A comparative experimental and molecular simulation study on the mechanical and morphological behaviors of adamantane-based polypropylene composites

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A B S T R A C T

The main objectives of this work were to construct and characterize polypropylene and adamantane (PP/ADM) nanocomposites experimentally and to identify their mechanical properties using molecular dynamics (MD) simulation. Samples with different contents of ADMs (0.5, 1, 2 and 4 weight percent (wt%)) were prepared using melt mixing method. It was observed that ADM nanofillers had significant effects on mechanical properties (Young's modulus) of PP nanocomposites. Furthermore an appropriate simulation model was developed to find mechanisms of dispersion and aggregation of the ADMs and to predict bulk properties of the nanocomposite. While former researches claimed that homogeneous filler dispersion exists only at the intermediate level of interfacial interaction between polymer and nanoparticle, according to results of current study entropy has substantial influence on dispersion process. In other words, entropy which controls the interfacial parameters such as how ADMs attach to the polymer chains (either by chain end or middle of the backbone), is a determining agent in dispersion and aggregation mechanism. Consequently chains entropy plays a significant role in enhancement of the nanocomposites Young's modulus. The trend of modulus alterations demonstrated that the entrance of ADMs at the chains contact point reinforced the polymer matrix and hence increased the modulus intensively. On the other hand, relative dispersion of ADMs and their small aggregates enhanced the modulus. However, ADMs aggregation caused by attaching to the joined ends, made a dramatic decline in Young's modulus.

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1. Introduction

Molecular diamond products called diamondoid materials or diamondoids, found in natural gas/petroleum streams, are thermodynamically stable molecules [1]. ADM ($C_{10}H_{16}$) is the smallest member of this group and since its first convenient synthesis by Schleyer [2] in 1957, extensive studies have been devoted to the use of ADMs as nanofillers [3–5]. It is due to the fact that ADM groups improve the properties such as stiffness, glass transition temperature and solubility of the composite [6–8]. In comparison with inorganic fillers (silica, clay, ZnO, etc.), wholly organic diamondoids are potentially more easily dispersed in organic polymer systems. Therefore, with high compatibility, ADMs can be incorporated into the backbone of many polymers like poly(olefins), poly(esters), poly(imides) and poly(benzyl ethers) [9]. PP is one of the most commonly used polyolefins, for its good balance between properties and cost, as well as its processability and low density. However, the mechanical properties, particularly its stiffness and tensile strength, are poor. Thus, to discover some reinforcing components, various studies have been performed [10,11].

Recently, diamondoids have been used as special nanofillers to prepare PP/diamondoids nanocomposites. This has introduced a new way to obtain high performance PP as an engineering plastic. However, the physical properties of PP/diamondoids nanocomposites such as crystallization, mechanical and morphological behavior have been rarely studied [3]. Since it is difficult to control and measure all of these properties experimentally, computational modeling is considered as an alternative technique to provide some crucial insights. For this purpose, molecular level computational methods, like MD simulation, have been widely applied to visualize the deep insight of nanocomposites properties [11–15]. MD simulations have been utilized in predicting both the structure and the elastic mechanical properties of polymer and polymer based nanocomposites so far [16–18].

Specially, in order to explain the mechanical properties, a vivid insight into the interface between polymer and nanofillers is necessary. For example, an efficient load transfer from polymer matrix to nanofiller is required to take advantage of high Young's modulus. On the other hand it is impossible to study the nanofiller-polymer interface with current laboratory equipment, therefore MD simulations have been considered as an important tool for investigation of reinforcement mechanisms in nanocomposites [19–22].

For prediction of nanocomposites mechanical properties and examination of their reinforcement mechanisms, three different MD simulation models; a united atom (UA) model (CH_2 and CH groups are considered as a unit), a coarse grained (CG) model (six united atoms are taken as one bead) and an explicit atom (EA) model (all the hydrogen atoms are taken into account explicitly) have been developed [23]. To evaluate the structure and conformational properties using the first two models (UA and CG), it is necessary to reintroduce the missing atoms before comparing to the experimental data. Additionally these models are inefficient for observing chain rotation too [24] and their dynamic evolution is faster than the corresponding EA model or experiments [25].

Regardless of the mentioned problems, the EA model more closely resembles the dynamic experimental data when compared to the UA and CG simulations models [24]. However, in the EA model, samples typically have significant number of atoms. As a consequence, to reduce the total size of a model, simulation works have focused only on nanocomposites with large volume fractions of nanoparticles (NPs) and to predict the lower NPs volume fraction enhancement, extrapolation has been applied [21].

