STUDY OF EFFICIENCY OF HALLOYSITE NANOTUBES DISPERGATION IN POLY(VINYL ACETATE) MATRIX

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Abstract

Nanocomposite system formed by poly(vinyl acetate) (PVAc) matrix and halloysite nanotubes (HNT) filler was prepared in three different ways. The first method was kneading the composite melt in laboratory kneader. The second one was direct emulsion polymerization of vinyl acetate in the presence of HNT. The third method of composite preparation was to disperse HNT in toluene solution of PVAc in planetary ball mill. The filler content was 10 wt. % in all composites. The samples from all three preparation methods were subjected to the observation of nanoparticles dispergation efficiency within the bulk material using SEM. The best level of particles dispersion was achieved using the ball mill. The particles were effectively dispersed, forming the agglomerates in the range from below one micrometer down to single nanotubes.

Keywords: Nanocomposite, halloysite, dispergation, ball mill

1. INTRODUCTION

The usage of nanometric size filler is keeping its supreme position thanks to the specific properties of the output nanocomposite. Nanotubular clay mineral Halloysite (HNT) is composed of aluminosilicate naturally structured in layers. It has significant reinforcing impact on polymer composites. It has large influence to tensile strength of polymer composites even in small contain - less than 7 % [1]. The unique structure of HNT allows its usage as filler for nanocomposites for medical application. For example as a drug deliverer [2] or reinforcing material for tissue replacements with very low cytotoxicity [3].

A sufficient nanofiller dispersion and preparation of nanocomposites remains a large problem till present time. There exist a large number of nanocomposites preparation methods. The simplest method is to disperse nanofiller in polymer melt mechanically, most often using twin screw extruder [4]. The less common way how to disperse filler can be by high energy planetary ball mill. The dispersion of the filler in matrix can be than performed while dry phase [5] or in the polymer solution [6]. Other ways to disperse the particles can be performed by ultrasonication of particles in the polymer solution [7], or radical grafting of the polymer matrix directly to particle surface. It is about the matrix polymerization with the filler directly present [8]. In this paper three methods of nanocomposite preparation will be introduced: To disperse filler in the polymer melt by laboratory kneader, direct polymerization of poly(vinyl acetate) with the HNT present and to disperse the HNT filler in polymer solution using planetary ball mill.

The sample preparation by laboratory kneader introduces a low-volume composite sample preparation by mixing of the matrix and the filler in the melt. It also simulates the most common way of composite production - twin screw extrusion. In the laboratory kneader the particles are dispersed in matrix by shear rate. It is caused by mixing segments affecting the polymer melt directly and nanofiller particles indirectly.

During the vinyl acetate polymerization with presence of HNT, better level of nanofiller dispersion was assumed, than during preparation in the polymer melt. Low molecular vinyl acetate has a better diffusion to nanofiller agglomerates than high molecular PVAc. Moreover, the HNT has a certain amount of hydroxyl groups on its surface which causes it partly more polar. That is why the particles are sufficiently dispersed in the polar solvent - the water.

The HNT filler was to disperse in toluene PVAc solution using the planetary ball mill, considering its high milling efficiency. The particles are dispersed in high viscous polymer matrix solution by the effect of high speed movement of milling segments. At the same time the particles agglomerates are grinded by impaction of the milling segments to the wall of the milling jar and their rolling alongside the milling jar wall. The combination of those effects provides a highly effective mixing method.

2. MATHERIALS AND METHODES

2.1. Used material

Poly(vinyl acetate) Vinnex® 2525, kindly provided by Wacker. Halloysite nanotubes, poly(vinyl alcohol), dodecyl sulfate sodium salt, benzoyl peroxide and ammonium iron(II) sulfate hexahydrate purchased by Sigma Aldrich. Sodium pyrophosphate decahydrate and toluene was obtained from Penta s.r.o.

2.2. Preparation of testing samples

HNT in the amount of 10 wt % was used to prepare all of the PVAc based composites.

