The effect of MWCNT on dynamic mechanical properties and crystallinity of in situ polymerized polyamide 12 nanocomposite

Farzaneh Faridirad | Mohammad Barmar | Shervin Ahmadi

Iran Polymer and Petrochemical Institution, Pazhouhesh Blvd., Pazhouhesh Science Park, Km 15, Tehran-Karaj Highway, Tehran, Iran, 1497713115

Correspondence
Shervin Ahmadi, Iran Polymer and Petrochemical Institution Pazhouhesh Blvd., Pazhouhesh Science Park, Km 15, Tehran-Karaj Highway, Tehran, Iran, 1497713115.
Email: sh.ahmadi@ippi.ac.ir

This work aims at investigating the dynamic mechanical properties of in situ anionic ring opening polymerized polyamide 12 in the presence of multi-walled carbon nanotubes (MWCNT). According to the dynamic mechanical thermal analysis results, the addition of only 0.1 wt.% of MWCNTs led to 30% enhancement in modulus at room temperature which exhibited improved mechanical behavior of the nanocomposites. Test results showed that by the presence of 1.2% wt MWCNTs, the modulus is almost doubled, and it did not show any tangible changes by the addition of more nanotubes. Also, the effect of different frequencies on the viscoelastic behavior was investigated in order to determine the thermal transitions occurred in the synthesized nanocomposites. After that, the crystallinity of the samples has been studied using differential scanning calorimetry and X-ray diffraction data in order to investigate the effect of MWCNT content on the crystals' dimension.

KEYWORDS
crystallinity, dynamic mechanical thermal analysis, in situ polymerization, multi-walled carbon nanotubes, polyamide 12

1 | INTRODUCTION

Aliphatic polyamides are engineering plastics. An important difficulty during the usage of such polyamides is their hydrophilic character. This feature is provided by the amide linkage. Increasing the number of —CH2 units inhibits this matter.1 They bring together good processability and thermal stability, and also they are highly available in the market. Commercially available polymers, such as Nylon (polyamide) 12 (PA12), rises, which can be easily produced by ring-opening polymerization of Lauroylactam monomer.2

PA12, the lowest water absorbing Polyamide, is associated with excellent resistance towards solvents, abrasion, and environmental stress cracking and high processability.3 Polyamides (PA 12 and 11) are often used as pressure sheaths for flexible pipes in oil exploration, along with polyvinylidene fluoride and polyethylene.4

Several additives, such as fillers, can be dispersed in the matrix, in order to improve the mechanical properties of polyamide 12.2,5 The nanocomposites exhibit also reduced permeability to gases, enhanced thermal stability, and improved stiffness and deformation properties. One of the key research topics in the field of polymer materials is to enhance the mechanical properties of polymers by incorporation of nanofillers.6 The final properties of polymer composites depend on both material composition and morphology obtained.7

Multi-walled carbon nanotubes (MWCNTs) are unique nanostructured materials indicating remarkable physical, mechanical, and electrical properties8-10 which make them attractive for many applications such as polymer composites.11 The prospect of obtaining high-performance MWCNT-based polymeric nanocomposites has attracted the efforts of researchers.12 MWCNTs have been successfully compounded with different thermoplastic13,14 and thermoset15 matrices through different conventional polymer processing technology. There are varieties of nanocomposite materials which are normally manufactured based on the applications.16 According to the acceptable performance of carbon nanotube (CNT), the synthesis of nanocomposites based on polymer-CNT is becoming increasingly affordable.17 There are many studies carried on polymer-CNT nanocomposites. The commercial products of polyamide 6 or polyamide 12 reinforced with MWCNT are available for applications such as

Received: 15 December 2017 | Revised: 20 February 2018 | Accepted: 22 March 2018
DOI: 10.1002/pat.4322

electrically conductive parts, automotive fuel filters, and connectors. They can deliver extended wear, lower friction resistance, increased load capacity, and mechanical strength. Also, flame-retardant materials and conducting materials could be synthesized by using these nanotubes.

Organic polymer components combination with MWCNT fillers has extraordinary significance for the development of advanced materials representing enhanced mechanical and thermal properties. However, these enhanced properties can only be achieved by homogeneous dispersion of the MWCNTs within the polymeric matrix. The strength of nano filler-polymer interactions is another key parameter to obtain a nanocomposite with interesting mechanical and physical chemistry properties. Nevertheless, enhancing the toughness of polymers by nano fillers is still in debate.

