Tensile and Relaxation Properties of PA6/Nanoclay Nanocomposites

M.Golzar*, A.R. Khalighi

Abstract—**Mechanical tensil and relaxation tests were performed to examine the effect of nanoclay content and its dispersion on viscoelastic behavior of nanocomposites. Master-batch of PA6/Clay was prepared via melt mixing. Doing sensitivity analysis on the results of the tensile tests with regarding to cross head speed revealed that in spite of monotonically increase in elasticity modulus and yield stress with nanoclay weight fraction increase, by exfoliation of nano clay sensitivity to strain rate will decrease intensively, this effect in intercalated specimen is not as much as the exfoliated ones. Also, it seems that this degree for higher quantities of nanoclay approaches to a distinct limit. The results of the Analysis of stress-relaxation test by generalized Maxwell model indicated that existence of nanoclay on polymer matrix has an effect on both viscosity and elasticity behaviors of matrix. The effect of exfoliation of clay on elastic property is much more than its effect on viscosity behavior. When the layers are exfoliated, by increasing weight fraction of clay in formulation, time constants of Maxwell model leads to a decrease, while its elastic constants increase. Intercalation of clay more affected viscose behavior.**

I. INTRODUCTION

Using polymer, instead of metal, is increasingly being developed due to some benefits such as low density, good thermal insulation, and high resistance to corrosion and chemical attacks. The vast differences between polymer and metal properties and some disadvantages like polymer's higher viscoelasticity than metal, which results in creep and relaxation behavior in polymer, its very lower elasticity modulus and low fracture stress than metal, high thermal expansion coefficient (which is 10 times more than metals), low dimensional stability, water absorption from environment by some polymers like PA6 and variable properties of polymer have prompted the researchers to strive in approaching polymer to metal characteristics [1-3]. Nano fillers, regarding their high aspect ratio (10 ~ 1000) [4] and their effect on polymer chains have made great improvements in some properties like: elastic modulus, yield stress, Uv stabilization, and fire retardant effect [5-7]. The complex performance of polymer nanocomposites can only be understood deeply by a proper interaction between experimental studies and mathematical modeling. Therefore, modeling and simulation of polymer-based nanocomposites have become an essential issue aimed at expanding the application of these materials in potential engineering capacities. In the recent years, many modeling studies have been carried out that the majority of them have been focused on the prediction of elastic modulus, interfacial bonding [8-11] or load transfer for carbon nanotubes [12].

By increasing loading time, e.g., creep or fatigue (must be taken into account in design, especially in aviation and automotive applications [13]) the material must remain in service for an extended period of time. Therefore, it is necessary to predict the probable behavior of material in service by modeling and extrapolating the information obtained from relatively short-term laboratory tests [14]. This paper is aimed at the theoretical and experimental investigations of the effect of nanoclay and its degree of dispersion in polymer matrix on time-dependant properties of polymers. The selected material for filling and matrix phases are nanoclay and PA6, respectively. The reason for selecting nanoclay is its platelet structure, which causes reinforcement in two directions [15], and its good compatibility with PA6.

Since nanoclay platelet structure tends to assemble and produce agglomerate and tactoid, developing a process for exfoliating silica layers in to nylon matrix and production of nanocomposite by expanding interlayer, is of high significance [16]. As it was mentioned, the extent of nano phase dispersion and distribution in polymer matrix has an effective role in the degree of nanoclay reinforcement. High degree of dispersion, because of increase in both aspect ratio and the interface are an influential factor in improving properties. There are numerous articles investigating and presenting different methods for obtaining the more exfoliation of nanoclay in PA6 [17-18], and also examining the effect of dispersion degree on mechanical properties [19]. Master-batching has been done due to lake of enough accuracy in feeding clay along with granules into extruder, gaining confidence in nanocomposite formation during the next compounding process, and finally doing the least operation on polymer during the process of nanocomposite formation and refraining from polymer degradation.

The authors are from the Department of Mechanical Engineering of Tarbiat Modares University (TMU) P.O. Box 14115-111 Tehran, Iran
*Corresponding author:Tel:+98-2182884320
Email address: m.golzar@modares.ac.ir

II. Theory

Almost, all materials possess viscoelastic properties, and operate differently in tensile and compression strength and loading styles. Viscoelasticity in polymer is more sensible than metals. That is, deformation in polymer is not only a function of applied tensile, but it also depends on time (loading rate). The materials which their deformation depends on time, as viscoelastic materials, have both solid and fluid like behaviors [20-21].