The first of testing composite samples had been prepared in melt on laboratory kneader Plasti-Corder BRABENDER with temperature of 140°C and 45 RPM of sigmoid kneading segments. The PVAc had been brought to kneader and plasticized by kneading for 1 minute. Then HNT filler was added and sample had been mixed for 11 minutes. After that the melt had been removed from the kneader and leaved to cool down to the laboratory temperature.

The second sample was prepared by polymerization of vinyl acetate with presence of HNT filler using following procedure: An emulgator containing poly(vinyl alcohol) and dodecyl sulfate sodium salt dispersed in water was prepared in reaction container. The initiator benzoyl peroxide, catalyzer ammonium iron(II) sulfate hexahydrate and the free ion catcher sodium pyrophosphate decahydrate were added to the emulgator under the nitrogen atmosphere. After complete dissolution of all parts, vinyl acetate and HNT filler were added. The mixture had been heated for two hours and stirred intensively, then cooled down. PVAc composite precipitate was done by freezing. Catalyzers and dispersants were separated and removed in the form of a green precipitate. The required white composite was dried in the dry box at 40°C to the constant weight value.

The third composite sample was prepared by milling of PVAc solution with HNT filler in planetary ball mill. Commercial PVAc was dissolved in toluene to get 10 % solution and placed to steel milling jar containing the milling balls together with HNT filler. The milling balls weight was calculated as 10 times the weight of the polymer mass. Two steel milling jars was placed into Retch planetary mill and the milling was repeated in 6 cycles, each for 30 minutes. 20 minutes breaks were set in between the milling cycles to let the milling jars to cool down. At the end of milling process the output composite solution was precipitated to water and filtered. Then it was dried in the drying box to constant weight.

2.3. Scanning electron microscopy

Samples for the scanning electron microscopy were first cryogenically broken under liquid nitrogen to create fracture area. Then they were covered by thin Pt/Pd layer using Chemical Vapor Deposition method in argon atmosphere. For the particle distribution analysis, scanning electron microscope JEOL 7500F with resolution of 1 nm and acceleration voltage of 10 kV was then used.

3. RESULTS AND DISCUSION

Photography **Figure 1** is showing the fracture area of composite sample prepared on laboratory kneader. On picture on the left a large agglomerate of undispersed particles can be seen. Particle agglomerates in range of size of several tens of micrometers was observed on the photographs. A detail view of matrix - halloysite

particles agglomerates interface can be seen on the figure left. Nanotubes on the edges of the agglomerates are relatively well soaked with matrix. This is the indication of sufficient adhesion of untreated HNT to PVAc matrix. The presence of large particle agglomerates is then not caused by low interfacial compatibility in the composite, but by insufficient ability of the kneader to disperse the filler. Still, even individual nanotubes was observed in the sample.