Moreover, the mechanical properties of viscoelastic polymers are limited to picosecond (ps) or nanosecond (ns) time scales, using the available computation resources. Accordingly, large over estimations have been observed in prediction of the Young's moduli compared to the experimental results [26].

In current research, by generating samples with the desired NPs volume fraction and the densities close to the experimental value, the EA model was modified to improve the simulation results, Furthermore the potential energy of samples was equilibrated regardless of the simulated time so the Young's modulus was calculated based on the material behavior over a vague time interval By this improvement, the simulated moduli could forecast the experimental result well.

2. Material and experimental techniques

2.1. Materials

In this study, PP with extrusion grade of PI0800 was used as the matrix polymer (Bandar e Imam petrochemical Co. (Iran)).

Table 1
Physical properties of adamantane.

Diamondoid chemical formula	Molecular structure	Mw	MP (°C)	aBP (°C)	ρ (g/cc)	Crystal structures
Adamantan C10H16		136.240	269	135.5@ 10 mmHg	1.07	Cubic, fcc

aBP = apparent boiling point, MP = melting point, Mw = molecular weight, ρ = normal density.

Polypropylene with Molecular formula of $(C_3H_6)_n$ has molecular weight of 42.08 g/mole for repeat unit. The examined ADM was a SIGMA–ALDRICH 100277 Adamantane which is white, solid, crystalline powder with a molecular weight of 136.23 g/mol. The name adamantine is derived from the Greek language word for diamond since its chemical structure is like the three-dimensional diamond subunit. It is chemically and thermally stable and strain-free. These characteristics cause high melting points (MP) in comparison to other hydrocarbons. However it sublimes easily, even at atmospheric pressure and room temperature. Its carbon–carbon bond length is 1.54 Å and is almost identical to that of diamond, and the carbon–hydrogen distance is 1.112 Å. Some physical properties of adamantane are shown in Table 1 [27,28].

2.2. Nanocomposite preparation

The PP was blended with different percentages (0.5%, 1%, 2% and 4%) of the ADM by a Brabender Internal Mixer. The PP blending experiments were carried out at 190 °C and 60 rpm screw. Compounds were fulfilled by first feeding PP into the mixer. After 3 min of mixing and melting the PP pellets, a specified amount of ADM was poured into the mixer. The maximum length of the mixing period was 15 min. In order to perform mechanical testing on the samples, a hydraulic press was used to mold the samples into films (2–3 mm thickness) under a pressure of about 100 bar, at 200 °C and for 5 min.

2.3. Characterization

In order to investigate ADM particle size distribution, SEM image of PP/ADM (0.5%) was chosen. It can be seen in Fig. 1 that 25 adamantane particles are shown which 5 particles have more than 200 nm size and 15 particles are with diameters below 100 nm. These particles size distribution are listed in Table 2. In general, around 80 percent of adamantane particles are in the range of 60–150 nm size. By morphological tests we can conclude that the melt mixing method, which can simply be used at industrial scale, has relatively proper yield.
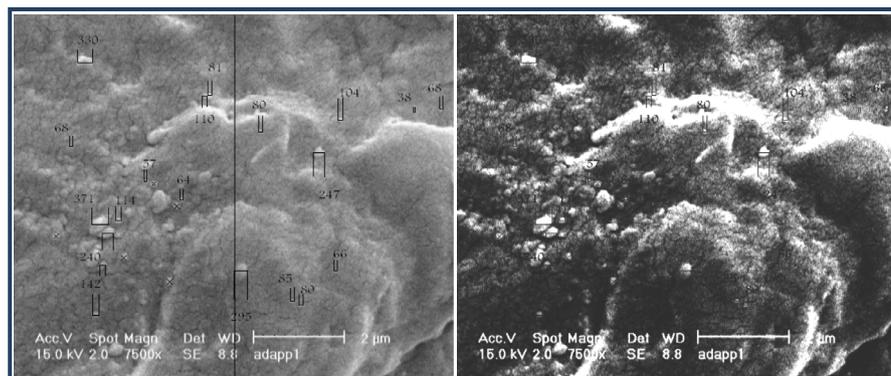
Fig. 1. Particle size distribution analysis for 0.5 wt% ADMs composite.