Many studies were done on improving the MWCNT dispersion in a polymer matrix and lowering the MWCNT loading to overcome the dispersion and distribution problem. Techniques including high shear processing, sonication during extrusion, and surface functionalization have been applied. Twin-screw extrusion is an appropriate method in the industrial processes of the thermoplastic materials, and it is economical for the preparation of MWCNT nanocomposites. Unfortunately, the common melt mixing in many cases makes an incomplete dispersion of MWCNT agglomerates. In situ polymerization has been considered as a possible way to solve this problem. The filler is usually mixed into the monomer, and the polymerization is initiated by the addition of activator and catalyst. Due to the initially very low viscosity of the matrix, a good penetration of the MWCNT results in an easier dispersion within the monomer.

In one of the works done by Cheng et al., a high volume fraction of highly aligned CNTs were homogeneously dispersed in an epoxy matrix in order to investigate the thermoset nanocomposite containing CNT.

The properties of samples made by both melt compounding and in situ polymerization process are reviewed by Byrne and Gun’ko. Also, in another study done by Deng et al., improved dispersion of the MWCNTs in the polyamide 6 by in situ polymerization was shown. An improvement of 138% in the strain at break was achieved for the in situ polymerized polyamide 6 nanocomposites comparing with the same nanocomposites synthesized by melt mixing.

The influence of the nanofillers on the rheology properties of the polymer matrix was carried out by J. Bai et al. through the investigation of PA12 nanocomposite. The effect of the CNTs on the modulus and the damping of the PA12 samples were analyzed by them. They reported that the PA12-CNT nanocomposite had an increased elastic modulus compared with neat PA12.

Beside the works mentioned earlier, it is valuable to investigate the dynamic mechanical properties of polyamide 12 nanocomposites. In order to evaluate the mechanical properties Dynamic-mechanical thermal analysis (DMTA) is a suitable method that enables the effect of frequency and temperature to be studied. The relaxation processes of polymers at various temperatures affect the physical and mechanical properties of these materials. The relaxation mechanisms in semi-crystalline polymers are more complicated by the presence of crystalline and amorphous phases in comparison to fully amorphous polymers. Generally, there are 2 or 3 types of relaxations for semi-crystalline polymers which are indicated by Greek letters α, β, and γ (high to low temperature, respectively). For the polymers that represent all 3 types of relaxations, α relaxation is occurred at the highest temperature and refers to the polymer crystalline phases. The β relaxation is lower than α and higher than γ and is related to the polymorphic regions. This relaxation is also known as glass transition temperature. γ Relaxation is occurred at the lowest temperature and refers to the very small movements of the chains (or lateral branches) in the amorphous or crystalline region. For polymers with only 2 types of relaxations, α is related to the amorphous region and the glass transition temperature, and β is also related to the partial movements of the chains.

Several groups have investigated the crystalline behavior of polyamide 12. In the early 1970s, Northolt et al. observed monoclinic and triclinic structures in polyamide 12, which is very similar to the crystalline structure observed in polyamide 11. Researches have shown that 4 different crystalline forms are found in polyamide 12: γ phase, γ’ phase, α phase, and α’ phase. Among these, the gamma phase is the most stable and most frequent phase in terms of thermodynamics and is characterized as a triclinic phase with a melting point of approximately 179°C.

The aim of the present work is to precisely study the dynamic mechanical properties of polyamide 12-MWCNT nanocomposites, by means of dual cantilever bending mode. Also, the effect of frequency on the viscoelastic properties such as storage modulus (E’), loss tangent (tan δ), and different transitions was investigated. Furthermore, the effect of the incorporation of CNTs to the polyamide 12 matrix on the dynamic properties was evaluated. In the second part, the crystallinity of the samples was studied through the calculation of crystals’ thickness using different equations.

## EXPERIMENTAL

### 2.1 Materials

The monomer used in this project was Laurolactam supplied by Evonik Co., Germany. Toluene disocyanate (TDI), used as an activator, was obtained from Karoon Co., Iran. The catalyst, sodium caprolactam, was obtained from Karangin Co., Iran. Multiwall carbon nanotube (MWCNT) was used as filler and obtained from Nanosany Co, America, with the average diameter of 20 to 30 nm.

### 2.2 Preparation and processing

The effect of MWCNT was investigated through different formulations (Table 1). All the samples were prepared by using 2% activator and 1% catalyst. An amount of 100 g of each kind of composite was produced by this method. The filler loadings were in the range between 0.10 and 3.5 wt%. Monomer and catalyst were dried at 60°C for 24 hours in the vacuum oven. A master-batch of mono-mer/MWCNT (4 wt%) was prepared by physical mixing for 24 hours, at 160°C. For the preparation of the PA12 samples via the reactive extrusion, the master-batch containing monomer and MWCNT and catalyst were compounded in a 50-ML chamber of a Haake type
internal mixer model Sys 9000. The materials were premixed for 3 minutes at 200°C with a screw speed of 60 rpm under a nitrogen atmosphere. Then, the activator was introduced into the mixture. During the polymerization, the axial torque generated by the molten mixture on the transducer was recorded and used to evaluate the completeness of the polymerization and the achieved melt viscosity level. The polymerization reaction was continued for approximately 2 minutes after reaching the torque maximum level. The nanocomposite samples were coded as follows: PA12, PA12/C-0.1, PA12/C-0.3, PA12/C-0.7, PA12/C-1.2, PA12/C-2, and PA12/C-3.5; for the polyamide nanocomposite samples containing 0, 0.1, 0.3, 0.7, 1.2, 2, and 3.5 wt% filler loading, respectively.

