EFFECT OF SOME ADDITIVES ON PROCESSABILITY, MECHANICAL PROPERTIES AND MORPHOLOGY OF POLYOXYMETHYLENE/SILICA NANOCOMPOSITES

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ABSTRACT

In this paper, the effects of some additives such as ethylene-vinyl acetate copolymer (EVA), linear low density polyethylene (LLDPE), polylactic acid grafted with 5 wt.% polyethylene glycol (PELA) and zinc stearate (named UTF) on processability, mechanical properties and morphology of polyoxymethylene/silica (POM/SiO$_2$) nanocomposites were investigated. The obtained results showed that the processing of the POM/SiO$_2$ nanocomposite was more easily in the presence of PELA, UTF and EVA indicated by a lower torque and mixing energy. The incorporation of PELA caused the decrease in the Young-modulus and hardness but increased elongation at break as well as tensile strength of the POM/SiO$_2$ nanocomposites. The SEM images showed that POM and EVA, LLDPE, UTF were incompatible in the POM/SiO$_2$ nanocomposite by observing phase separation. By the incorporation of PELA in the nanocomposite, no phase separation between POM and PELA was observed. Using some additives for POM/SiO$_2$ nanocomposites is one of the suitable solutions to improve the processability and the mechanical properties, especially the elongation at break of the material.

Keywords: POM, PELA, EVA, LLDPE, nanosilica, nanocomposites.

1. INTRODUCTION

Polyoxymethylene (POM) is one of commonly engineering thermoplastics used in many fields such as automobile, electronic, biomedical applications and mechanical engineering, etc. POM has many good advantages such as good fatigue resistance, dimensional stability, high stiffness, creep resistance, high impact strength, and good wear-resistant properties. However, low friction coefficient, low impact toughness, low heat-resistance, and sensitivity to notch limit its applications. To overcome these disadvantages, nano-additives which have high specific surface area, high thermal and weather stability, for example, organoclays [1], alumina [2], layered silicates [2], hydroxyapatite [3], nano-Al$_2$O$_3$ [4], and ZnO [5] have been added into

POM. Nevertheless, some modification methods were also applied for POM nanocomposites. Thontree Kongkhlang et al. used organically modified bentonites[MxMg$_6$(Si$_8$xCax)Si$_8$O$_{20}$(OH)$_4$] with different alkylamine surfactants to prepare POM/organomodified bentonite nanocomposites [6]. The authors indicated that the elasticity of POM/organo-modified clay nanocomposites were better than that of the pristine POM at low frequency (below 1 rad/s) and lower than that of the pristine POM at higher frequencies (10-100 rad/s). G.N. Tomara et al. reported that the dielectric α-relaxation of polyurethane (PU) remains unaffected by the introduction of PU into POM matrix while the adding of layered silicates (LS) leaded to the separation of γ- and δ-modes of POM in the direct melt compounding system. By using the melt compounding and a latex-mediated masterbatch (MB) technique to produce the POM/PU/LS systems, the α-mode of POM was shifted to higher frequencies [7]. Kinga Pielichowska et al. prepared the composites based on hydroxyapatite (HAp) grafted with poly(ethylene glycol) (PEG) (HAp-*g*-PEG)and POM using melt processing methods. The obtained results showed that the introduction of HAp-*g*-PEG to POM matrix has a slight influence on the melting temperature and degree of crystallinity of POM. The authors also confirmed that the POM/HAp-*g*-PEG nanocomposites can be used for biomedical applications [8]. Up till now, the study on the mechanical properties and processability of POM/silica nanocomposites in the presence of some polymers and additives are presented not so much.

