

STUDY ON THE DYNAMIC MECHANICAL, FLEXURAL STRENGTH AND SOME CHARACTERISTICS OF POLYOXYMETHYLENE/SILICA NANOCOMPOSITES

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Abstract. Similar to thermal analysis measurements such as differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA) and thermo-mechanical analysis (TMA), dynamic mechanical thermal analysis (DMTA) is also a technique that provided information on the thermo-mechanical properties of polymeric materials. This work focuses on the reinforcement of polyoxymethylene (POM) by nanosilica particles (NS) in order to increase flexural strength and hardness of the POM matrix. Thermo - mechanical properties of the POM/NS nanocomposite were investigated by using dynamic mechanical thermal analysis (DMTA). The loss modulus and storage modulus of POM/NS nanocomposites were increased in comparison with the POM. The glass transition temperature for POM and POM/NS composites was observed at around -70 °C. POM/NS composites have good thermal stability, less deformation at high temperature. The results of flexural tests showed that the POM/1 wt.% NS nanocomposite presented the highest flexural values with flexural strength and modulus strength of 93.8 MPa and 2.416 MPa, respectively. Flexural strength tends to reduce when NS content exceeds 1 wt.%. On the other hand, the hardness of POM/NS nanocomposites was higher than that of POM and reached maximum hardness value (83.5 shore D) at 1 wt.% NS content. The NS particles also improved solvent/chemical resistance of neat POM. The results indicated that the mass changes of POM/NS nanocomposites were about 3 % less than that of neat POM. Mass of POM/1.5NS nanocomposite changed markedly after soaking in solvents of acetone and xylene. POM and POM/NS nanocomposite are stable with solutions such as: acetic acid 10 wt.%, HCl 10 wt.%, NaOH 10 wt.% and toluene. The durability of POM/NS nanocomposites in solvent and chemicals is improved when NS is added to POM.

Keywords: polyoxymethylene, nanosilica, dynamic mechanics, flexural, hardness.

Classification numbers: 2.4.4, 2.9.3, 2.9.4.

1. INTRODUCTION

Polyoxymethylene (POM) is formaldehyde-based thermoplastics that had attracted increasing interest in research and development due to its mechanical properties (high tensile strength and stiffness) and chemical resistance as well as excellent thermal properties. Moreover,

it is one of the few polymers that can be synthesized through non-petroleum route at low cost. Therefore, POM is widely used in mechanic, automotive, and electric-electronic industries, etc. [1-3]. However, the high crystallinity and brittleness of POM, accompanied with the low thermo-oxidative stability are the limiting factors of its applications in different fields [1 - 2].

In recent years, there have been many studies aiming to further improve the mechanical and some properties of POM by combining with additives such as carbon nanotubes [4 - 6], montmorillonite [7 - 10], CaCO₃ [11], graphite [12], ZnO [13], Al₂O₃ [14], hydroxyapatite [15 - 16], polyhedral oligomeric silsesquioxane [17 - 18] and carbon fibers [19]. Unlike fillers which are micro-size additives, nanoscale additives can improve thermal properties and inhibit polymer combustion when they are added into polymer matrix without losing mechanical properties. In a study of Xu *et al.* [20], carbon fibers (CF) and nanosilica (NS) were used to increase the toughening and flexural properties of POM. The POM matrix composites displayed the enhancement of average coefficient of friction and flexural of POM by CF and NS. In other report, Xiang *et al.* [21] have synthesized nanocomposites based on POM and NS by melt compounding method. The addition of NS into POM raised the degradation temperature of the nanocomposites in inert gas or air. NS has outstanding properties such as high tensile strength, small expansion coefficient, high reflexes of UV light and so on. It is widely used in plastic, paints, coatings, rubber, etc. [22 - 24]. Although the addition of silica particles to various polymers significantly reduced heat release rate of the polymers, there are no previous studies on the flame-retardant effectiveness of the NS addition.

In our previous work [25 - 27], some characteristics of POM/NS nanocomposites via a melt compounding method such as mechanical properties, thermal and UV stability have been studied. The results showed that the properties of POM/NS nanocomposites have been improved, especially mechanical and thermal properties [24 - 25]. For instance, the POM/NS nanocomposites were more thermally stable than neat POM (the thermal resistance of POM/NS nanocomposites increase by about 30 °C compared with neat POM), and the tensile strength, elongation at break and UV stability improved.