2.3 | Material characterization

2.3.1 | Tensile modulus analysis

Tensile properties were evaluated on a LR50K Plus, Lloyd Instruments tensile testing machine at a constant crosshead speed of 5 mm/min, at room temperature according to ASTM D638 standard test method for pure polyamide 12 and its nanocomposite. Specimens were injection molded at a pressure of 150 MPa and at a temperature of 230°C. At least 3 tests were conducted for each formulation. In this analysis, Young’s modulus (E) will be determined.

2.3.2 | Dynamic mechanical thermal analysis

Dynamic properties of the specimens were determined by DMTA (DMA-Triton, Tritec 2000, England) in dual cantilever bending mode over the temperature range from –150°C to 150°C at a heating rate of 2°C min⁻¹. Different frequencies of 0.1, 1, 5, and 20 Hz were applied during the test. Dynamic mechanical analysis (DMA) applies a small oscillatory stress at a set frequency to the sample and examines changes in modulus and damping. The storage modulus (E') and loss tangent (tan δ) were recorded as a function of temperature. Strain amplitude was constant at 0.05%. All the tests were carried out under the nitrogen atmosphere. DMTA samples (35 mm × 12 mm × 1 mm) of PA12 nanocomposites were prepared by preheating each nanocomposite up to 200°C followed by pressing under 30 MPa and then cooling the sheets.

2.3.3 | Differential scanning calorimetry (DSC) analysis

Thermal behavior of the samples was investigated using a differential scanning calorimetric (DSC 200F3 Maila) manufactured by NETZSCH. The approximate weight of the tested samples was 11 mg. Prior to testing, all the specimens were exposed to a vacuum oven at 80°C for 24 hours in order to prevent from any possible moisture absorption. In order to eliminate the heat history of the samples, they were heated rom the ambient temperature up to 250°C at the heating rate of 20°C/min. The samples then were cooled from 250°C to 25°C at the same rate to allow the crystallization behavior of the melt to be recorded at a non-uniform temperature. Next, they were again heated to 250°C to allow the melting behavior of the samples to be investigated. In this test, Tc is the temperature of crystallization, Tm₂, the melting point extracted from the second heating cycle, ΔHc, the latent heat of crystallization, ΔHf, the melting heat of the second melting cycle, and Xc,% is the calculated crystallinity of different percentages. It should be noted that these values of crystallinity are calculated using Equation (1).

\[ X_c = \frac{\Delta H_f}{\Delta H_{f0}} \]  

where \( \Delta H_f \) is the latent heat of 100% crystalline polyamide 12 and \( \Delta H_{f0} \) is the latent heat of the sample.

2.3.4 | X-ray diffraction (XRD) analysis

In order to measure the crystallinity and the dimensions of the crystalline plates and also the evaluation of the polyamide nanocomposites crystallinity prepared by the in situ melt mixing reaction, X-ray diffraction analysis was done at the range of 5° to 40° (WAXD) using Philips X pert device at the speed of 1°/min. The electric current of the device was 30 mA, and its voltage was 40 KV. The copper atomic beam with a wavelength of 1.54°A was used in this device as a detector. All specimens were dehumidified for 24 hours before being tested in a vacuum oven at 60°C. In this test, the samples were sheets of 40 × 40 and 1.6 mm in thickness.

3 | RESULTS AND DISCUSSION

3.1 | Tensile modulus results

Tensile test results for the pure polyamide 12 and its nanocomposites are presented in Table 2. It can be seen that ultimate tensile strength increases with increasing the MWCNT up to 0.7 wt%, and after that the tensile strength is approximately doubled.