In our previous publication, LLDPE [9], EVA [10], UTF [11], EVA-grafted-maleic anhydride [12], EVA-g-acrylic acid [13] were used as additives for high density polyethylene/fly ash composite, polylactic acid/TiO$_2$nanocomposites, EVA/silica nanocomposites. These additives exhibit a good improvement for properties of the above composites and nanocomposites, especially their mechanical properties, processability, thermal stability and weather stability. Moreover, in a recent publication, the relative melt viscosity, FTIR, tensile strength, TGA, DSC, dielectric properties and morphology of POM/silica nanocomposites (nanosilica has the particle size of about 12 nm) were investigated and discussed. The obtained results showed that 1.5 wt.% of nanosilica exhibited the best improvement for POM [14]. In the same fashion, in this work, effect of some additive EVA, LLDPE, PELA and UTF on the mechanical properties and processability of POM/silica nanocomposites were investigated and discussed.

2. EXPERIMENTALS

2.1. Materials

Polyoxymethylene (POM, code F20-03, Korea Engineering Plastics Co., Ltd., Korea): density of 1.41 g/cm^3, melt flow index of 9 g/10 min. LLDPE (density of 0.926 g/cm^3, MFI (2.16 kg/190 ^{o}C) of 50 g/10 min, Korea), EVA (containing 10 wt.% of VA, density of 0.93 g/cm^3, MFI (2.16 kg/190 ^{o}C) of 1.8 g/10 min, Korea), PELA (PLA grafted with 5 wt.% PEG, Korea), UTF (containing 10 wt.% of zinc, density of 1.1 g/cm^3, Korea). Silica nanoparticles (NS, code 637238, Sigma-Aldrich Co., USA): 10-20 nm particle size (determined by TEM method). EVA, LLDPE, PELA, UTF and silica nanoparticles were used as received.

2.2. Preparation of POM/silica nanocomposites with additives

POM/silica and POM/additive/silica nanocomposites were prepared by melt-mixing method using internal mixer (Haake Rheomixer, Germany) at the same conditions: mixing temperature of 190 ^{o}C, mixing time of 6 min and mixing speed of 60 rpm. The weight

ratio of POM/additives/silica was fixed at 93.5/5/1.5. The filled coefficient of mixing chamber is 0.7. A mixture of additives and silica nanoparticles was added into the mixing chamber in 2nd min after POM melting. After melt mixing, the samples were formed to the sheets using press machine (Toyoseiki instrument, Japan) at 195 ^{o}C and at a pressure of 12–15 Mpa for 2 min. The abbreviation of the obtained samples containing 5 wt.% of EVA, LLDPE, UTF and PELA is 5EVA, 5 LLDPE, 5 UTF and 5 PELA, respectively.

2.3. Characterizations

2.3.1. Determination of processability of POM/additive/silica nanocomposites

The processability is reflected through the relative melt viscosity or mixing torque of nanocomposites by the melt-mixing process. The mixing torque values of the nanocomposites were recorded by Polylab 3.1 software connected to the internal mixer during melt-mixing process.

2.3.2. Fourier transforms infrared spectroscopy (FT-IR) of POM/additive/silica nanocomposites

FT-IR spectra of the nanocomposites in the thin film shape were recorded on the Nicolet/Nexus 670 spectrometer (USA) at room temperature by 32 scan with 8 cm^{-1} resolution and wave number rangingfrom 400 to 4000 cm^{-1}.

2.3.3. Tensile testing

Tensile properties (tensile strength, elongation at break and Young's modulus) of the nanocomposites were measured on Zwick Tensile2.5 Machine (Germany) according to ASTM D638 standard with cross-head speed of 10 mm/min at room temperature. The specimen has a thickness of 4 mm or less.

2.3.4. Morphology analysis

The fracture surface of the nanocomposites after breaking was examined by using S-4800 Field Emission Scanning Electronic Microscopy instrument (Hitachi, Japan) (FESEM).

