increase in temperature cannot make polymer chains to be mobile because of the presence of SiO₂ nanoparticles. In simple term, the modulus of polymer which is a symbol of the resistance to deformation, still high in the presence of nano silica, implying the higher efficiency particularly at higher temperatures.

By looking at in more details on the Figure 3 one may conclude that the behavior of loss modulus as a function of temperature below and above glass transition temperature is almost different. In fact the value of loss modulus increases as the polyethylene and its nanocomposites approaches from low temperatures toward the glass transition temperature. Besides the value decreases after the polymer temperature become higher than its glass transition temperature. The short answer for this variation can be attributed to the fact that in the region of the glass transition there is enough energy to move or activate the segments of polymer chains. However below which motions occur with

difficulty because of molecular friction implying more dissipation of the energy as heat. This is why the loss modulus increases as temperature approaches toward glass transition temperature. It is worth noting that in this condition much less energy can be stored since the molecular chains consume the energy and rapid decline in storage modulus can be observed.

The situation above glass transition temperature is a little be different of what happened below that. Indeed an elastic modulus (also known as modulus of elasticity) is the unit of measurement of resistance of an object or substance to being deformed elastically (i.e., non-permanently). It is clear that both storage and loss modulus should decrease with temperature. As temperature continues to increase above the glass transition the molecular frictions are reduced gradually implying the less energy is dissipated along with decreasing the loss modulus. It seems more decreasing occurs at temperature which is called glass transition temperature. In fact the maximum dissipation of energy occurs at glass transition temperature and in such temperature loss modulus appears to be at maximum value. It is worth noting that the behavior of a viscoelastic material depends strongly on both storage and loss modulus and in order to clarify the role of temperature on thermal and mechanical behavior of the material the relative changes in storage and loss moduli must be taken in to account. For this reason their ratio ($Tan \delta = \text{Storage modulus/Loss modulus}$), the so called the loss tangent or damping factor, can be used to find the exact location of glass transition temperature.

Figure 4 and 5 show the dependency of storage modulus (E') and loss modulus (E'') for pure polyethylene (sample A) and polyethylene reinforced with different content of SiO₂ (Sample B, C, D and E) on frequency at 25 °C. It is clear from the graphs that both the storage and the loss modulus can vary significantly as a function of the deformation frequency, which has very important implications in the context of viscoelastic behavior. The figures illustrate that both storage modulus and loss modulus depend on the frequency. Indeed from low to high frequency, E' and E'' increase with frequency and the slope depends on the silica content. In the case of low content of silica there is no any interaction between particles. It means they are separated enough to avoid any interaction, no possibility of collision by Brownian motion, no

repulsion or attraction potential such as London/van der Waals forces. It is a very interesting result at which the dependency of storage modulus on the silica content will be appeared in more intensity at high frequency. This is because at higher silica content the behavior of composite is more as an elastic material and in such case increasing frequency has more effect on the deformation and movement of the chains [17]. In fact at higher frequency the tendency of polymer chains to move is less than lower frequency because of increasing the rigidity of the system. It means the viscous items of the PE and its nanocomposite approach toward the lower value as frequency becomes greater. It is worth noting that the loss modulus of PE nanocomposite has not any significant difference with that of pure PE at low frequency. But this difference becomes more as frequency increases gradually. For example the difference between loss modulus of pure PE and PE/1Wt% SiO₂ at 50 Hz and 250 Hz are about 8 and 15 MPa respectively.

Figure 6 shows the dependency of Tan delta of PE and its nanocomposite on the temperature (i. e. -150 to 120 °C) at constant frequency (1 Hz) and Figure 7 illustrates the variation of Tan delta of the mentioned materials at different frequency (1 to 300 Hz) at 25 °C respectively. It is worth noting that increasing the weight percent of silica along with improvement in interfacial interactions between silica and polyethylene chains promote their dispersion in a matrix, which can be reflected through an increase in storage modulus of the composite. Moreover, this will also lead to a reduction in mobility of polymer chains, which means that higher energy will then be required for transitions. Certainly,