<table>
<thead>
<tr>
<th>MWCNT %wt</th>
<th>Yang Modulus (Gpa) at Room Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.41 ± 0.14</td>
</tr>
<tr>
<td>0.1</td>
<td>0.50 ± 0.26</td>
</tr>
<tr>
<td>0.3</td>
<td>0.65 ± 0.62</td>
</tr>
<tr>
<td>0.7</td>
<td>0.74 ± 0.48</td>
</tr>
<tr>
<td>1.2</td>
<td>0.90 ± 0.69</td>
</tr>
<tr>
<td>2</td>
<td>0.97 ± 0.77</td>
</tr>
</tbody>
</table>
3.2 Dynamic mechanical thermal analysis results

It is valuable to predict the behavior of nanocomposite materials through dynamic mechanical tests such as DMTA. The viscoelastic behavior of a material could be studied through DMTA technique as a function of time, temperature, and frequency, while it is subjected to a cyclic loading. Dynamic mechanical properties may be investigated in terms of a dynamic storage modulus, a dynamic loss modulus, and a mechanical damping factor called "tan δ".

Figure 1A-F shows the storage modulus of pure PA12 and its nanocomposite at different frequencies as a function of temperature. It should be mentioned here that the sample containing 3.5% wt. MWCNT was so brittle that it could not be prepared for DMTA tests. Therefore, it could be concluded that this sample is not processable and has not an acceptable efficiency due to the presence of much amount of MWCNTs. These nanotubes increase the strength but inversely decrease the flexibility of the nanocomposites.

Comparing the storage modulus of the PA12 pure sample with its nanocomposites shows that the modulus increased when the nanotube was incorporated into the polyamide matrix as the reinforcing fillers. This effect is clearly shown in Figure 2. A 30% increase in the storage modulus at room temperature can be reached by dispersing only 0.1% of MWCNT. It should be mentioned that in the first step of the polymerization, the MWCNT was appropriately extrapolated within the monomer and the uniform and nanometric distribution of MWCNT was occurred. The evidences such as SEM results showed that during the in situ polymerization no agglomeration will be occurred. Figure 3 shows the SEM results for monomer/MWCNT and PA12 nanocomposite sample containing 2%wt. MWCNT.

Therefore, a uniform nanostructure will be achieved in the final nanocomposite product. This uniform nanosstructure network increases the mechanical properties of the nanocomposites which appeared in the values of the modulus.

The main benefit of this work is the dominance of the penetration to the tension mechanism during the distribution process, which prevents length shortening of MWCNT and maintains better the quality and efficiency of the MWCNT. Decreasing the effect of tension and keeping the MWCNT length to be constant is an important reason which enhances the mechanical properties of the samples in fewer contents of the nanotubes.

The effect of nanotubes on the storage modulus of nanocomposites at room temperature (25°C) is tabulated in Table 3. It is clear from this table that the modulus increased considerably up to the MWCNT loading reached to 1.2%wt. For higher percentage, just 12% increase

---

**FIGURE 1** Storage modulus (E') versus temperature of A, PA12, B, PA12/C-0.1, C, PA12/C-0.3, D, PA12/C-0.7, E, PA12/C-1.2, F, PA12/C-2 nanocomposites at different frequencies during the run of DMTA
was occurred regarding to the previous sample. It can be interpreted as the addition of more MWCNT can be toxic to the chemical reaction or the probability of agglomeration formation increases within the polymeric matrix, which causes the strength of nanocomposite to be decreased.

The changes of tan δ are shown in Figure 4A–F. Tan δ, which is also called, damping factor, represents the ratio of the viscous to elastic response of a viscoelastic material or in another word the energy dissipation potential of the material which is related to the molecular motions. The elastic nature of the network increases by the incorporation of MWCNT to the matrix.

The maximum tan δ of the nanocomposite is higher than its value for the pure PA12 sample (this effect is shown in Figure 5). By introducing the nanotubes into the polymeric matrix, the damping factor will be affected by 2 different factors, the first is the existence of MWCNT and the other one is the molecular weight of the nanocomposites. During the in situ polymerization of laurolactam in the presence of nanotubes, the polyamide 12 chains will be formed, and by grafting the chains on the MWCNT, the movement of the polymeric chains will be restricted, which leads the damping factor to be decreased. On the other hand, by increasing the MWCNT content, the molecular weight distribution will become broader. This competitive factor increases the mobility of polymeric chains and consequently the damping factor.

These 2 factors compete with each other. At lower contents of MWCNT, the first factor is dominated, and therefore damping factor was downtrend and approximately constant up to the addition of 0.7% wt. nanotubes. By increasing the MWCNT content up to 1.2 and 2%wt, the second effect is dominant and makes the damping factor to be increased significantly, which is clearly shown in Figure 5.