Generalized Maxwell model is a suitable model to illustrate stress-relaxation in plastic products. This model is composed of series connection of spring and dashpot. Two or three-parameter models usually predict an accurate approximation of the polymer behavior. Equation 1 illustrates the parallel connection of three-parameter Maxwell model with a single spring parameter:

$$E(t) = \xi_1 e^{\frac{-t}{\tau_1}} + \xi_2 e^{\frac{-t}{\tau_2}} + \xi_3 e^{\frac{-t}{\tau_3}} + \xi_e \qquad (1)$$

In this equation, $E(t)$ is a function of modulus reduction in time, ξ_n and τ_n are elastic coefficient and relaxation time respectively. Relaxation time is defined as $\tau_n = \eta_n / \xi_n$ in which η_n is the viscosity of the liquid in the dashpot. Stress-relaxation curve is as a function of viscoelastic properties of polymer. One of the advantages of Maxwell model in this research is the possibility of separation of viscose and elastic components of samples. According to what was mentioned, the tests used in characterization of viscoelastic behavior must contain an independent time factor that is able to investigate the variation of material behavior. In the present paper, tensile and stress-relaxation tests is used to study the viscoelastic behavior of polymer.

Tensile test is one of the most common tests in perception of mechanical properties of materials. As it was expressed above, because of viscoelastic character of polymers it shows different behavior with varying the speed of given force. This factor can be considered as a good parameter to study polymer's time-dependant behavior and the effect of nanoclay on it. By doing tensile test, at different crosshead speeds, and sensitivity analysis, the effect of nanoclay and its degree of dispersion on viscoelastic behavior can be detected. The purpose of doing sensitivity analysis is to measure the effect of input variations on systems output. In the present paper, cross head speed is considered as input parameter, and mechanical feature of elasticity modulus is considered as the material's response to the input. By using equation 2, which is one of the common equations in this field, the material's sensitivity to cross head speed variations can be measured:

$$s_{ij} = \frac{k_j}{c_i}\frac{\partial c_i}{\partial k_j} = \frac{\partial \ln c_i}{\partial \ln k_j} \qquad (2)$$

In the above equation, s_{ij} is regarded as the sensitivity of parameter j to input i, and the variation of k_j respect to c_i is measured. In order to non-dimensioning the resulted number, it is multiplied by k_j / c_i. The less obtained value, the less sensitivity of output parameter to input parameter.

III. Experiment

Material and Equipments

The polyamide-6 used in this study was Tecomid *NB50 NL IT*, ($\bar{M}_w = 5.2999*10^4 \quad gmol^{-1}$) purchased from Eurotec Co. Organoclays Cloisite 30B was purchased from SouthernClay Company. Finally the last material that is called Irganox 1010, obtained from Clarinet Co. ruled as a stabilizer was added about 0.5 wt% to polymer in all processes to avoid polymer thermal degradation. Before combining, the materials were vacuum dried at 80^{o}C for 48-hr to remove any absorbed water.

Master-batching performed with 10 wt% of clay in counter-rotate Haake internal mixture (Brabender Co.*)* with 50 cm^3 capacity, 100rpm screw speed and the temperature of 230^{o}C were considered equal for each of three heating zones, while the resistant time was 5 minutes. Then, the outcome mixture granulated and then was diluted to 1, 2, 4, 6, and 8 wt% by Brabender co-rotating twin-screw Extruder, model DSE-25. Dilution process was done at screw speed of 200 rpm, barrel temperature of (220, 225, 230, 235, and 240)^{o}C, from hopper, and feeding speed was 2.5 kg/hr. Mean resistance time with the above conditions was 138 seconds. The output granule was injection molded in to standard 4mm thick tensile (ISO 527-2/1A) bars using a KraussMaffei (model 150-700C2) injection molding machine. To remove any versatile residual stress and homogenizing the crystalline structure, annealing was carried out on injected specimens at 80° C and for 48-hr in vacuum oven. This performance however removed the moisture effect in test results. The nanocomposites samples prepared with this procedure are referred to herein ac NC_X (where X is the silicate loading). All specimens were kept in sealed desiccators until mechanical tests were carried out. The values reported for tensile and stress-relaxation test reflect an average from at least five measurements.

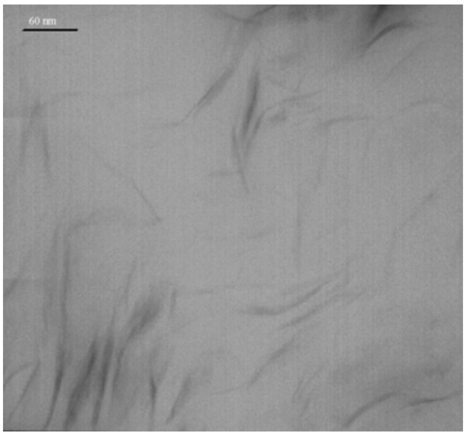

Figure 1. TEM image of NC-4.