From the literature and our previous works, the goal of the present study is to improve some other properties such as dynamic mechano - thermal, flexural properties, and hardness of POM and POM/NS nanocomposites. These properties of POM/NS nanocomposites were determined and compared with those of the neat POM.

2. EXPERIMENTAL

2.1. Materials

Polyoxymethylene (Lupital ® F20-03) was supplied by Mitsubishi Engineering-Plastics, Ltd. Co. (Japan) with the density of 1.41 g/cm³, melt flow index (MFI) of 9 g/10 min. Nanosilica powder with particle size about 12 nm was supplied by Sigma-Aldrich Co. (USA).

2.2. Preparation of POM/NS nanocomposites

The POM and NS particles were preliminary dried at 80 °C in vacuum for 4 hours. Then, nanocomposites based on POM and 0.5 - 2 wt.% NS (compared with total weight of two components) were melt mixed by using a Haake Rheomixer (Germany) at 190 °C for 5 minutes and screw speed 60 rpm. After melt mixing, the nanocomposites were molded by hot pressured machine (Toyoseiki, Japan) at 190 °C, pressing pressure of 12-15 MPa for 2 minutes.

Table 1. Symbol of nanocomposite samples with contents of NS change from 0 to 2 wt.%.

Samples	POM	POM/0.5NS	POM/1NS	POM/1.5NS	POM/2NS
The content of NS (wt.%)	0	0.5	1	1.5	2

The samples in sheet shape were allowed to be cooled and stored at room temperature for 48 hours before determining their properties. These samples were denoted as shown in Table 1.

2.3. Determination of dynamic mechanical thermal analysis of POM/NS nanocomposites

Dynamic mechanical thermal analysis (DMTA) of POM/NS nanocomposites were performed on DMTA MCR302 Instruments (Australia) in three – points bend at the frequency of 1 Hz according to ASTM D 4065 standard. The samples were cooled to -100 °C with a function of temperature (T = -100 °C to + 125 °C). The temperature was allowed to stabilize, then increased with rate of 3 ± 1 °C/min until 125 °C. The specimen dimensions (width × length × thickness) were 10 × 50 × 1 mm. The storage modulus, loss modulus (G' and G'') and loss factor ($\tan \delta$) were recorded as functions of temperature.

2.4. Determination of flexural strength of POM/NS nanocomposites

Flexural strength test of POM/NS nanocomposites were performed at a test speed of 2 mm/min according to EN ISO 178 using a Zwick Tensile 2.5 Machine (Germany). All the tests were performed at room temperature (25 °C). The specimens were of bar shape with length of 60 mm, width of 12.7 mm and thickness of 3 mm.

2.5. Determination of hardness of POM/NS nanocomposites

Hardness of POM and POM/NS nanocomposites was measured by Shore D at room temperature.

2.6. Determination of solvent and chemical resistance of POM/NS nanocomposites

The solvent/chemical resistance of POM/NS nanocomposites was evaluated by immersing 2 mg pieces of the sample into solvents and chemicals such as: acetone, toluene, xylene, solutions of acid acetic 10 wt. %, HCl 10 wt.%, NaOH 10 wt.% and CH₃COOH 10 wt.% within 28 days. The solvent and chemical resistance were evaluated by measuring the change of mass in each period times of 7, 14, 21 and 28 days. After each period times, test samples were withdrawn, dried and reweighed. Change of mass was calculated according to the formula:

$$\text{Change of mass (\%)} = (M_s/M_o) \times 100$$

M_s and M_o correspond to mass of sample at period time t and initial mass.

All above tests were performed at Institute for Tropical Technology, VAST.

3. RESULTS AND DISCUSSION

3.1. Dynamic mechanical thermal property

Dynamic mechanical thermal analysis (DMTA) data of POM/NS nanocomposites were recorded as a material temperature - dependent viscoelastic property and contributed to

determine modulus of elasticity and damping values by applying an oscillating force to the sample. The diagrams presented in Fig. 1 - Fig. 3 show correspondingly storage modulus, loss modulus, and loss factor of the POM, POM/0.5NS and POM/1.5NS nanocomposites. Figure 1 and Figure 2 describe the storage modulus (G') and loss modulus (G'') as a function of temperature for POM and POM/NS (with 0.5 and 1.5 wt.% of NS content). A direct comparison of G' plot between POM and POM/NS nanocomposites reveals a difference in the curve characteristics. It can be noticed that the G' of the composite is enhanced by adding NS compared to neat POM. This is explained by nanoscale silica particles dispersion in POM matrix leading to the formation of physical interaction between hydroxyl groups on the surface of NS and the end-chain aldehydes of POM.