On the other hand, regarding to Figure 1A–F, Pure PA12 and PA12/ MWCNT nanocomposites showed higher storage modulus and more elastic-like behavior with increasing the testing frequency. Storage modulus vs temperature curve for PA12 and PA12/MWCNT nanocomposite specimens showed 2 drops during the run of DMTA, one at the region of low temperatures (−100°C to 40°C) and the other at the region of approximately high temperatures (40°C to 200°C). These 2 transitions shifted gradually to higher temperatures by increasing the frequency. The transitions (Figure 4A–F) are also confirmed by the corresponding peaks in the tan δ vs temperature curves. These peaks are seen to shift towards the higher temperatures with increasing the frequency.
E modulus could be obtained through mathematical analysis using the rule of mixture. This relation is shown in (2) assuming randomly oriented short nanotubes. In this equation, $E_C$ represents the predicted modulus of the composite, $l$ is the mean length of the nanotubes (25,000 nm), $d$ is the average outer diameter of the nanotubes (25 nm), $E_{NT}$ is the modulus of the CNTs (800 GPa), $E_M$ is the modulus of the polyamide matrix (1.2 GPa), $t$ is the thickness of nanotubes (9 nm), and $V_N$ is the volume content of the MWCNT. The volume content of the MWCNT was estimated according to the density of the polyamide, 1.01 g/cm³ and the density of neat modulus at room temperature (25°C).

**TABLE 4** The values of volume fraction for MWCNT in the synthesized PA12 nanocomposites

<table>
<thead>
<tr>
<th>MWCNT %wt</th>
<th>$\rho$ nanocomposite</th>
<th>$V_N$ (Volume Fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.01</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>1.01109</td>
<td>0.000481</td>
</tr>
<tr>
<td>0.3</td>
<td>1.01327</td>
<td>0.001448</td>
</tr>
<tr>
<td>0.7</td>
<td>1.01763</td>
<td>0.003392</td>
</tr>
<tr>
<td>1.2</td>
<td>1.02308</td>
<td>0.005846</td>
</tr>
<tr>
<td>2</td>
<td>1.0318</td>
<td>0.009827</td>
</tr>
</tbody>
</table>

**FIGURE 4** Loss tangent (tan δ) versus temperature of A, PA12, B, PA12/C-0.1, C, PA12/C-0.3, D, PA12/C-0.7, E, PA12/C-1.2, F, PA12/C-2 nanocomposites at different frequencies during the run of DMTA.

**FIGURE 5** Loss tangent (tan δ) versus temperature of pure PA12 and its nanocomposite at the frequency of 1 Hz during the DMTA analysis.

**FIGURE 6** The comparison of experimental and predicted values of modulus at room temperature (25°C).
MWCNT, 2.1 g/cm³. At this point it is valuable to compare the experimental E modulus values with those predicted from the rule of mixtures. The values for volume fraction of MWCNT in the nanocomposites are presented in Table 4.

\[
    E_c = \frac{3}{2} \left( 1 + 2 \left( \frac{1}{d} \right) \frac{E_N/E_M - d/4t}{E_N/E_M + d/2t} \right) V_N \left( 1 - \frac{E_N/E_M - d/4t}{E_N/E_M + d/2t} \right)^{-1}
\]

\[
    E_M = \frac{5}{2} \left( 1 + 2 \left( \frac{1}{d} \right) \frac{E_N/E_M - d/4t}{E_N/E_M + d/2t} \right) V_N \left( 1 - \frac{E_N/E_M - d/4t}{E_N/E_M + d/2t} \right)^{-1}
\]

(2)

Figure 6 demonstrates a comparison of modulus values obtained experimentally and the values predicted by the rule of mixture at room temperature. According to Figure 6, the experimental values are lower than those predicted by the rule of mixtures at filler loadings higher than 1.2 wt.%. Therefore, it must be confirmed that the predictions due to the rule of mixtures may be an over-estimation of the E modulus of such nanocomposites. Because the amount of crystalline material in the nanocomposite is only somewhat less than the neat polyamide 12, the E modulus of the matrix should remain fairly unchanged by introducing the nanotubes. This fact shows the potential of MWCNTs as the reinforced agents for polyamide 12.

Figure 7 represents the effect of MWCNT content on the loss modulus of polyamide 12 and its nanocomposites at the frequency of 1 Hz.
of 1 Hz. A gradual shift of the glass transition temperature was observed according to the tan δ (loss factor) or loss modulus curves (see Figures 5 and 7, respectively). Valuable information could be extracted from the transitions at lower temperatures (β transition), which is related to the movements of short chain segments. This transition is more sensitive to the changes in inter-molecular interactions between filler and matrix. Similar to the α transition, the intensity and the place of the peak associated to the β transition increased noticeably, as illustrated by the loss modulus curves. The effect of frequency on loss modulus for all synthesized samples is shown in Figure 8.