Thickness of the injected and master-batch specimens was $4mm$ and $2mm$, respectively. It is essential to say that Preparation of the master-batch specimen (denoted MB_5min) to undergo the test was performed by compression molding at 230^{o}C and a pressure of 1000kPa. To avoid shrinkage, warpage and obtaining a necessarily smooth surface for the test, the pressing specimen was cooled form 230^{o}C to 60°C under the pressure in $20\min$ and then it releases to reach ambient temperature. TEM test was performed on NC_4 to verify XRD test results. Thin section (60nm) were cut from tensile specimen perpendicular to flow direction under temperature -130^{o}C using a C.Reichert Co - (OMU3) Ultra Microtome and observed by transmission electron microscopy (TEM) Philips EM 208S 120kv to evaluate intercalated and exfoliated structure of nanocomposites.

The mechanical tests used to investigate time-dependent properties of nanocomposites are as follows: (1) Tensile test is done at room temperature according to ISO 527-2/1A, in three different cross head speeds ($10 \quad 50 \quad 100 \quad mm/\min$), on injected samples along injection direction by Instron model 5500. (2) Relaxation test, which is in accordance with the condition mentioned in Last research reported by Dennis up to 10 % strain, by means of Instron model 5500 [22].

IV. Results and discussion

Appearance of a sharp peak in the patterns related to nanocomposite specimens compared to pure matrix confirms nanoclay's role as an effective nucleating agent in polymer matrix. Numerous articles have covered nanoclay nucleation agent and intensification roles in γ formation. Comparing Figs. 1 and 4, it can be concluded that: (a) Nanoclay available in PA6 as a nucleating agent plays an important role in determining the amount of crystallization phase and enhances the crystallization. (b) Process factors have a more determinant effect on the type of crystal structure dominant on polymer matrix.

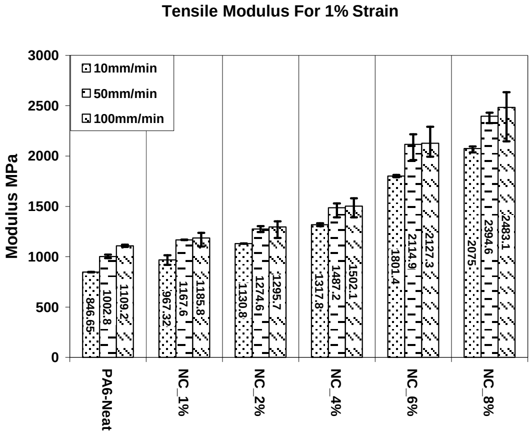

Figure 2. Column chart of elastic modulus below 1% strain

Results of tensile test

Fig 2 illustrates the results of tensile test with cross head speed of 50 mm/min up to 20% strain. Increasing nanoclay's weight percent enhances the amount of yield stress and elasticity modulus. This process, at the three cross head speeds is the same, so presentations of other cross head speeds' diagram are abandoned. To evaluate the sensitivity of the material's behavior to cross head speed, elasticity modulus is chosen as the mechanical indicator of the samples, and the parameter value is found, in three different cross head speed, by tangent of curve method respect to strain of less than 1%. Column chart related to this parameter is illustrated in Fig 3. S_{ij} Values as the results of sensitivity analysis are displayed in Fig 4. Clearly, the sensitivity of elasticity modulus to cross head speed in full exfoliated specimens is noticeably decreased with increasing of nanoclay weight percent. The best condition of insensitivity which is near zero occurs in NC_4. In intercalated specimens also sensitivity to cross head speed is reduced, but its quantity is less than exfoliated ones, and it seems that this quantity, in lieu of higher clay content, has a bias to a limited value.

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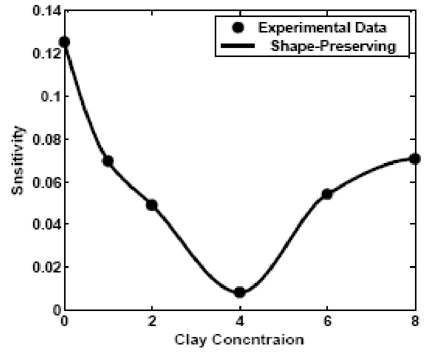

Figure 3. Sensitivity analysis result.

