Applied Clay Science 140 (2017) 10–16

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

High energy ball milling for the processing of organo-montmorillonite in bulk

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ARTICLE INFO

Article history:
Received 1 July 2016
Received in revised form 14 January 2017
Accepted 18 January 2017
Available online 1 February 2017

Keywords:
Organo-montmorillonite
Ball milling
Clay polymer nanocomposite
Gas barrier
Defence inflatables

ABSTRACT

The key issue for improving the barrier properties of clay polymer nanocomposite (CPN) is to obtain an effective dispersion and exfoliation of the clay platelets into the polymer matrix. Processing of nanoclay in bulk for industrial application still is a challenge. This paper aims to investigate high energy ball milling as an easy technique to achieve the exfoliation of organo-montmorillonite (OMt). OMt was ball-milled under different conditions and the structural changes have been characterized through XRD patterns, HR-TEM images, SEM images, particle size analysis and FT-IR spectra. A series of polyurethane based nanocomposite coating was prepared using these ball-milled OMt and the functional performances, specifically resistance to helium gas permeability and tearing strength were explored targeting inflatables for defence applications.

1. Introduction

Clay polymer nanocomposite (CPN) is a potential area of nanoengineered materials, providing lighter weight alternatives to conventional filled polymers with value added properties. As compared to neat resin, nanocomposites have been reported to provide enhanced physical properties (Ray and Okamoto, 2003; Joshi and Bhattacharyya, 2011; Hintze-Bruening and Leroux, 2012) and at the same time to impart some special functional properties such as resistance to gas or vapour permeability (Joshi et al., 2006; Morgan, 2012). Having layered structures with large aspect ratio, nanoclays present a torturous path (Joshi et al., 2006; Tiwari et al., 2008; Choudalakis and Gotsis, 2009) for the gas/vapour and thereby retard its rate of passage through the polymer matrix. The improved barrier property is of significance to applications where retention of gases or air is very critical e.g. packaging, inflatables such as balls, tyres etc. and specialty applications like the envelope for aerostats, radomes, floatation systems and other inflatable aerial delivery systems used for defence applications (Joshi et al., 2006; Pal et al., 2011; Morgan, 2012). These kinds of structures are generally made up of high strength woven textiles coated with polymer (generally, polyurethane), where incorporation of nanoclay into the polymer could lead to a significant property enhancement (Chatterjee et al., 2016).

The common practices for successful preparation of CPN are: *chemical route* e.g. by organically modifying the clay mineral layers to make it compatible with polymers or by using a compatibilizer and *physical route* e.g. by using ultrasonicator or homogenizer, high shear mixing using twin screw extruder or by using high energy ball milling etc. (Riess and Schauberger, 2015). However, processing of nanoclay in bulk for industrial application still is a challenge.

Recently, a number of researchers have studied the structural changes of various clay minerals by high energy ball milling. Frost et al. (2001) used a planetary ball mill to grind kaolinite (Kaol) up to 10 h. The XRD patterns showed that ball milling attenuated the basal reflection until its almost disappearance, indicating the delamination of the Kaol particles. The breaking of the hydrogen bonds between adjacent Kaol layers might be the reason behind this. Later, in another study, Frost et al. (2003) reported the effect of ball milling on the intercalation of Kaol with formamide. In this case also, XRD patterns of the ball-milled Kaol showed the decreasing trend in intensity of basal reflection with grinding time. Formamide was subsequently used to intercalate the ball-milled Kaol. XRD diffraction patterns of the intercalated Kaol showed expanded interlayer spaces indicating the intercalation of the formamide molecules. Mani et al. (2003) combined ball milling with ultrasonication to produced nano-sized clay mineral particles of organo-montmorillonite (OMt) with narrow particle size distribution. Prior to sonication, however, no significant increase in the specific surface area was observed which was attributed to the aggregation of the particles. Lee et al. (2007) reported intercalation of various alkylammonium ions using ball milling, with water and kerosene as solvents and this technique was again found to be effective in increasing the basal spacing

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http://dx.doi.org/10.1016/j.clay.2017.01.019
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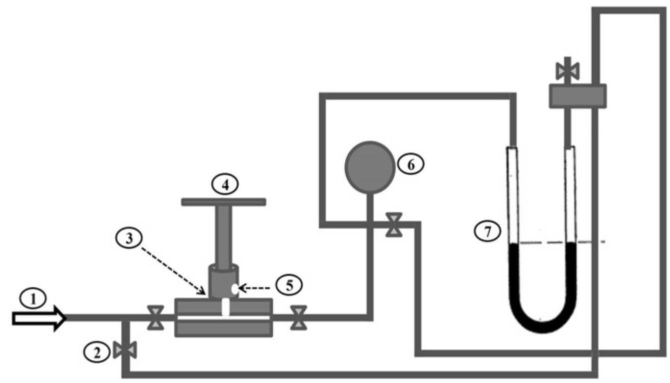

Fig. 1. Schematic of gas permeability tester: (1): helium gas supply, (2): valve, (3): sample to be clamped here, (4): ram, (5): air escape, (6): pressure gauge, (7): manometer.

of montmorillonite (Mt). In the work of Ramadan et al. (2010), the effect of different conditions of ball milling on the structure of Na^+-montmorillonite (Na-Mt) and OMt was investigated. It was observed that ball milling increased the structural disorder by peeling off of layers followed by the exfoliation of the particles as indicated by the disappearance of the basal reflection. Recently, Zhuang et al. (2015) have studied on modification of Ca^{2+} montmorillonite (Ca-Mt) with anionic and nonionic surfactants by using ball milling in a planetary ball mill at 500 rpm, 5 to 1 ball-to-materials, and this technique was also found to be helpful in increasing the basal spacing of the clay mineral layer.