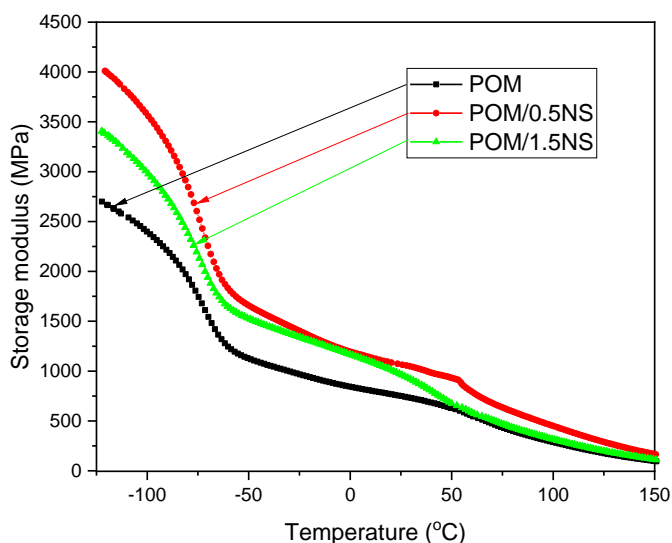


Figure 1. Storage modulus diagrams of POM and POM/NS nanocomposites.

From Figure 1, the glass transition temperature (T_g) for POM and POM/NS composites was observed at around -70°C corresponding to the variation of G' . Besides, the G' has tendency to reduce with increasing temperature due to rising the flexibility of polymer at high temperature and reaching maximum rate at the glass temperature. The G' of POM/NS composites is always greater than that of neat POM at glass and elastic state, indicating that POM/NS composites have good thermal stability, less deformation at high temperature. The impact stress is evenly distributed over the phases in the materials, due to the good adhesion interaction between polymer matrix and nanoparticles, the polymer structure becomes more stable at high temperature. The G' of composites is only slightly changed when the NS content is varied.

Figure 2 depicts the loss modulus (G'') of POM/NS nanocomposites also as a function of temperature. There are two peaks of the phase transition corresponding to the phase transition from the glass to the elastic region (1) and from the elastic to melting region (2) of POM and POM/NS nanocomposite as seen in Figure 2. The first peak located at around -72°C was the phase transition of POM [15] in which the material transitioned from glass region to elastic region. The next transition that observed at temperature peak in range from 93 to 100°C was attributed to melting transition of POM. Consequently, the POM/0.5NS and POM/1.5NS samples show the first peaks at -79 and -102°C , respectively. By adding nanosilica particles into POM, the transition energy from glass region to elastic region is increased and the peak is

shifted to the high temperature region. This can be explained by the interaction between hydroxyl groups of nanosilica with carbonyl group with aldehyde terminal group in POM macromolecules.

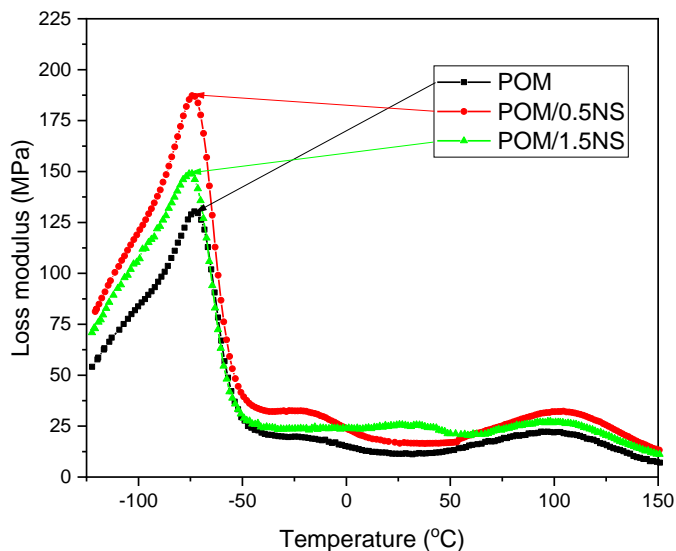


Figure 2. Loss modulus diagrams of POM and POM/NS nanocomposites.