To study the effect of nanoclay on strain at break, the average value of this parameter in lieu of three different cross head speeds is presented in Fig 7. As it can be seen, with increasing cross head speed, elongation at break is reduced. Most interestingly, elongation at break, in spite of increase in Yong modulus, does not noticeably decrease up to NC_2. Over than this wt%, a sharp decrease is observed in this value. The obtained results agree with other researchers findings [27]. Cho (2000) in his investigations about compact strength reported similar trend to strain at break for PA6 nanocomposites. This behavior, maybe, is due to the effect of nanoclay's surface modifier as a plasticizer agent in PA6 matrix. To research in this case, dynamical-mechanical behaviors of specimens will be evaluated.

Stress-relaxation

Fig. (5) illustrates the results of stress-relaxation test. The curve fitting between two-parameter Maxwell model (equation 1) and experimental data, to determine coefficients of this equation, was done by Matlab software. With increasing in silica loading, the model follows the material's behavior perfectly. The coefficients obtained from this method are summarized in Table 1.

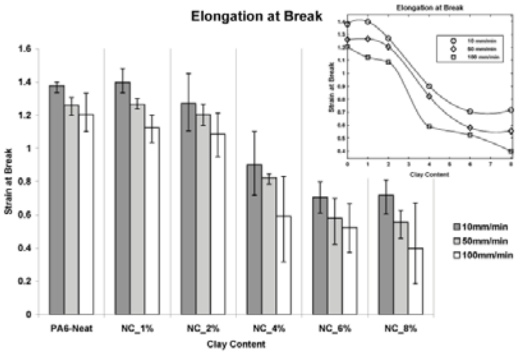

Figure 4. Average elongation at break.

The study of rising and falling behavior of Maxwell model shows that in exfoliated specimens, Maxwell's stiffness constants increase while time constants decrease with increasing of clay wt%.

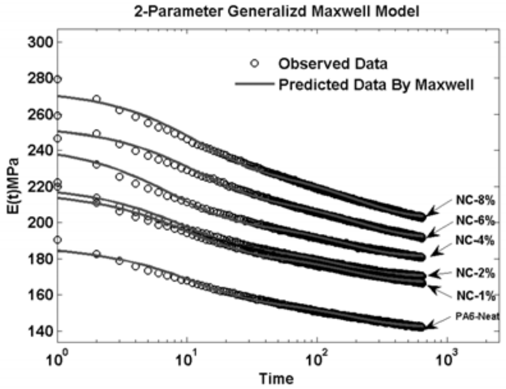

Figure 5. Stress-relaxation test results in 10% strain.

It means that the polymer material caused by an applied force is relaxed in a short time, while its strength is kept at high levels. With investigating mathematical concept of relaxation time from Eq. 1, we can conclude that exfoliation of nanoclay in polymer matrix affects on both viscose and elastic behaviors of PA6. chemical bounds between surface modifier of nanoclay sheets and PA6 chains, reduce chains mobility, decrease the number of crystalline structures of PA6 chains, and hinder their slip and movement over each other. This phenomenon explains variation of viscose and elastic response of composite to applied force. Elasticity modulus is significantly dependent on quantity and quality of distribution and of nanoclay sheets [18]. In exfoliated state, which leads to a nanocomposite formation, ionic bounds between nanoclay's surface modifier and polymer chains, in volume unite increase significantly. It is because of increasing aspect ratio [19], and so forming a huge interface between nanoclay sheets and polymer chains. This feature, which is particular to nano reinforcers, has a great influence on physical-mechanical properties of polymers. In exfoliated condition, the effect of nanocomposite formation on elastic properties is very much more than viscose properties. This feature leads the material to a solid-like behavior. Examining the results of sensitivity analysis can lead us to the above result. Increasing the percentage of nano filler and saturating the polymer matrix, no adequate space for exfoliation of clay layers will remain, so the created structure in specimens has a bias to an intercalated structure.

Table 1. Two-part Maxwell model coefficient based on stress relaxation test.

Coef.	$\xi_1(MPa)$	$\tau_1(sec)$	$\xi_2(MPa)$	τ_2(sec)	$\xi_3(MPa)$
PA6_Neat	16.42	176.70	28.43	10.5	142.2
NC_1%	17.86	165.90	31.96	9.546	167
NC_2%	18.37	144.00	32.47	8.573	170.5
NC_4%	21.01	140.90	40.71	7.399	181.3
NC_6%	24.47	192.70	37.7	11.64	191.6
NC_8%	42.18	188.50	28.96	11.7	202.6

In intercalated condition, compared to exfoliated ones, due to the larger size of clay masses, there is a smaller interface between polymer chains and clay. It seems that this small interface in saturated polymer and so the limitation in ionic bounds formation between surface modifier and polymer chains cause the formation of free surface modifier. Migration of the modifier to matrix phase leads to plasticization of the consequent composites and reinforcement of viscose property for specimens with higher silica loading.