Generally, from the X-ray diffraction (XRD) pattern of the clay it has been established that the decrease in intensity of the basal reflections is indicative of the separation of the clay mineral layers while disappearance of that peak is widely taken as an indication of particle exfoliation (LeBaron et al., 1999; Chen, 2004). Also, TEM imaging of clay minerals has mainly focused to observe the changes of the interlayer space (Lee et al., 2007; Zhou et al., 2008; Ramadan et al., 2010). However, the above mention literatures are mainly found to emphasise on the structural changes of the clay mineral due to different conditions of ball milling. Its direct consequence on the ultimate property in CPN form has hardly been discussed. On the other hand, in the majority of the studies, dealing with CPN systems, mixed intercalated/exfoliated morphology has been obtained (Yao et al., 2002; Kim et al., 2003; Rehab and Salahuddin, 2005; Salahuddin et al., 2010; Barick and Tripathy, 2011). However, an aligned exfoliated structure of CPN is expected to achieve maximum barrier performance.

In this paper high energy ball milling was investigated as an easy technique to achieve maximum exfoliation of OMt (Cloisite 30B) and its effect on resistance to gas permeability, which is the ultimate functional property in CPN coatings form was also explored, targeting defense inflatables. A series of ball-milled clay was prepared under different conditions and the structural changes have been characterized through XRD patterns, HR-TEM images, SEM images, particle size analysis and FT-IR spectra. Several coating formulations of thermoplastic polyurethane (TPU) with untreated and treated OMt were synthesized via solution intercalation route and applied on high strength polyester (PET) fabric as a coating, particularly aiming the inflatable envelope material. The coated fabrics were evaluated for special functional properties such as helium gas permeability and tearing strength. The functional properties of the CPN were finally correlated to the ball milling conditions that affects the exfoliation of the clay mineral layers.

2. Experimental

Powdered OMt (Cloisite 30B) was procured from Southern Clay Products, Inc., USA. The clay material was put into stainless steel jar together with stainless steel balls (10 mm in diameter) keeping ball-to-powder mass ratio of 5 to 1 and were dry-milled in a planetary ball mill (Retsch PM-100, Germany) under milling speeds of 200 rpm and 400 rpm separately. In each case milling was continued until the disappearance of the basal reflection, or for a maximum milling time of 4 h. Samples were coded as “C milling speed- milling time”; e.g. “C 400-2” refers to clay mineral milled at 400 rpm for 2 h.

XRD patterns were collected using Cu Kα in Phillips X'Pert PRO PANalytical diffractometer, operated at 40 kV and 30 mA. XRD patterns were collected for each sample, with particular attention given to the 2θ region of 3° to 10° where the basal reflection occurs. TEM analysis was conducted on Phillips CM12 operated at 100 kV. Pristine as well as selected ball-milled OMt were analyzed. Samples were prepared by sonicating a small amount of clay powder in methanol for 5 min, then placing a drop of the mixture on a TEM Cu grid having a carbon support film. A scanning electron microscope (ZEISS, EVO50) was used to observe the particle morphology. Before examination, the sample surfaces were sputtered with an Au-Pd coating. Particle size of the clay was

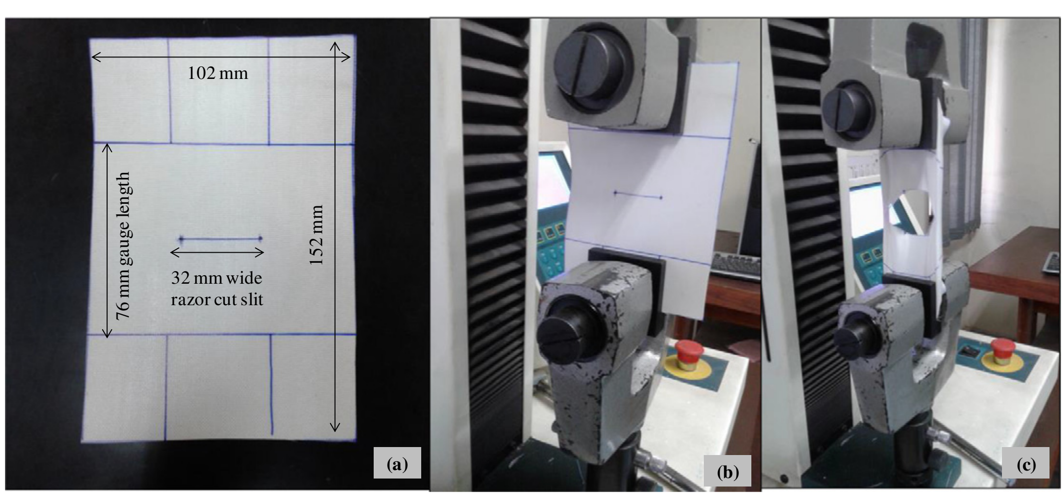

Fig. 2. Tearing strength testing: (a) test specimen, (b) mounting of sample in Instron, (c) tearing of the sample.