3. RESULTS AND DISCUSSION

3.1. Processability of POM/additive/silica nanocomposites

The processability of POM/additive/silica nanocomposites has been reflected through mixing torque by the preparation of the materials during the melt- mixing process. Figure 1 displays the torque versus time curves of the materials during the melt-mixing process. The torque of POM reaches to maximum value after 0.5 min of mixing time and POM melts completely after 1.5 min of mixing time. The maximum torque values of the investigated nanocomposites are different due to the unlike friction between POM particles and twin screws of chamber. As adding silica nanoparticles, and additive into the POM at 2nd min, the torque of mixture increases slightly and reaches steady state at 3rd min. In steady state, the torque of POM/silica nanocomposite is lower than that of POM/LLDPE/silica nanocomposites and higher than that of POM/EVA/silica, POM/PELA/silica, and POM/UTF/silica nanocomposites. It means that the EVA, PELA, and UTF play a role of a plasticizer or a processing aid agent and lubricant. They contribute to the increase in mobility of POM macromolecules, leading to reduction of internal friction in melt mixing process of POM and silica nanoparticles. Therefore,

melt mixing process of POM/EVA/silica, POM/PELA/silica and POM/UTF/silica nanocomposites was carried out more easily than POM/silica and POM/LLDPE/silica nanocomposites [15-17]. The torque of the POM/silica, POM/LLDPE/silica, POM/EVA/silica, POM/PELA/silica and POM/UTF/silica nanocomposites at the stable state gets to 4 Nm, 4.4 Nm, 3.9 Nm, 3.7 Nm and 3.2 Nm, respectively. EVA, PELA or UTF exhibit a better processing effect for POM due to the existence of carbonyl groups in their macromolecules which can interact with carbonyl groups at the beginning of the POM chain. In addition, the C-O groups in EVA, PELA and UTF can combine with C-O groups in the POM. In contrast, LLDPE only contains C-C bond which is difficult to interact with C-O or C=O in POM, thus, LLDPE reveals a less compatibility and poor processing effect for POM containing nanosilica.
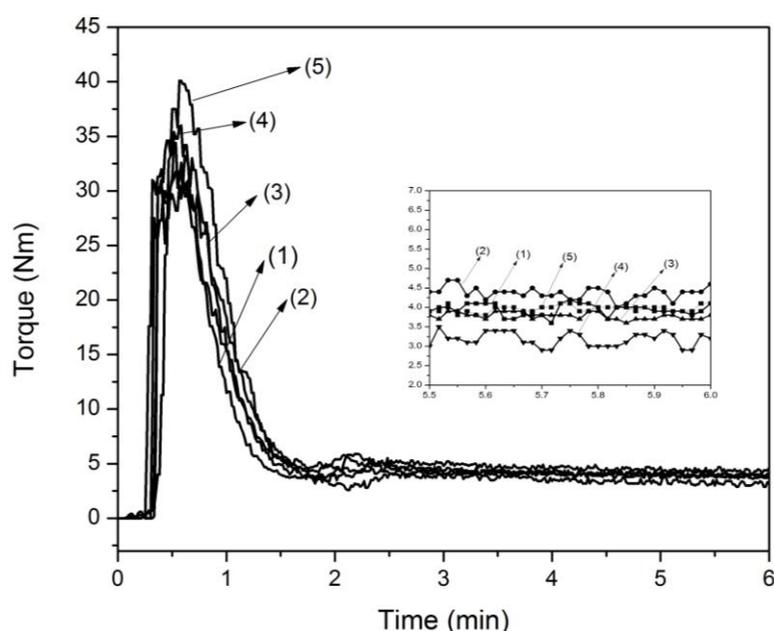
*Figure 1.*Torque curves of POM/EVA/silica (1) (-■-), POM/LLDPE/silica (2) (-●-), POM/PELA/silica (3) (-▲-), POM/UTF/silica (4) (-▼-) and POM/silica (5) (-■-) nanocomposites.