Investigation of coefficient diagram in Table 1 shows that single spring stiffness factor in Maxwell model, like elasticity coefficient of tensile test has a rising behavior and increases monotonically with increasing clay content. The first stiffness coefficient, which is an indicator of polymer behavior in short times, increases up to NC_4 and decreases for higher wt%. The above phenomenon, which may caused by the free surface modifier, is against the anticipated behavior for the nanocomposite .The above behavior doesn't occur at long time.The second stiffness coefficient, which is an indicator of polymer behavior at long time, has a treatment like single spring stiffness factor, but has more rising slop for NC_8. This enhancement in nanocomposite long-term behavior can be caused by connections between clay surface modifier and polymer chains and also saturation of matrix with clay which limit in polymer chains mobility.

Table 1 also indicates relaxation-time coefficients for two-parameter Maxwell model. Both of relaxation-time coefficients have falling behavior for NC_1, NC_2, and NC_4. This falling procedure for the second relaxation-time is more prominent. An interesting point is the rising treatment of the above coefficients at higher percentages of nanoclay. Referring to Eq. 1 and regarding simultaneous increase in time and stiffness coefficients of Maxwell model, we can conclude that both viscose and elastic behavior of polymer are affected by the existence of nanoclay in polymer matrix. The effect of exfoliation of nanoclay on elastic behavior is much more than its effect on viscose behavior, however an intercalated structure is formed and the effect of nanoclay on elastic behavior is lowered, the reinforcement of viscose phase will be more prominent. Presence of free surface modifier intensifies the above condition.

V. Conclusion

In this study viscoelastic behavior of nanocomposite PA6/nanoclay was investigated. Various mechanical and morphological tests were employed in order to investigate nano structure formation and its effect on polymer's short-term mechanical behavior. At the next step by the means of generalized Maxwell model, we tried to generalize the results of short-term mechanical tests to longer time. Performed Morphological and mechanical tests were tensile and stress-relaxation testes respectively. At the next section of this paper, in order to examine the accuracy of the used mechanical tests, DMTA was employed to measure mechanical damping of experimenting specimens in linear viscoelastic zone. The results of this test were used for more exact investigation on some of mechanical responses observed in tensile and stress-relaxation testes.

By a general evaluation of the results of the mechanical tests, we can infer that existence of nanoclay in polymer matrix leads to solid-like behavior, but surface modifier of nanoclay sheets, after extraction and migration to polymer, act as a plasticizer and enhance the viscose behavior. Mechanical short-term tests like tensile test lonely can not reveal the modifier effect on mechanical properties. Adding time factor to this test, or doing tests, in which time factor is an independent variable, we can reveal the effects on viscose phase.

Separated comparison of mechanical characteristics, like Yang modulus or yield strength, at different specimens with different cross head speeds, can not identify the effect of nanoclay on viscoelastic behavior, however studying the results with altogether and entering time factor by doing sensitivity analysis on the results of tensile test respect to cross head speed, it is perceived that in spite of monotonic increase in elasticity modulus with silica loading the polymer's sensitivity to strain rate is significantly affected by the distribution of nanoclay. In exfoliated condition, the material's sensitivity to strain rate, obviously, decrease with increasing in clay loading. While, this effect in intercalated specimens is not as much as exfoliated ones, and also it seems that insensitivity, in lieu of high wt% of clay has a bias to a constant value. According to DMTA results, an increase in sensitivity of strain rate in lieu of higher wt% of clay can be a consequent of the effect of surface modifier as a plasticizing factor.

Using generalized Maxwell model in analyzing the results of stress-relaxation test, we can verify the above findings. The presence of nanoclay at polymer matrix influences polymer's both viscose and elastic behavior. The effect of clay's exfoliation on elastic behavior is much more than its effect on viscous behavior. If an intercalated structure is formed, and the effect of clay on elastic behavior is lowered; then viscose phase reinforcement will be more prominent. The existence of free surface modifier intensifies the above condition. Although modification of nanoclay's surface leads to more exfoliation of clay sheets, extra modification can weaken the mechanical properties. In fact, according to the literature [30], if unmodified clay can be dispersed in polymer matrix, a nanocomposite with the most enhancements in mechanical properties will be obtained.

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