### 3.3 Activation energy

The storage modulus versus temperature curve for all samples shows a glassy state followed by the rubbery state. The activation energies of the transitions were then calculated from the Arrhenius-type plots. To clarify the nature of the 2 transitions in Figure 4A-F, the log of the frequency against 1/T₁ and 1/T₂ in Kelvin was drawn (Figure 9 A-F and 10A-F, respectively), in which T₁ and T₂ refer to the temperatures of the first and second peak, respectively. The plot gives different slopes for (T_g) and (T_β) and the activation energy of the transitions could be estimated.\(^3^7\)

\[
\ln f = \ln A - \frac{E}{RT}
\]

where \(f\) is frequency, \(A\) is pre-exponential constant, \(E\) is the activation energy, \(R\) stands for the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), and \(T\) is temperature in K.

The activation energy is approximately 300 to 400 kJ.mol\(^{-1}\) for α transition (T\(_g\)), while it is approximately 20 to 30 kJ.mol\(^{-1}\) for a β transition and 3 to 4 kJ.mol\(^{-1}\) for a gamma transition.\(^2^9^,3^7^,4^0\) The activation energy for the first transition in the region of low temperatures (Table 5 and Figure 9A-F) indicates that this is a beta transition, and it might be due to the more gamma phase formation and therefore the existence of less crystals in the samples. This transition at low temperatures became intensive in the nanocomposite in comparison to the pure polyamide 12. Thus, by increasing the MWCNT content, crystallinity decreased, which led to more activation at lower temperatures. The transition at high temperatures (Figure 10A-F) was
assigned to the glass transition temperature ($T_g$) of the pure PA12 and nanocomposite samples.

The extrapolation of results was done in order to gain a sense of elastic modulus in static conditions. According to the literature,$^{41-43}$ the storage modulus at room temperature and the frequency of 0 Hz were appropriately closed to the results of elastic modulus obtained from static test. Due to the point that static test mode is similar to the long time duration or in the other hand extra small frequency condition, therefore it could be a benchmark in order to estimate the static modulus from data obtained for dynamic modulus at the frequency equal to 0 Hz. To investigate the storage modulus obtained by dual cantilever bending mode of DMTA and estimate the static modulus, the storage modulus of the specimens at the room temperature was plotted against the test frequency. The storage modulus at the frequency of zero was then estimated by extrapolation (Figure 11). The extrapolation approximates values of 1.14, 1.03, 0.97, 0.73, 0.57,

### TABLE 5 The activation energy of 2 peaks for synthesize PA12-MWCNT samples

<table>
<thead>
<tr>
<th>MWCNT %wt</th>
<th>$E_a$ 1, kJ/mol</th>
<th>$E_a$ 2, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$65.66 \pm 0.21$</td>
<td>$496.41 \pm 0.52$</td>
</tr>
<tr>
<td>0.1</td>
<td>$82.80 \pm 0.24$</td>
<td>$404.95 \pm 0.15$</td>
</tr>
<tr>
<td>0.3</td>
<td>$59.30 \pm 0.41$</td>
<td>$268.75 \pm 0.39$</td>
</tr>
<tr>
<td>0.7</td>
<td>$66.48 \pm 0.32$</td>
<td>$335.65 \pm 0.72$</td>
</tr>
<tr>
<td>1.2</td>
<td>$71.11 \pm 0.53$</td>
<td>$540.52 \pm 0.19$</td>
</tr>
<tr>
<td>2</td>
<td>$66.27 \pm 0.60$</td>
<td>$550.58 \pm 0.78$</td>
</tr>
</tbody>
</table>

**Figure 10** Arrhenius plot to calculate the activation energy of the second transition

**Figure 11** The storage modulus against frequency for unfilled polyamide 12 and polyamide 12-MWCNT nanocomposites at 25°C
and 0.46 GPa for 2, 1.2, 0.7, 0.3, and 0.1% wt PA12-MWCNT nanocomposites and pure PA12 specimens, respectively. The results indicate that the dynamic storage modulus approaches the static elastic modulus (Table 2) with decreasing the test frequencies. Test results are shown in Figure 10 at room temperature.

3.4 Evaluation of the crystallinity in the PA12-MWCNT nanocomposite samples using XRD results

The presence of filler can lead to nucleation effects and can partially inhibit the crystallization of the polymer matrix. This can affect the displacement properties. The permeability depends on the penetration and solubility and therefore the concentration of the amorphous region. The crystalline structure of nanocomposites was investigated through XRD. As we know, nylon 12 is made up of both α and γ crystals, in which the dominant crystalline structure is γ. Two reflections are observed at 2θ = 6° and 21.5° in the results of XRD.