Figure 2 presents mixing energy consumption (MEC) of the nanocomposites obtained in melt-mixing process. The MEC is derivate of torque curves of the nanocomposites. In fact, the MEC can be influenced by friction of materials with mixer screw rotation, the melting ability of materials and the percent weight of components. It can be noticed that the MEC of all prepared nanocomposites ranges 0 to above 150 kJ for 6 min of mixing process, and increases with the mixing time due to increased levels of more efficient heating from viscous shearing. The MEC of POM/silica nanocomposite is much higher than that of the others containing additives. In general, lower MEC is observed for lower torque; however, the torque and MEC have not a direct correlation, highlighting the complex nature of melting in polymer extrusion [15]. In this case, the initial friction of melt mixing process could cause change in the MEC. Among four additives, EVA has lowest melting temperature. Thus, the melt mixing process of POM/EVA/silica nanocomposite consumes smallest energy. The melting temperature of PELA, LLDPE and UTF is similar to each other, but PELD can be best compatible with POM, leading to the MEC of POM/PELA/silica nanocomposite lower than that of POM/UTF/silica or

POM/LLDPE/silica nanocomposites. Combined to the above torque result, it can be to confirm that PELA exhibits the most compatible effect for the nanocomposites.
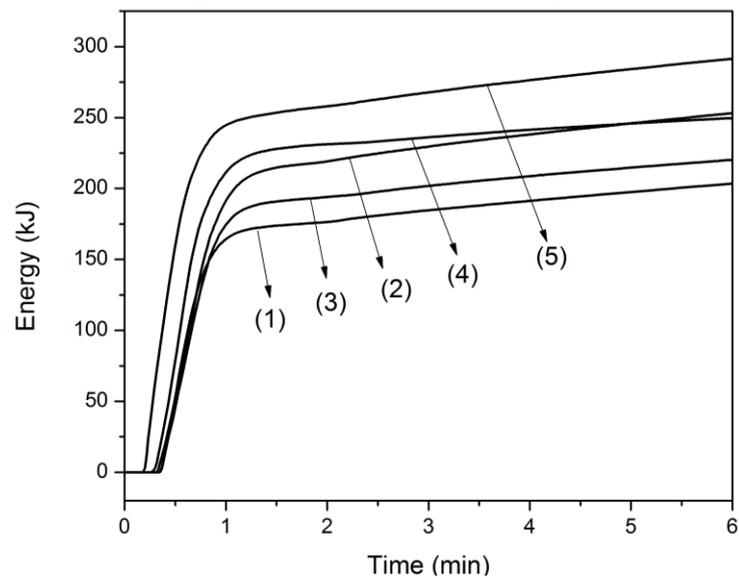
*Figure 2.*Mixing energy consumptionof POM/EVA/silica (1), POM/LLDPE/silica (2), POM/PELA/silica (3), POM/UTF/silica (4) and POM/silica (5) nanocomposites.

3.2. Tensile properties of POM/additive/silica nanocomposites
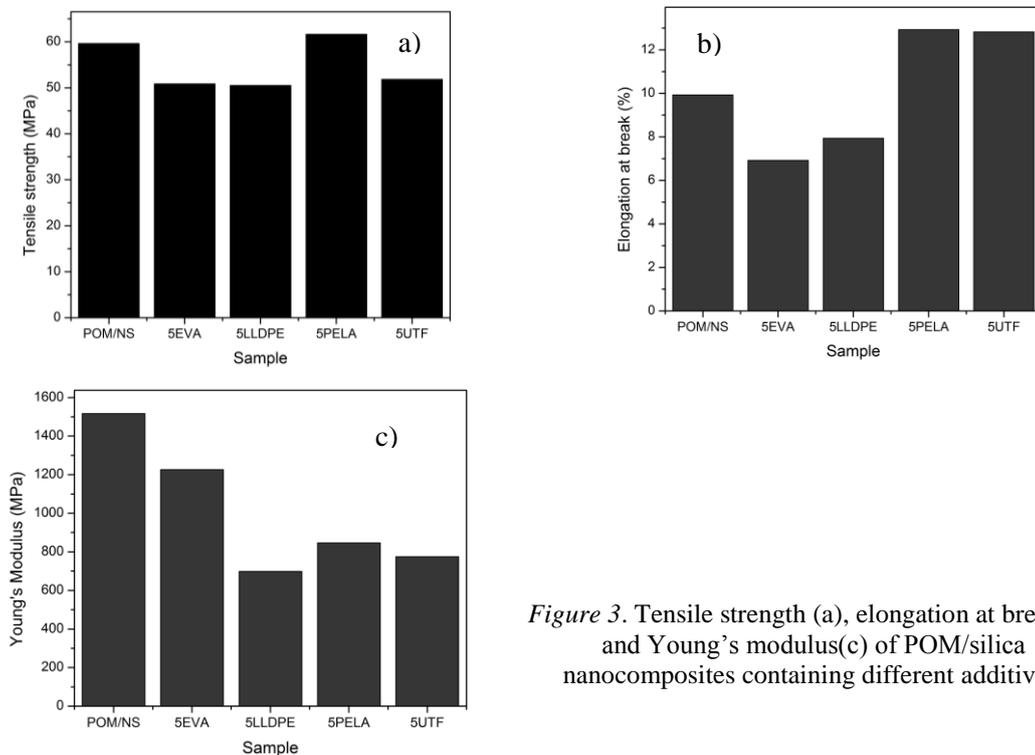
Figure 3. Tensile strength (a), elongation at break (b) and Young's modulus(c) of POM/silica nanocomposites containing different additives.