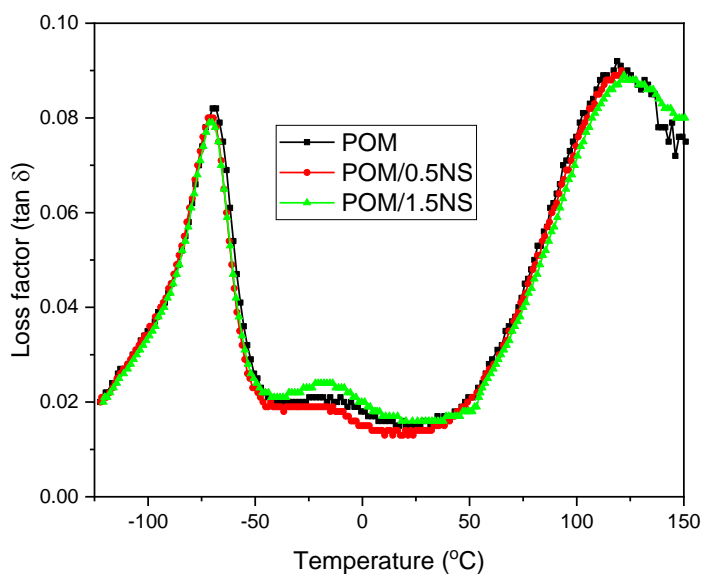


Figure 3. Loss factor ($\tan \delta$) diagrams of POM and POM/NS nanocomposites.

The DMTA diagrams characterizing the properties of POM and the POM/NS nanocomposites present a fairly typical trend of changes, especially the glass transition temperature range. The POM/NS nanocomposites had a characteristic shape similar to that of neat POM, the nature of the glass transition was not changed when increasing the NS content in the nanocomposites.

The loss factor ($\tan \delta$) is an important parameter in relation to the dynamic behavior of neat POM and POM/NS composite. The $\tan \delta$ diagrams of POM and POM/1.5NS nanocomposites are represented in Figure 3. It is clear that the $\tan \delta$ is increased with rising temperature at low temperature and reached maximum value at temperature of $-70\text{ }^{\circ}\text{C}$ in the glass region of the material. The $\tan \delta$ value is less than 1, which indicates that G'' is smaller than G' . $\tan \delta$ can be used to determine glass transition temperature T_g of the samples. The T_g of POM, POM/0.5NS and POM/1.5NS are -68 , -72 and $-71\text{ }^{\circ}\text{C}$, respectively. The T_g of POM/NS nanocomposites decreased slightly compared with POM, which may be due to the thermal conductive ability of NS. The small reduction of T_g shows that NS has a little effect on recovery properties of POM. This is explained by supposing that most of NS particles inside the bulk composite were impacted by tension force while a little nano particles at the surface of the polymer–particle phase were deformed [26]. Therefore, the energy at the interface of polymer and nano particles is low. On the other hand, in Figure 3, the NS content does not influence the behavior of nanocomposites nor their elastic deformation [15].

3.2. Flexural strength

The flexural properties of POM and POM/NS nanocomposites are shown in Figure 4 and Table 2. It is found that the flexural strength and modulus of POM/NS nanocomposites are higher than those of neat POM, and they increase with increasing NS content, because matrix can transmit stress to NS through interface, and NS with high modulus can withstand stress significantly better than the POM matrix. The POM/NS composites have high flexural modulus compared to neat POM. The POM/NS composites have high flexural modulus compared to neat POM. Figure 4 indicates a gradual increase of flexural modulus from 1837 MPa to 2416 MPa with the contents of NS varying from 0 to 1 wt.%, respectively.

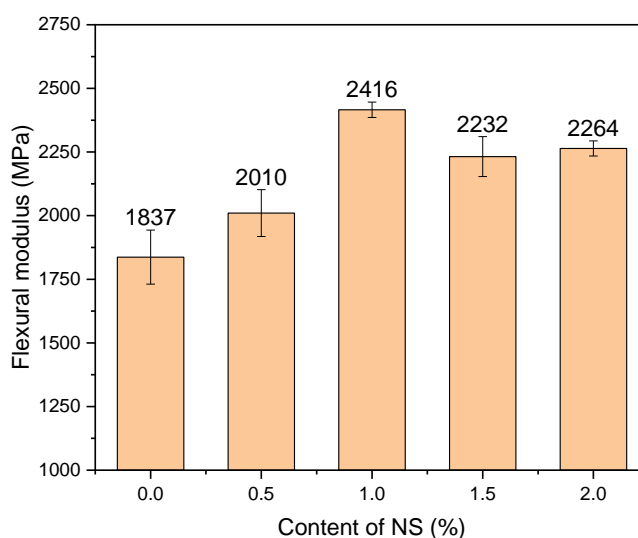


Figure 4. Flexural modulus of POM and POM/NS nanocomposites with different NS contents.

