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Inorganic fullerene-like IF-WS_2/PVB nanocomposites of improved thermo-mechanical and tribological properties

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HIGHLIGHTS

- Poly(vinyl butyral)/tungsten disulfide nanocomposites were examined.
- Different solvents and deagglomeration methods affect the properties of composites.
- Nanoindentation and scratch test, PSD, SEM, DSC and DMTA were analyzed.
- Thermo-mechanical and antifriction properties of composite material are improved.

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ABSTRACT

The subject of this research is to explore the possibility of preparation of nanocomposite material of improved thermo-mechanical and tribological properties, using inorganic fullerene-like tungsten disulfide nanostructures (IF-WS_2) as reinforcement in poly(vinyl butyral) (PVB). This paper also reports investigation of the effects of using different solvents in preparation of PVB/IF-WS_2 nanocomposite on the thermo-mechanical behavior of the resulting material. PVB was dissolved in ethanol, isopropanol, n-butanol and ethyl acetate. IF-WS_2 nanoparticles were added to these PVB solutions and dispersed by different deagglomeration techniques. Samples were dried and thin films were obtained. Their microstructure and the quality of IF-WS_2 dispersion and deagglomeration in PVB matrix was analyzed by scanning electron microscope (SEM). The reinforcing effect of IF-WS_2 is examined by determining hardness, reduced modulus of elasticity and coefficient of friction, by nanoindentation and nanoscratch test, in terms of the different solvents applied in preparation of the samples, mode of stirring and different contents of IF-WS_2. The glass transition temperature (T_g) was determined for the prepared samples using differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMA). Storage modulus and mechanical loss factor were observed in a defined temperature range using DMA.

1. Introduction

Composites with nanofillers are promising materials that combine the advantages of the matrix (usually a polymer) and the fillers. This work represents investigation of composites made of poly(vinyl butyral) - PVB, and inorganic fullerene-like nanoparticles of tungsten disulfide - IF-WS_2 of particle sizes in the range of 40–300 nm, quasi-spherical shape, closed-cage layered structure, and chemically inert. PVB resin is a thermoplastic polymer which has wide application due to its excellent properties [1]: well soluble in alcohols and many other organic solvents, fast drying, fast solvent release and low solvent retention, good film formation, transparent and colorless, good barrier properties, tough polymer with excellent flexibility, broad compatibility with modifying resins and additives, non toxic and low odor, good adhesion to many substrates and strong binding, impact resistance, good tensile strength and elasticity, freezing and aging resistance. Due to these properties, there are many applications of PVB: safety glass, metal primers and coatings, printing inks, temporary binders (ceramics), ballistic protection [1–3].

Transition metal dichalogenides are well known for their solid

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lubricating behavior, even for high-temperature applications, and they can be used as a multifunctional reinforcement for improvement in thermal and mechanical properties of polymers [4–6]. Compared to MoS_2, WS_2 exhibits higher thermal stability and higher maximum operating temperature [5]. For the first time, Tenne and coworkers researched inorganic fullerene-like materials other than carbon in 1992 [7], and tungsten disulfide was among them. The metal sulfides bond into a sheet which forms nearly spherical, hollow shape. These structures have properties that can be exploited in many applications. One of the most common uses for inorganic fullerenes is, as mentioned, as solid lubricants [8–11]. Each of the layers forming the fullerene is loosely attached to the layers above and below by secondary bonding with covalent bonding in plane. The application of shear stress will cause a surface layer to be sloughed off preventing wear on the lubricated component. The natural spherical shape of the particles causes them to function as nanometric ball bearings rolling with the motion of the components. The excellent mechanical properties of the fullerene prevent them from flattening and breaking down as they roll until a number of surface layers have been removed [7,11,12]. It has also been shown that multilayer tungsten disulfide has outstanding shock resistance properties superior to those of even carbon nanotubes. In contrast to organic (carbon-based) fullerenes, IF-WS_2 is easier and much less expensive to produce, as well as chemically stable and much less reactive and less flammable. Organic fullerenes are highly toxic, unlike IF-WS_2, as most other inorganic fullerenes [11–13]. Inorganic fullerene IF-WS_2 nanoparticles, and their potential usage as fillers in polymer matrix to produce nanocomposites with improved mechanical properties was subject of a small number of researches. Small amount of IF-WS_2 gave great results in reinforcement of nylon-12 and nylon-6 [14–16]. The combination of PPS/SWCNT-PEI with inorganic fullerene-like tungsten disulfide (IF-WS_2) nanoparticles was earlier examined and improvement in the thermal properties of PPS/SWCNT-PEI nanocomposites was observed with the addition of IF-WS_2. As previously observed in PEEK hybrid systems, the dispersion, morphology and thermal properties of PPS/SWCNT nanocomposites could be enhanced by the introduction of small amounts of IF-WS_2 [17]. This filler also provided significant improvement of mechanical, tribological and rheological properties in isotactic polypropylene (iPP) [18]. WS_2 fillers have also provided significant reduction of the wear rate and friction coefficient of hybrid PTFE/Kevlar fabric composites [19].