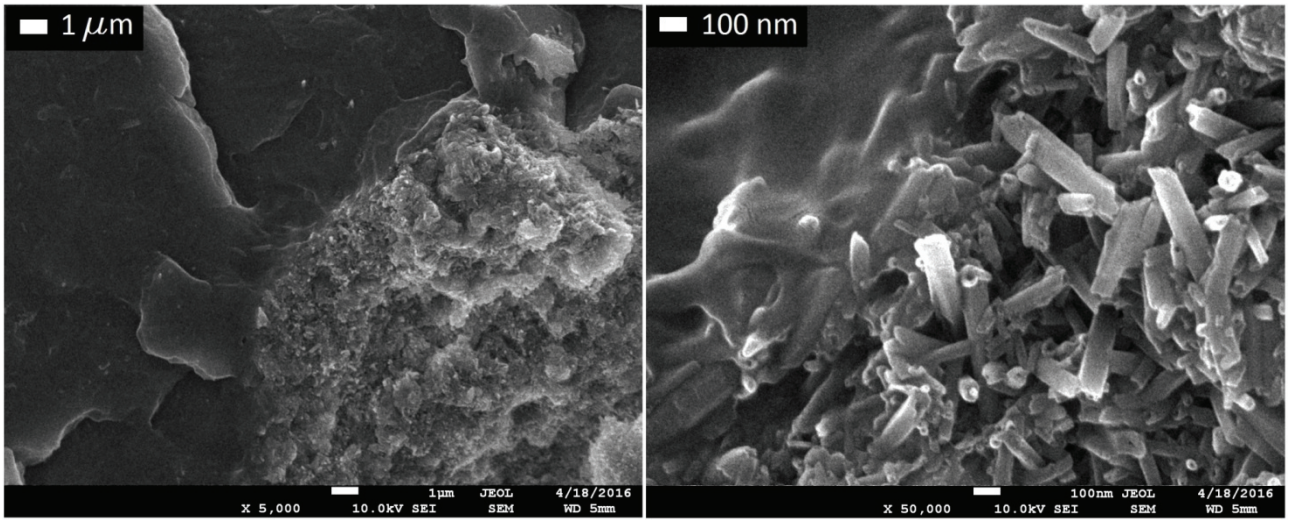

Figure 1 SEM photograph of the PVAc - HNT samples prepared by melt kneading

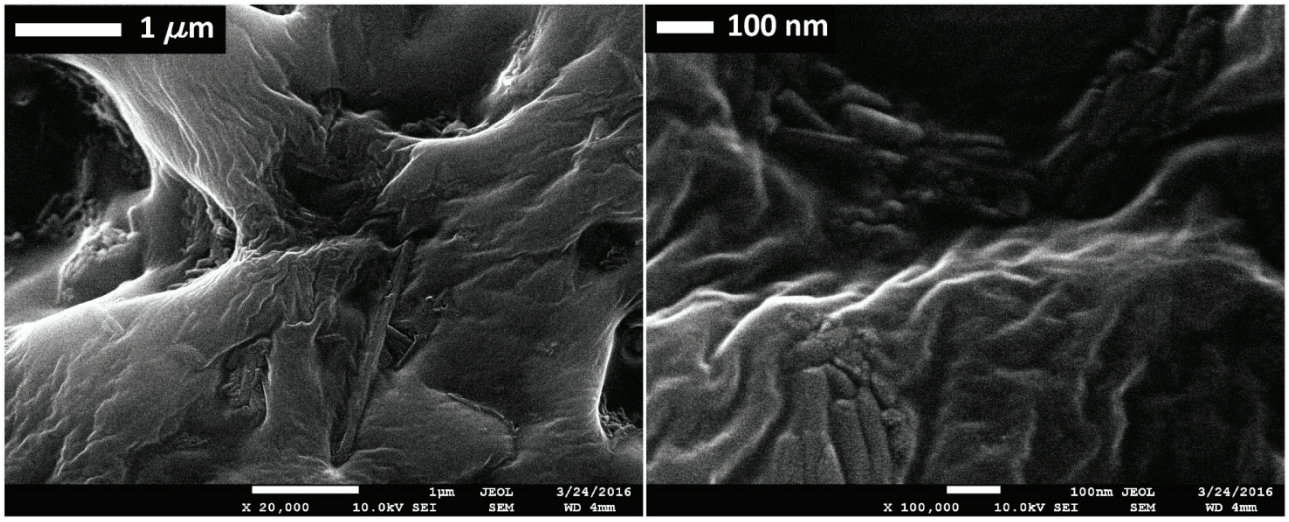

Figure 2 SEM photograph of the PVAc - HNT samples prepared by direct polymerization

The fracture area of composite sample prepared by emulsion polymerization of PVAc with HNT present is displayed on picture **Figure 2**. On a picture on the left sponge structure of the sample can be seen. It is due to the method of preparation. This state of sample makes the nano reinforcement observation more complicated. The particle agglomerate densely covered with PVAc matrix is visible on the upper and the left side of the photograph. A large, vertical needle shaped agglomerate of size of several micrometers can be seen at the picture's front. This indicates a lower compatibility of prepared PVAc matrix to the nanofiller. A detail of HNT and PVAc matrix interface is shown on the picture on the right. The particles of the filler are covered by the matrix but with worst soaking. The interface adhesion is not ideal then. That can be related to good vinyl acetate diffusion to the particle surface in the agglomerate, but with bad wettability of the individual particles by the vinyl acetate solution. That's why the PVAc is then separated from the particle surface during

polymerization process. Incorrectly dispersed agglomerates of nanofiller are also appearing during this composite sample preparation method, even if these agglomerates are significantly smaller than those prepared in the laboratory kneader.