The effect of additives on tensile properties of POM/silica nanocomposites is demonstrated in Fig. 3. The tensile strength of POM/silica nanocomposite is 59.65 MPa. When using EVA, LLDPE and UTF, the tensile strength of the nanocomposites decrease remarkably, about 15 %. For example, the tensile strength reduces from 59.65 MPa for POM/silica nanocomposite to 51.84 MPa for POM/UTF/silica; 50.85 MPa for POM/EVA/silica and 50.52 MPa for POM/LLDPE/silica nanocomposites. Noticeability, the tensile strength of POM/PELA/silica nanocomposite increase 3 % in comparison with that of POM/silica nanocomposite. Thus, PELA exhibits a positive effect in the enhancement of tensile strength of POM/silica nanocomposite. This can be explained that PELA could improve the dispersion and interaction between nanosilica and POM by the formation of hydrogen bonding between C=O, C−O−C groups of PELA and OH groups on the surface of silica nanoparticles as well as C=O, C−O−C groups of POM. In this case, PELA is a compatibilizer for the POM/silica nanocomposites.

It is well known that POM has poor elongation at break because it is very brittle. Meaningfully, the incorporation of UTF or PELA in POM/silica nanocomposites can improve the elongation at break of POM/silica nanocomposites. From these results, PELA can improve both the tensile strength and the elongation at break of POM/silica nanocomposites that could reconfirm the compatibilizer effect of PELA in POM/silica nanocomposites.

The Young's modulus of the nanocomposites containing other polymers and additives is lower than that of POM/silica nanocomposite. It means that the POM/additive/silica nanocomposites are more flexible.

3.3. Morphology of POM/additive/silica nanocomposites

Figure 4 is FESEM images of fractured surface of the nanocomposites. It can clearly observe that the fractured surface of all samples is roughly with many small cracks. For POM/EVA/silica, POM/LLDPE/silica and POM/UTF/silica nanocomposites, the appearance of phase separation with the spherical domains (domain size of 2-3 μm) indicate that the components in the nanocomposites are incompatible. By contrast, by POM/PELA/silica nanocomposites the phase separation is not observed. This result indicates that PELA is good compatible in POM/silica nanocomposites. Combination of all results above, it can be seen that PELA is the suitable compatibilizer for POM/silica nanocomposites.

