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Influence of fullerene-like tungsten disulfide (IF-WS_2) nanoparticles on thermal and dynamic mechanical properties of PP/EVA blends: Correlation with microstructure

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ABSTRACT

Compatibilized and non-compatibilized polypropylene/ethylene vinyl acetate copolymer (PP/EVA) blends loaded with 5 wt% of fullerene-like tungsten disulfide nanoparticles (IF-WS_2) as an inorganic nano-filler were prepared by melt mixing process and their thermal and dynamic mechanical properties were determined. TEM investigations revealed that the IF-WS_2 nanoparticles were mainly located within the EVA phase of the blend. Also, microstructure of blends studied by SEM showed that incorporation of IF-WS_2 into the blends led to reduction of dispersed domain size attributed to reduction of interfacial tension due to the filler presence. Melting temperature of PP loaded with 5 wt% of IF-WS_2 was increased up to 13 °C as compared to the neat PP. Addition of IF-WS_2 and PP-g-MAH as compatibilizer to PP/EVA blend increased melting and crystallization temperatures determined by DSC. DMTA studies showed that addition of IF-WS_2 into the blends had no positive effect on the storage modulus of nanocomposites while, their loss modulus were higher than that of the neat PP. Moreover, the β transition temperature of PP phase in the blends loaded with IF-WS_2 and compatibilizer was about 6 °C higher than the neat PP. The thermo-oxidative and thermal degradation behavior of developed nanocomposites determined by thermal gravimetric analysis (TGA) showed that thermal stability of nanocomposites was improved and their rate of degradation was reduced which were attributed to network-like structure formation of nano-fillers in the blends.

1. Introduction

Polymer nanocomposites are relatively new-class of materials which take advantage of nano-materials in exhibiting distinguish properties. The shape and type of nanomaterials are among important characteristics in classification of these materials. According to a traditional criterion, nano-materials can be categorized into organic and nonorganic substances. This division is based on presence or absence of structural carbon element [1,2]. Tungsten disulfide (WS_2) is one of the inorganic nano-materials having similar structure to fullerene commonly known as inorganic fullerene (IF). The shock-absorbing ability of the IF enables them to survive pressures up to 25 GPa at temperatures as high as 1000 °C without any significant structural degradation or phase change [3]. Also, the reported popular stiffness for individual IF is 350–360 Nm^{-1} and the compression stress being 1–2.5 GPa [4]. These nanoparticles have ultra-low friction properties and can be used as solid lubricants [5]. Also, WS_2 nanoparticles can be used as thin layer between two surfaces and reduce the friction. On the other hand, WS_2 is inert, non-toxic, and non-corrosive therefore this material can be applied to all medical equipments. From an application point of view the superb self-lubricating properties of IF

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nanoparticles open application possibilities for this material to be used in car industries, aerospace, biomedical, micro-electronics and numerous other industries [6–10]. Given their unique physico-chemical and mechanical properties, these nanoparticles drawn enormous attention shortly after their discovery in 1992 by Tenneet. al [11–14]. Incorporating of these nanofillers into polymeric matrices, for instance, has been studied for more than a decade and wide variety of polymers such as poly(ether–ether–ketone), poly(phenylene sulfide), (PPS), poly(methyl methacrylate), polyamide and epoxy resins have been used [14–17]. Naffakh and coworkers studied role of nanoparticle concentration in morphology and thermal properties of poly(phenylene sulfide) nanocomposites. They showed that addition of WS_2 with concentrations greater than or equal to 0.5 wt% had high impact on mechanical properties of nanocomposites [18].

Xu and coworkers reported that introduction of IF-WS_2 into polyamide-12 increases its toughness [19]. They claimed that the increase in mechanical properties can be derived from well dispersion of WS_2 nanoparticles in polymer matrix. Also the large interfacial area between nanoparticles and polymer plays important role in stress transfer from weak polymer matrix to the reinforcing nano filler [19].

The effect of IF-WS_2 nanoparticle on crystallization of various polymers has been studied. Isothermal crystallization behavior of PPS nanocomposites containing IF-WS_2 was investigated by Naffakh et al. They showed that, crystallization behavior of PPS is controlled by presence of IF-WS_2 and its content [20]. The effect of IF-WS_2 on crystallization of isotactic PP (iPP) was also studied by Naffakh and coworkers. Their results indicated that IF-WS_2acts as nucleation agent and it is responsible for formation of α-crystals of iPP [21]. Their results showed that surface folding free energy of crystals domain of polymer matrix decreased with increasing amount of WS_2 and from these results they suggested that high amount of WS_2 can create a new surface of crystals with low energy [21].