The effect of the NS particles on the flexural properties of POM/NS nanocomposites is also displayed in Table 2. In comparison with neat POM, there is a little change of the flexural strength for POM/NS nanocomposites. The flexural strength of POM/NS nanocomposites gradually is increased along with rising NS contents and reaches a maximum value of 93.8 MPa at 1 wt.% NS content. However, flexural strength tends to reduce when NS content exceeds 1

wt.%. Because the nanoparticles have high surface energy and surface area, so they have a strong tendency to agglomerate. They are prone to agglomeration to form micro-size or much bigger size particles leading to the stress concentration in composites. Thus, this region is under much more stress and would reach the flexural strength first and then rupture apart when subjected to force.

Table 2. Flexural properties and hardness of POM and POM/NS nanocomposites.

NS content (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Hardness (Shore D)
0	88.8 ± 1.3	1837 ± 106.1	82
0.5	90 ± 0.9	2010 ± 92.1	82.8
1	93.8 ± 0.3	2416 ± 30.1	83.5
1.5	89.6 ± 1.2	2232 ± 78.5	82.25
2	90.8 ± 0.4	2264 ± 29.9	83

3.3. Hardness

Hardness of nanocomposites is an important property among their mechanical properties. The hardnesses of neat POM and POM/NS nanocomposites are listed in Table 2. It can be seen that the hardness of POM composites is increased slightly in comparison to that of neat POM. This means the addition of NS particles could enhance the stiffness of the nanocomposites. The POM/1NS nanocomposite demonstrates the highest hardness value of 83.5 (Shore D) among four investigated nanocomposite samples.

This might be explained by the presence of nanoparticles inhibiting the movement of macromolecular chains, that enhancing the hardness of POM macromolecules. Moreover, the NS has high specific surface areas and surface energy due to the effect of their small scales. Thus, the nanoparticles can interact with macromolecular chains when added the polymer to enhance the interaction between macromolecular chains.

3.4. Solvent/chemical resistance

The mass change of POM and POM/1.5NS nanocomposites after 7, 14, 21 and 28 days in solvents/chemicals at 25 °C is shown in Figure 5.

The results indicate that POM and POM/NS nanocomposite are stable with solutions such as: acetic acid 10 %, HCl 10 %, NaOH 10 % and toluene. Their mass changes less than 3 % compared with the initial mass before soaking in above solutions [1]. However, mass of POM/1.5NS nanocomposite change markedly when soaking in solvents of acetone and xylene. It can be seen that the mass increase of POM and POM/NS nanocomposites when immersed in these two solvents, especially in acetone. The increase in mass is the osmolality of acetone into POM matrix and silica (due to the hydrogen and dipole interaction).

Table 3 performs the mass change of POM and POM/NS nanocomposites with various NS contents after 28 days of soaking in solvents at 25 °C. It can easily be seen that the mass increases slightly when soaked in solvent and chemicals. The mass increase of POM can be

attributed to the swelling of POM in polar solvents. Besides, POM has end-of-circuit functional groups containing aldehydes, so it can interact with polar groups in the solvent, and keep the solvent molecules in the polymer structure. When NS is added to POM, the durability of POM/NS nanocomposites in solvent and chemicals is improved. This can be due to the NS particles have limited penetration and permeation of solvent molecules into POM.