The picture **Figure 3** is showing a surface structure of cryogenically broken composite sample, prepared in planetary ball mill. The SEM analysis did not show significant agglomerate of HNT particles. The largest particles agglomerates found is shown on the picture on the left, where the agglomerates are composed only by a few nanotubes. A detailed view of matrix and nanofiller interface is depicted on the picture on the right. The agglomerate found is well covered with polymer matrix. Processing of composites in the planetary ball mill has no negative impact on interfacial adhesion then.

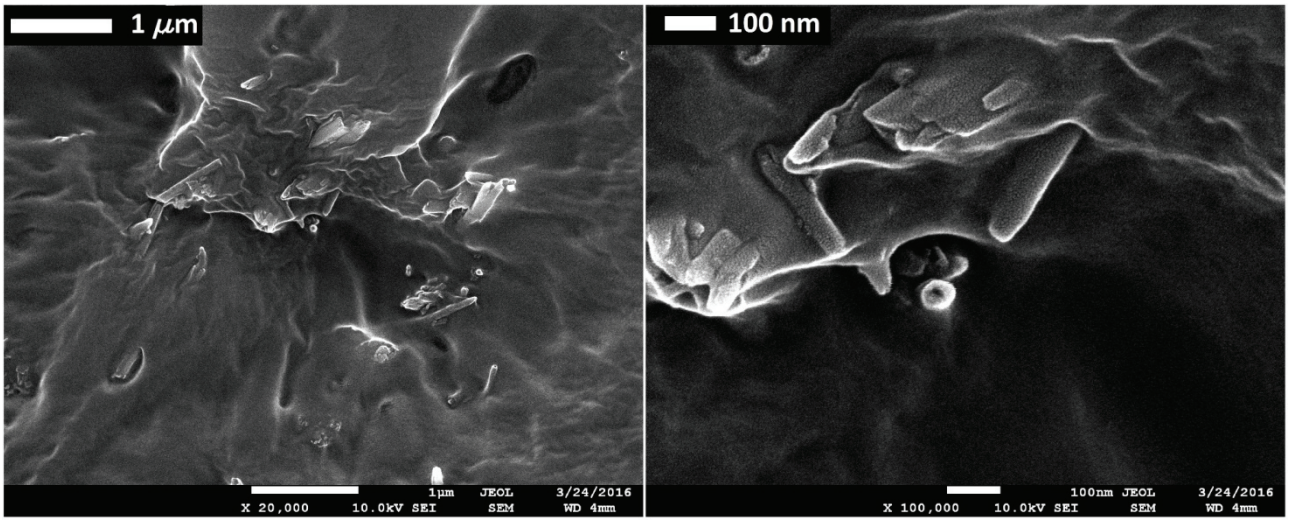

Figure 3 SEM photograph of the PVAc - HNT samples prepared from toluene solution, dispersed by ball mill

4. CONCLUSION

In this paper three methods of nanocomposites preparation were compared and level of particle dispersion in matrix was observed. Composite preparation by kneading in polymer melt is the least time consuming method. Unfortunately, large number of insufficiently dispersed particles is appearing in the composite structure. This method is not very suitable for nanocomposite preparation then.

Composite preparation using direct polymerization with presence of the filler was favorable because of its low demands of laboratory equipment. It was medium time consuming in comparison with other methods. It also produces an average affectivity of dispersion, but the composite structure is strongly porous. In theory good results could be reached by combination of both methods mentioned, meaning directly polymerized composite is then fabricated by extrusion.

Ball mill method of filler dispersion in polymer solution provides the highest level of HNT dispersion compared with previously discussed composites preparation methods. This method allowed dispersing the filler in polymer almost to the level of individual nanotubes. Due to the high time requirement for milling, this method of composite preparation remains highly ineffective.

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