Since this kind of nanoparticles often comes aggregated, it is important to emphasize that there is a high spread of the friction results of the lubricants containing IF-WS_2 nanoparticles with the size of IF-WS_2 aggregates in the lubricant. Their influence on the friction and wear were studied in oil-based lubricants, and it was demonstrated that the repeatability of the antifriction results depends on the homogeneity of the dispersion, of the size of the IF-WS_2 nanoparticles in the lubricant and the size of the IF-WS_2 aggregates [20]. Deagglomeration of nanoparticles by ultrasonic irradiation is very often applied technique, already investigated and prooved to have an impact on improving reinforcing effect of the fillers in composites, leading to enhanced mechanical performance of the composites [21–23]. High intensity ultrasound is used to very effectively disperse powder in a liquid, but it is more complex to achieve dispersion of nanoparticles in high viscosity polymer solutions. We may find very different or even opposite results about the optimum processing conditions of nanoparticle dispersion in polymer solutions, like in epoxy resin [24]. The dispersion quality is usually characterized from transmission electron microscopy or scanning electron microscope image analysis or by measuring the particle size in diluted suspensions. The cluster size in suspensions can be affected by various parameters including particle content, colloidal stabilization (electrical charges, absorbed surface layers, polymer interaction) [21]. The influence of the main parameters of ultrasonication such as time, power and irradiation modes (continuous, pulsed) on the cluster size of different nanoparticles was investigated in low concentration suspensions in different solvents for polymers such as poly(vinyl alcohol) and polyvinyl butyral [21–26]. Sonication method and duration were optimized through examination of behavior of MoS_2, IF-WS_2 and BN [13,27]. Nanomechanical and nanotribological properties of polymer composites prepared by these techniques (steering and ultrasonic irradiation) have been studied using the nanoindentation and nanoscratch technique [26,28]. The high-intensity ultrasonic processor was used in examinations of the effects of agglomerated versus deagglomerated multi-walled carbon nanotubes on the thermal and mechanical characteristics of polyethylene oxide, and significant differences were observed [28]. Generally, observing the effect of ultrasonic duration and amplitude it is established that longer ultrasonic irradiation is better for nanofluid preparation, and that higher sonicator amplitude is better for proper dispersion of nanoparticles.

Different solvents are often used in this dispersion and deagglomeration methods, and there is also a significant influence of the chemical structure of the used solvent, polymer and nanoparticles. When working with fullerene-like nanoparticles, the aim is to achieve certain exfoliation of the layers. The sonication of the layered compounds in solvents generally gives few-layer nanosheets with lateral dimensions of a few hundred nanometers [29], and taking into account the high surface energy of these layered inorganic materials, the success of the dispersion depends on surface tension and on solubility parameters of the used solvent and polymer (Hansen and Hildebrand solubility parameters) [30,31]. Hansen Solubility Parameters are useful in prediction of the molecular affinities, solubility and solubility-related phenomena. The idea is based on the concept of “like dissolve like” as each molecule is assigned with three parameters following attractions forces: dispersion forces (δ_D), permanent dipole-permanent dipole forces (δ_P), and hydrogen bonding (δ_H) [32].

The goal of this work is to produce PVB/IF-WS_2 nanocomposite of enhanced mechanical properties, i.e. to reinforce PVB by adding a small quantity of IF-WS_2 nano-particles, and to determine how different kinds of solvents and ultrasonic deagglomeration techniques affect thermo-mechanical behavior of poly(vinyl butyral)/tungsten disulfide nanocomposites, that might find further application in more complex composite systems.

2. Materials and experimental

2.1. Materials

PVB/IF-WS_2 nanocomposites were prepared by the solvent-casting technique: fine-grained white powder PVB (Mowital B60H, Kuraray GMBH) was first dissolved (10 wt%) in different solvents: ethanol (Zorka Pharma, Serbia), 2-propanol (LachNer, Chech Republic), ethyl-acetate (CentroHem, Serbia), n-butanol (BetaHem, Serbia). Inorganic fullerene-like tungsten disulfide nanoparticles (IF-WS_2, NanoLub™ - ApNano Israel) were added into the PVB solutions in 2 different contents: 1 and 2 wt% of IF-WS_2 in PVB. Homogenization and particle deagglomeration were achieved by:

1) stirring (magnetic stirrer),
2) ultrasonic irradiation during 30 min, with pulsations (1 s ON/1 s OFF), at 600 W of power,
3) ultrasonic irradiation during 30 min, without pulsations, at 300 W of power.

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