3.4. FTIR spectra of POM/additive/silica nanocomposites

Figure 5 demonstrates the FTIR spectra of POM/silica nanocomposites with and without additives. The peaks characterized for main functional groups of POM and silica nanoparticles are appeared in FTIR spectrum of POM/silica nanocomposite [1]. For instance, peak assigned to stretching and bending vibrations of hydroxyl groups in silica nanoparticles are found at 3610 cm^{-1} (area A in Fig. 5) and 1638 cm^{-1} (area H in Fig. 5), respectively. The vibrations of methylene and ethylene groups are recognized at 2980, 2921, 2790, 1469, 1432, 1383, and 895 cm^{-1} (area B, C, I, J in Fig. 5). The band located at 1734 cm^{-1} (area G in Fig. 5) is due to C=O stretching vibration at the beginning of POM chains. The C-O-C bond is given at 1236 cm^{-1} (area J in Fig. 5). The peaks noticed to stretching vibrations of Si-O bond in silica nanoparticles are overlapped by C-O-C bond as shown in area J in Fig. 5 while bending vibration of Si-O bond in silica nanoparticles appears at 458 cm^{-1} [9]. Peaks at 2327, 2238, 2018, and 1819 cm^{-1} (area D, E, F in Fig. 5) are from the impurities in the nanocomposites.
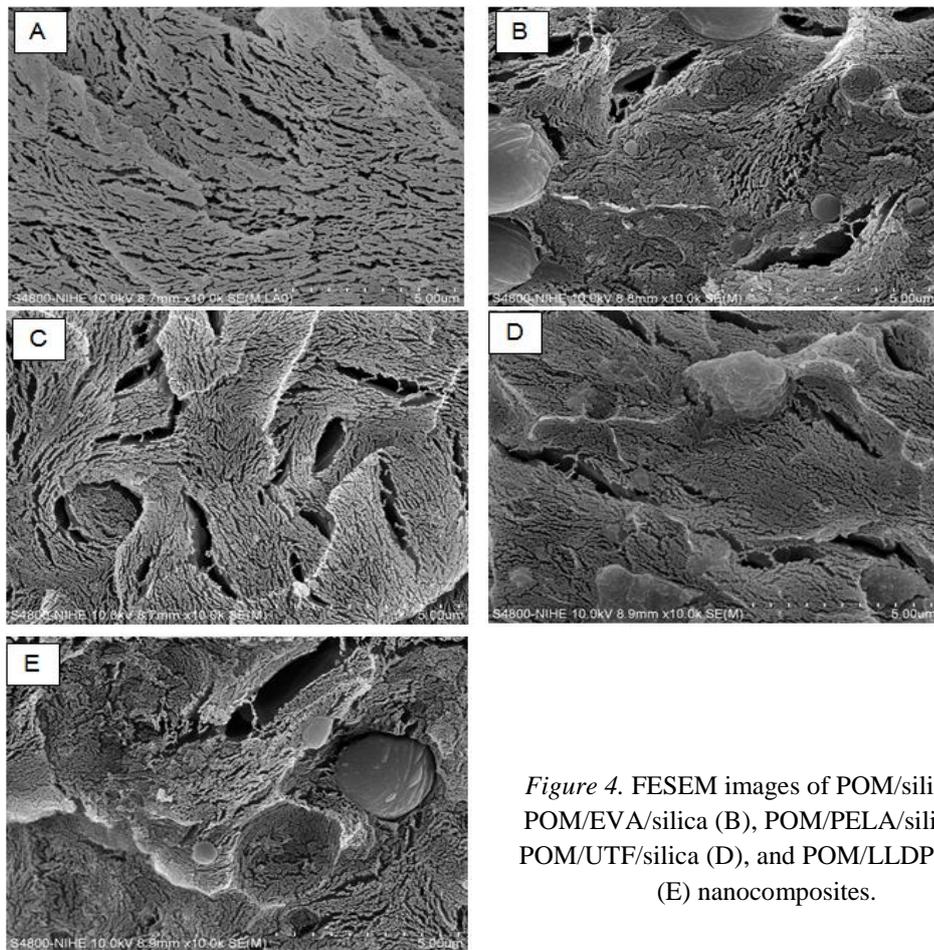
Figure 4. FESEM images of POM/silica (A), POM/EVA/silica (B), POM/PELA/silica (C), POM/UTF/silica (D), and POM/LLDPE/silica (E) nanocomposites.
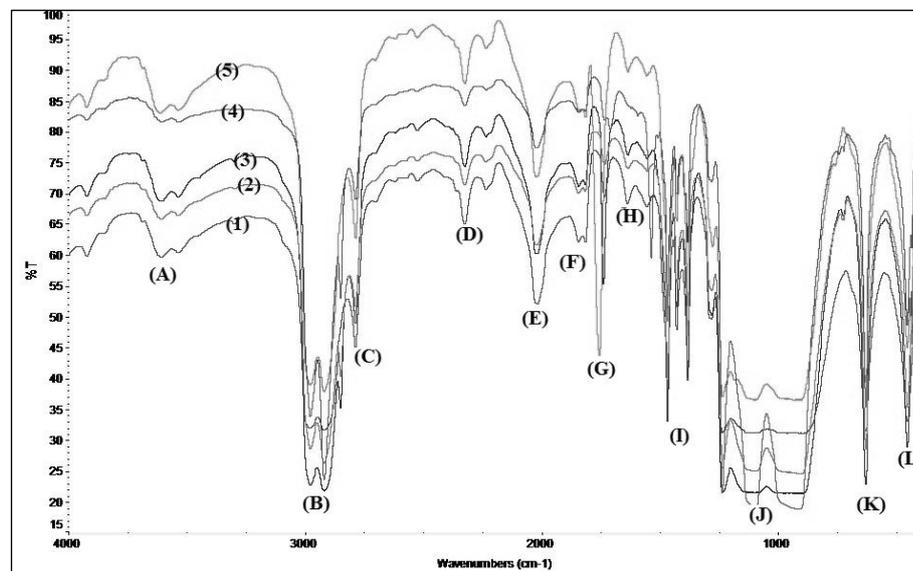
Figure 5. FTIR spectra of POM/silica (1), POM/LLDPE/silica (2), POM/EVA/silica (3), POM/UTF/silica (4), and POM/PELA/silica (5) nanocomposites.