They also studied the melting behavior and crystallization kinetics of Nylon-6/IF-WS_2 nanocomposites [22]. Asadi and coworkers investigated crystallization process of poly(ethylene succinate)/IF-WS_2 nanocomposites. They showed that IF-WS_2 nanoparticles have positive effect on crystallization behavior of polyethylene succinate [23]. This research indicated that, introducing WS_2 to PES led to increasing crystallization rate and formation of homogenous crystal morphology [23]. Naffakh and coworkers investigated the effect of organic (single wall carbon nanotubes) and inorganic (IF-WS_2) nanoparticles on properties of poly(ether–ether–ketone), PEEK. The studied samples were traditionally prepared and then morphology and thermal behavior of the prepared nanocomposites were evaluated [24,25]. Their results showed that, size and interactions between WS_2 nanoparticles and polymer chains can play importance role in nucleation activity of WS_2 [25]. The IF-WS_2 nanoparticles have much lower toxicity than other commonly used nanoparticles [26,27]. Anew polymer blend nanocomposite based on poly(L-lactic acid)/polypropylene (PLLA/PP) and WS_2 was introduced by Naffakh et al. The WS_2 and PP have been incorporated into PLLA as a biopolymer and their morphology, thermal and mechanical properties were investigated. Their study opened a new window for developing WS_2–based polymer blend nanocomposites for biomedical applications [28].

PP/EVA blend is one of the most important polyolefinic materials which is vastly used in automotive, furniture industries and electrical equipments housings. To further improve the properties of this blend various inorganic and organic nano-fillers have been examined [29]. The influence of an organo-modified nanoclay (OMMT) on various properties of PP/EVA blends was extensively explored in our previous works [30–34]. Considering the unique physico-chemical and mechanical properties of IF-WS_2, it seems incorporation of IF-WS_2 into PP/EVA blend can lead to development of a new class of blend nanocomposites having highly improved properties with outstanding performance. Therefore in the current work a new series of blend nanocomposites based on PP/EVA/IF-WS_2 are prepared. Accordingly, the influence of IF-WS_2 nanoparticles on morphological, dynamic mechanical and thermal properties of PP/EVA blends in absence and presence of a compatibilizer i.e. PP-g-MA will be explored. An attempt will be also made to establish a correlation between the thermal properties and microstructure of the developed nanocomposites.

2. Experimental

2.1. Materials

PP (Moplen HP501H; density = 0.9 g/cm^3, MFI at 230 °C and 2.16 kg = 2.1 g/10min) from Basell, EVA (Escorene Ultra UL00218CC3; density = 0.94 g/cm^3, MFI at 190 °C and 2.16 kg = 1.7 g/10 min, vinyl acetate content = 18 wt%) from Exxon Mobile Chemicals Company were used as received. A maleated PP (PP-g-MA Polybond 3200) consisting of 1 wt% maleic anhydride was obtained from Chemtura Inc. Inorganic fullerene-like WS_2 nanoparticles (IF-WS_2) were provided by Nano Materials Ltd. (Apnano) and used as filler. These nanoparticles have an onion-like structure composed of concentric layers of WS_2. A detailed statistical analysis on this material has been performed by Naffakh et al. [35] to determine distribution of particle sizes and shapes from SEM images. They reported that the particles are multifaceted polyhedrons with an apparent shape ranging from spheres to ellipsoids. The particle aspect ratio ranges between 1 (spheres) and 2.3, with a mean value of 1.4, standard deviation of 0.3, and a median of 1.36. The particle dimensions are in the range of 40–200 nm with a mean value of 80 nm, standard deviation of 30 nm, and median of 75 nm.

2.2. Sample preparation

PP/EVA/IF-WS_2 nanocomposites were prepared in a micro-compounder (DACA Instruments Santa Barbara CA, USA) under the following processing conditions: rotation speed of 150 rpm, mixing time of 5min and temperature of 210 °C. PP and EVA components and different amounts of PP-g-MA and IF-WS_2 were introduced to the micro-compounder in a single step. Prior to the mixing, all materials were dried in an oven at 50 °C for 24 h. The compositions of the prepared nanocomposites are shown in Table 1.

2.3. Characterization

Ultra-thin sections of the extruded samples (~80 nm thickness) were obtained under cryogenic conditions at −120 °C using an EM

Table 1
Compositions of the prepared PP/EVA/IF-WS_2 nanocomposites.

Sample Code	PP (wt%)	EVA (wt%)	Compatiblizer (wt%)	IF-WS2 (wt%)
P100	100	–	–	–
P95W5	95	–	–	5
P75E25	75	25	–	–
P75E25C5	75	25	5	–
P75E25W5	75	25	–	5
P25E75W5	25	75	–	5
P75E25C5W1	75	25	5	1
P75E25C5W5	75	25	5	5
P25E75C5W5	25	75	5	5