The size of the crystal (L) is measurable through XRD information. Similar to Scherrer equation, this method does not follow the dependency of (1 / cosθ), but the changes of tanθ are taken into account

\[ \beta = \beta_s + \beta_D \]  

(6)

\[ \beta = \left( \frac{K \lambda}{L \cos \theta} \right) + 4e \tan \theta \rightarrow \beta \cos \theta = \frac{K \lambda}{L} + 4e \sin \theta \]  

(7)

In this case, by drawing \( \beta \cos \theta \), via \( 4 \sin \theta \), the crystal size is obtained using the intercept value.

The other method is the modified Scherer. This method is based on the error reduction. In this approach, the logarithm is taken from the basic equation of Scherrer:

\[ \ln \beta = \ln \left( \frac{K \lambda}{L \cos \theta} \right) = \ln \frac{K \lambda}{L} + \ln \left( \frac{1}{\cos \theta} \right) \]  

(9)

By plotting the \( \ln (\beta) \) versus \( \ln (1/\cos \theta) \), a straight line will be obtained with slope of 1 and the intercept of \( \ln (K \lambda / L) \). It should be noted that each test was repeated 5 times for each nanocomposite.

<table>
<thead>
<tr>
<th>MWCNT wt%</th>
<th>20(°)</th>
<th>PWHM</th>
<th>1/FWHM</th>
<th>4sin(θ)</th>
<th>( \beta )</th>
<th>( \beta \cos \theta )</th>
<th>L (nm)</th>
<th>k/L</th>
<th>1/cosθ</th>
<th>ln(1/cosθ)</th>
<th>ln(K \lambda / L)</th>
<th>ln(1/\cos \theta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>21.32</td>
<td>1.29</td>
<td>0.931</td>
<td>1.454</td>
<td>1.203</td>
<td>0.070</td>
<td>0.0028</td>
<td>550.64</td>
<td>0.12</td>
<td>0.069</td>
<td>0.0024</td>
<td>0.0027</td>
</tr>
<tr>
<td>0.1</td>
<td>21.43</td>
<td>1.27</td>
<td>0.931</td>
<td>1.439</td>
<td>1.368</td>
<td>0.071</td>
<td>0.0024</td>
<td>550.64</td>
<td>0.12</td>
<td>0.069</td>
<td>0.0024</td>
<td>0.0027</td>
</tr>
<tr>
<td>0.3</td>
<td>21.46</td>
<td>1.26</td>
<td>0.930</td>
<td>1.387</td>
<td>1.261</td>
<td>0.071</td>
<td>0.0024</td>
<td>550.64</td>
<td>0.12</td>
<td>0.069</td>
<td>0.0024</td>
<td>0.0027</td>
</tr>
<tr>
<td>0.7</td>
<td>21.37</td>
<td>1.26</td>
<td>0.930</td>
<td>1.302</td>
<td>1.261</td>
<td>0.071</td>
<td>0.0024</td>
<td>550.64</td>
<td>0.12</td>
<td>0.069</td>
<td>0.0024</td>
<td>0.0027</td>
</tr>
<tr>
<td>1.2</td>
<td>21.80</td>
<td>1.27</td>
<td>0.930</td>
<td>1.387</td>
<td>1.261</td>
<td>0.071</td>
<td>0.0024</td>
<td>550.64</td>
<td>0.12</td>
<td>0.069</td>
<td>0.0024</td>
<td>0.0027</td>
</tr>
<tr>
<td>1.9</td>
<td>21.83</td>
<td>1.27</td>
<td>0.930</td>
<td>1.302</td>
<td>1.261</td>
<td>0.071</td>
<td>0.0024</td>
<td>550.64</td>
<td>0.12</td>
<td>0.069</td>
<td>0.0024</td>
<td>0.0027</td>
</tr>
<tr>
<td>2</td>
<td>21.77</td>
<td>1.27</td>
<td>0.930</td>
<td>1.302</td>
<td>1.261</td>
<td>0.071</td>
<td>0.0024</td>
<td>550.64</td>
<td>0.12</td>
<td>0.069</td>
<td>0.0024</td>
<td>0.0027</td>
</tr>
<tr>
<td>2.5</td>
<td>21.71</td>
<td>1.27</td>
<td>0.930</td>
<td>1.302</td>
<td>1.261</td>
<td>0.071</td>
<td>0.0024</td>
<td>550.64</td>
<td>0.12</td>
<td>0.069</td>
<td>0.0024</td>
<td>0.0027</td>
</tr>
<tr>
<td>3</td>
<td>21.69</td>
<td>1.27</td>
<td>0.930</td>
<td>1.302</td>
<td>1.261</td>
<td>0.071</td>
<td>0.0024</td>
<td>550.64</td>
<td>0.12</td>
<td>0.069</td>
<td>0.0024</td>
<td>0.0027</td>
</tr>
<tr>
<td>3.5</td>
<td>21.67</td>
<td>1.27</td>
<td>0.930</td>
<td>1.302</td>
<td>1.261</td>
<td>0.071</td>
<td>0.0024</td>
<td>550.64</td>
<td>0.12</td>
<td>0.069</td>
<td>0.0024</td>
<td>0.0027</td>
</tr>
<tr>
<td>4</td>
<td>21.65</td>
<td>1.27</td>
<td>0.930</td>
<td>1.302</td>
<td>1.261</td>
<td>0.071</td>
<td>0.0024</td>
<td>550.64</td>
<td>0.12</td>
<td>0.069</td>
<td>0.0024</td>
<td>0.0027</td>
</tr>
</tbody>
</table>