The FTIR spectra of nanocomposites containing additives also exhibit the similar peaks like the FTIR spectrum of POM/silica nanocomposite mentioned. However, the intensity of some peaks at area G and J in the FTIR spectra of POM/PELA/silica and POM/EVA/silica is stronger than that in the other FTIR spectra corresponding to the resonation of carbonyl in PELA or EVA with carbonyl at the beginning of POM chains. This is also an evidence for the existence of PELA or EVA in the POM/silica nanocomposites. In addition, the strong shift of peak characterized for carbonyl groups in the FTIR spectrum of POM/silica nanocomposite to similar peak in the FTIR spectrum of POM/PELA/silica nanocomposite, from 1734 cm^{-1} to 1759 cm^{-1}, is contributed to prove for the formation of hydrogen bonding between PELA and POM, silica nanoparticles as discussed above.

To evaluate quantitatively the content of the carbonyl groups existed in nanocomposites, carbonyl index (CI) has been determined by the following equation as described in Ref. [18]:

$$CI = \frac{A_{1750}}{A_{1368}}$$

(1)

The CI of the POM/silica, POM/EVA/silica, POM/PELA/silica, POM/LLDPE/silica, and POM/UTF/silica nanocomposites is 0.120, 1.883, 2.270, 0.173, and 0.321, respectively. It is clear that the CI of POM/EVA/silica and POM/PELA/silica nanocomposites is much higher than that of the others. This result confirmed that FTIR spectra can be used as an independent method to consider the dispersion of EVA and PELA in the POM/silica nanocomposites.

4. CONCLUSIONS

In this work, the effect of additives such as LLDPE, EVA, PELA and UTF on the processability, the tensile properties and the morphology of POM/silica nanocomposites is presented. The processability and mixing energy consumption by the preparation of POM/silica nanocomposite are more in favour by the incorporation of EVA, PELA and UTF. By the tensile properties, only PELA has a positive effect in the enhancement of tensile strength and the elongation at break of POM/silica nanocomposites. Among the additives, PELA is the most suitable additive for POM and nanosilica in the nanocomposites. Thanks to the formation of hydrogen bonding between C-O, C=O groups in PELA and C-O, C=O groups in POM, O-H group in silica nanoparticles, PELA can improve the dispersion and interface interaction of nanosilica in POM matrix.

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