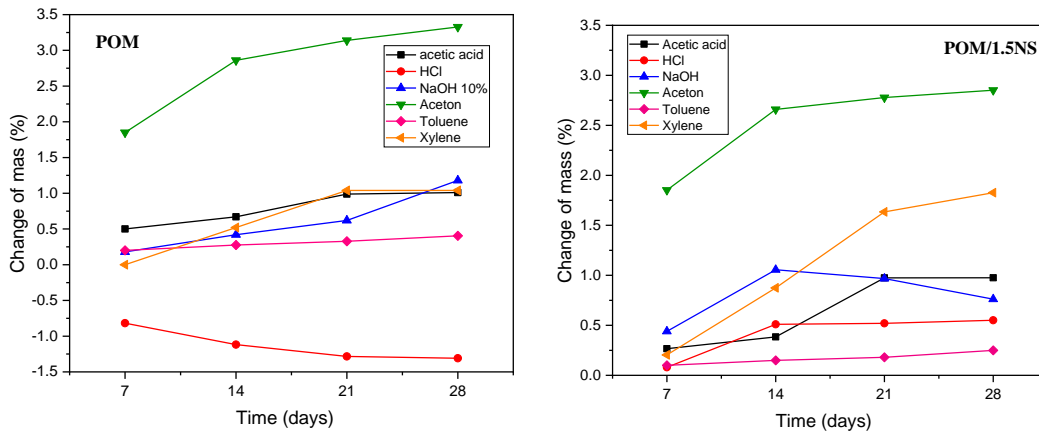


Figure 5. The mass change of POM and POM/1.5NS nanocomposite after soaking in different solvents/chemicals.

Table 3. Mass change of POM and POM/NS nanocomposites after 28 days soaking in solvents and chemicals at 25 °C.

Sample	Change in mass (%)					
	NaCl	Acetic acid	HCl	NaOH	Acetone	Xylene
POM	-1.11±0.12	1.01±0.02	-1.31±0.12	1.18±0.16	3.43±0.42	1.04±0.23
POM/0.5NS	-0.61±0.09	1.89±0.10	-0.85±0.17	1.12±0.09	0.85±0.08	1.23±0.18
POM/1NS	-0.30±0.13	1.62±0.04	-0.63±0.17	0.89±0.14	2.68±0.24	0.59±0.08
POM/1.5NS	-0.24±0.07	0.98±0.73	0.55±0.17	0.76±0.23	2.85±0.06	1.83±0.32
POM/2NS	-0.31±0.03	2.04±1.71	0.54±0.17	1.08±0.25	2.87±0.09	1.48±0.85

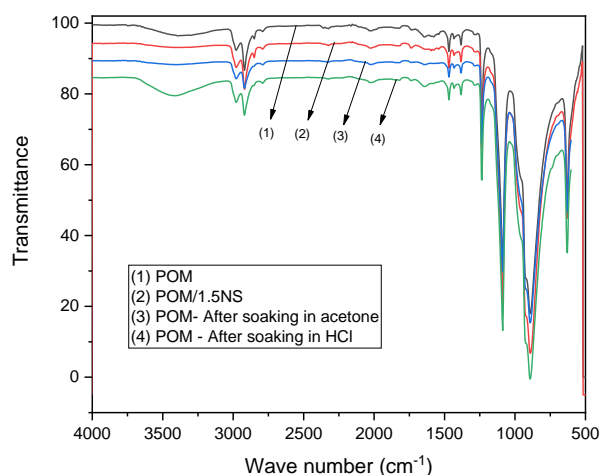


Figure 6. The FTIR spectra of POM before and after soaking in some solvents/chemicals.

The FTIR spectra of POM and POM/1.5NS before and after soaking in various solvents/chemicals are displayed in Figure 6. On the spectrum of POM after soaking in HCl, there is an additional peak at 3411 cm^{-1} corresponding to the valence oscillations of water. This demonstrates POM may have swelled when soaking in HCl. From Fig. 6, the FTIR spectra of POM before and after soaking in solvent/chemical are similar to each other, which indicates that the structure has no change.

4. CONCLUSION

In this study, the thermal dynamic mechanical, hardness, flexural properties and solvent/chemical resistance of POM/NS nanocomposites are investigated. The loss modulus peak heights and storage modulus of POM/NS nanocomposites are higher than those of POM, which indicate better adhesion between NS particles and polymer matrix. The addition of NS improves flexural strength and modulus of neat POM significantly. The flexural modulus is increased gradually from 1837 MPa to 2416 MPa. Similarly, the flexural strength reached a maximum value of 93.8 MPa at POM/INS nanocomposite. The hardness of POM/NS nanocomposite is higher than that of POM with the highest value of 83.5 (Shore D). The durability of POM/NS composites in solvent and chemicals is enhanced by adding NS particles.

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Declaration of competing interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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