corresponding effects can be observed through a reduction in the damping factor, broadening of tan δ peak, and/or increase in T_g. Since the variation of Tan delta and loss modulus versus temperature and frequency is the same, therefore all previous discussions can be repeated. It has been observed in the previous figures that the addition of silica improves the loss modulus of nanocomposites. This is mainly because of the large surface area per unit volume of reinforcing silica, which enables a significant increase in friction between the constituents of a composite. Therefore a lot of energy is transformed into heat when such composites are deformed under an applied load. Moreover, the increase in loading of reinforced PE increases the frictional forces until the nanoparticles exceed a particular limit where they begin to agglomerate within the matrix. The reason of agglomeration of nanoparticles can be attributed to adhesion of particles to each other by weak forces and can be occurred during the manufacturing of nanocomposites. This is because at high loading the surface free energy of the system will be increased and nanoparticle tends to be agglomerated to reduce the energy of system.

4. Conclusion

In the current research, the effect of addition of silica nanoparticles to polyethylene on its viscoelastic behavior has been investigated. The results are remarked as follows:

- the storage modulus of all materials including PE and its nanocomposites decreases as temperature increases .
- The value of loss modulus increases as the polyethylene and its nanocomposites approach

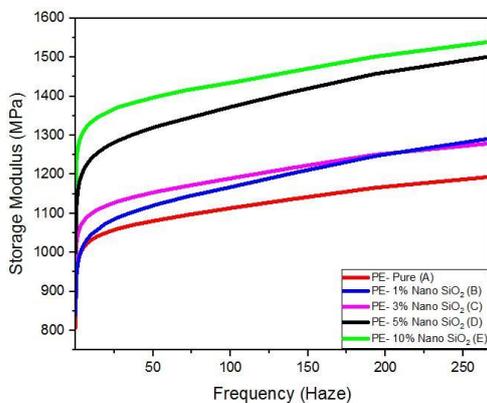


Fig. 4- Dependency of storage modulus on the frequency at 25 °C

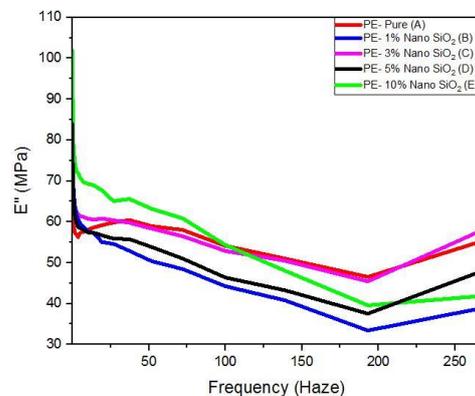


Fig. 5- Dependency of loss modulus on the frequency at 25 °C

from low temperatures toward the glass transition temperature.

c. The value loss modulus decreases after the polymer temperature become higher than its glass transition temperature.

d. The highest amount of $\tan\delta$ is for the pure polyethylene sample, and with the addition of SiO₂ nanoparticles, the decreasing trend of $\tan\delta$ is

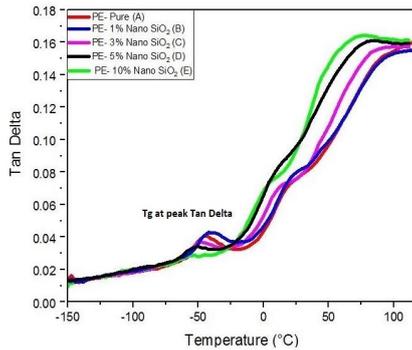


Fig. 6- Variation of $\tan\delta$ in the range of -150 up to 120 °C at constant frequency of 1 HZ.

observed and the damping curve moves towards the lower values of $\tan\delta$ indicating a reduction in the damping effect in nanocomposite samples compared to pure PE.

e. Both the loss modulus and $\tan\delta$ of PE nanocomposite have not shown big differences with those of pure PE at low frequency and the differences becomes significant as frequency increases gradually.

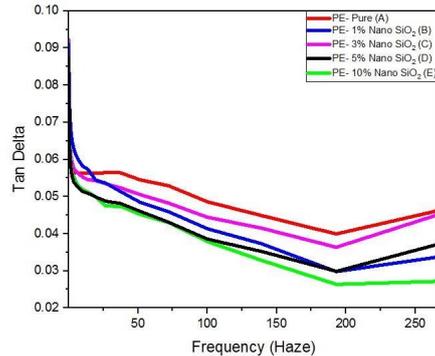


Fig. 7- Dependency of $\tan\delta$ on the frequency at 25 °C.

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