**Table 6** The effect of MWCNT wt% on the crystal dimension of PA12-MWCNT nanocomposites using Scherrer, modified Scherrer, and Williamson-Hall equations.
In this paper, $k$ was considered 1. The wavelength ($\lambda$) was considered equal to 1.5418 Å due to the copper anode. Also, the correction factor of the device is 0.1163. The obtained values for crystal dimension of the nanocomposites obtained from the 3 mentioned methods are presented in Table 6.

According to Table 6 by increasing the percentage of CNTs, the size of the crystals has been decreased. This can be explained by the fact that the nanotubes play the role of nucleus, the higher the number of these nuclei, the higher the number of crystalline nuclei, and more crystals with smaller size are created.

### 3.5 Evaluation of the crystallinity in the PA12-MWCNT nanocomposite samples using DSC results

The DSC results are shown in Table 5. It is clear that the CNTs increase the crystallinity content due to their nucleation effect. But on the other hand, more MWCNT decreases the chain mobility and their intercalation into the crystalline cells, due to more interaction between the chains and CNTs. The second effect prevents the formation and completion of the crystals. The results are similar to Fornes et al research for nano-clay.\(^{49}\)

In order to calculate the thickness of the crystal through DSC results, Thomson-Gibbs equation was applied. According to this equation, the thickness of the crystalline layer ($L$) can be measured as follows. $L$ is the distance between the 2 folding of the chains inside the crystal\(^{48}\):

$$L = \frac{2\sigma T_m^0}{\Delta H_f^0} \left( T_m - T_m^0 \right)$$ (10)

In this equation, $T_m^0$ is the equilibrium melting point, $T_m$ is the melting point obtained through DSC analysis, $\sigma$ is the surface free energy (m\(^2\)/m\(^2\)), and $\Delta H_f^0$ is the enthalpy of fusion for the 100% crystalline polyamide 12. According to this equation, if the melting temperature increases slightly, the thickness of the crystalline layer also increases gradually.

In order to calculate the thickness of the crystals, in this equation, $T_m^0$ was taken as 500 K, surface free energy was 40.7 mJ/m\(^2\), and the enthalpy of fusion for 100% crystalline polyamide 12 was 246 kJ/g. Also, the density was considered as 1.01 g/cm\(^3\). The values for crystals' thickness of nanocomposites calculated through Thompson-Gibbs equation and also other parameters from DSC analysis are reported in Table 7. It should be noted that the test for all samples was repeated 5 times and the average value of parameters is reported in Table 7.

The sample with the least crystal thickness has more side branches, and the branches could not go in to the crystalline cell which leads to the smaller crystals. As it can be seen in Table 5 by increasing the MWCNT content, the distance between the entanglements decreased. This fact could be explained as more MWCNT content creates more nuclei centers for crystalline formation which increases the number of crystals. This phenomenon let the number of nodes to be increased and simultaneously the distance between nodes to be decreased.

It is obvious that the results obtained from all methods showed the same procedure. Just a little difference between these methods was seen, which is related to the parameters of each approach and also the calculation methods.

### 4 Conclusion

The present work studies the mechanical properties of PA12 nanocomposites containing MWCNTs under dynamic conditions.

Comparing the storage modulus of the unfilled PA12 with nanocomposites exhibited a significant increase in the modulus of the nanocomposites. The nanocomposite specimens also showed lower tan $\delta$ in comparison with the unfilled PA12. By adding only 0.1 wt.% of MWCNT, the storage modulus increased up to 30% in comparison with the pure sample.

The effect of frequency on viscoelastic behavior of the samples was studied, and the related activation energy to each transition was calculated.

Also, the crystallinity of the synthesized PA12-MWCNT nanocomposites was investigated using the XRD and DSC results through Scherrer, modified Scherrer, Williamson-Hall, and Thomson-Gibbs equations. The results showed that by increasing the MWCNT content, the crystals’ thickness decreased.

**ORCID**

Shervin Ahmadi  
[http://orcid.org/0000-0003-1038-5146](http://orcid.org/0000-0003-1038-5146)

**REFERENCES**


