Structure Analysis of PVC Nanocomposites

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Summary: In this paper poly(vinyl chloride)/clay nanocomposites were prepared by melt intercalation using a single screw extruder. Problems with thermal stability of these nanocomposites during compounding were largely eliminated by pre-treatment of the organoclay with plasticizer (dioctyl phthalate), which created a barrier between polymer and quaternary amine. These nanocomposite materials were analyzed with respect to their morphology. The intercalation, exfoliation, nano-phase dispersion and orientation were investigated using Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and X-ray diffraction (XRD). Moreover, different types of sample preparation for these techniques were tested as well. It was found that partially intercalated and disordered structure arose in poly (vinyl chloride) composites containing sodium type of montmorillonite, while a fine dispersion of partial to nearly full exfoliation of individual montmorillonite layers in poly (vinyl chloride) matrix was observed when this clay was organically modified. Finally, the influence of different mixing time (in extruder) on nano-phase morphology was surveyed.

Keywords: melt intercalation; montmorillonite; morphology; nanocomposites; poly(vinyl chloride)

Introduction

Clays have long been used as fillers in polymer systems because of their low cost and improved mechanical properties of the resulting polymer composite. However, clay particles could only be dispersed on the micro-scale. In the early 1990's, Toyota researchers discovered that the treatment of montmorillonite clay with amino acids allowed the dispersion of individual 1 nanometre thick silicate layers of the clay on a molecular scale in polyamide-6, which was one of the latest evolutionary steps in polymer technology [1]. Therefore, many recent studies have focused on polymer-layered silicate

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nanocomposites, which can show very large improvements in mechanical, thermal and barrier properties, as well as in dimensional stability and remarkable increase in heat distortion temperature without a significant loss of transparency, toughness or impact strength [2, 3, 4]. The enhancement of these properties mainly depends on the interaction between the polymer matrix and the layered silicates. According to this interaction quality, the different types of nanocomposites ranging from intercalated to exfoliated states may be obtained. Thus, the radical improvement is ascribed to the nano-scale morphology, which means homogeneous dispersion and exfoliation of individual silicate layers in the continuous polymer matrix [5].

A great number of published papers deal with intercalation of monomers or polymers into layered silicate clay as one of the promising strategies for nanocomposites arrangement. In most cases, this synthesis involves either intercalation of a suitable monomer and then exfoliation of the layered silicate clay into individual nano-scale elements by subsequent polymerization or polymer intercalation from a solution. However, for majority of commodity polymers, both approaches are limited since neither a suitable monomer nor a compatible solvent is always available [5, 6]. Therefore, polymer-melt direct intercalation method can be a new approach to fabrication of polymer-layered silicate nanocomposites by using a conventional polymer extrusion process. In this particular case, the formation of nanocomposites depends upon the thermodynamic interaction between the polymer chains and the host silicate surfaces, and also upon the transport of the polymer chains from the bulk melt into the layered silicate clay. It was found that the result of polymer intercalation is determined by the interplay of entropic and enthalpic factors [5]. In fact, although the motion reduction of polymer chains inside the interlayer of silicate clay mineral results in a decrease in the overall entropy of macromolecular chains, this entropic decrement may be compensated by an increase in conformational entropic freedom of the tethered alkyl surfactant chains, which separate the silicate layers of clay. Since small increases in the basal spacing of layered silicate do not strongly influence the total entropic change, intercalation will rather be driven by the changes in the total enthalpy. Therefore, the driving force of this mechanism is the enthalpic contribution of interactions between polymer and organically modified clay [6, 7].

The literature contains numerous studies about melt intercalation method for nanocomposites preparation where polyamide, polystyrene, polypropylene, polyethylene and epoxy resin are mainly used as polymer matrix [8]. Only recently, polyvinylchloride nanocomposites have been prepared by polymer melt intercalation. However, few publications about PVC containing montmorillonite as a layered silicate clay have been advertised so far, despite the fact that polyvinylchloride is an important commercial polymer owing to its wide applications and low cost [9, 10, 11, 12, 13]. Wang et al. [11] primarily studied the influence of plasticizer (in this case dioctyl phthalate) and clay amount on thermal and mechanical properties of the nanocomposites. Their work contained several kinds of intercalated PVC nanocomposites. On the other hand, they were not interested in morphology, because XRD was the only method for observing the structure of their PVC nanocomposites. Wang et al. [12] mainly investigated the effect of silicate clay modification and its content on the relaxation behaviour, mechanical properties and morphology. In this publication XRD and TEM were two methods used for PVC nanocomposite structure observation.

None of the publications about PVC nanocomposites include techniques such as Scanning Electron Microscopy and Atomic Force Microscopy. However, these techniques are very important to characterize the resulting nanocomposites morphology and a lot of researchers use them together with TEM and XRD to confirm nanocomposites structure. Therefore, the aim of the present paper is to give information about the morphology of PVC nanocomposites using four basic methods: TEM, SEM, AFM and XRD. Two types of PVC/MMT nanocomposites were prepared by polymer melt intercalation with sodium type of montmorillonite and organically modified montmorillonite, in which dioctyl phthalate was applied as a plasticizer. In addition, the influence of two different retention times (single and double pass compounding) in extruder on PVC nanocomposites morphology is discussed.

Experimental

Materials

Two types of smectic clay, namely Cloisite Na+ and Cloisite 30B, from Southern Clay Products, USA were used in this study. The first one is sodium montmorillonite without any surface treatment, the second one is a commercial product modified by methyl tallow bis-2-hydroxyethyl ammonium chloride at a loading of 90 milliequivalent per 100 grams of neat clay to form the lamellar clay/tallow core layered structure. As a polymer matrix the suspension type of polyvinylchloride (PVC) Neralit 652 (K-value 65) supplied by Spolana Neratovice, Czech Republic, was utilized. Dioctyl phthalate (DOP) was used as a

PVC plasticizer. All samples were stabilized with 2 wt. % of Lankromark LZB 968, which is quite often industrially used in the field of flexible PVC flooring. The main characteristics of the PVC composition used in this study are listed in Table 1.

Table 1. Main characteristics of the PVC compound.

Component	*Commercial name*	*Concentration*
Polyvinylchloride	Neralit 652 (K-value 65)	74 wt. %
Plasticizer	Dioctyl phthalate (DOP)	24 wt. %
Stabilizer	Lankromark LZB 968	2 wt. %

Sample preparation

First co-intercalation of Cloisite Na+ and Cloisite 30B by dioctyl phthalate was carried out at the temperature of 80 °C in a laboratory mixer for 30 minutes. In the next step PVC blend containing plasticizer, stabilizer and also modified layered silicate (5 wt. %) was mechanically mixed and thereafter compounded in Buss KO-kneader MKS 30 single screw extruder. The polymer melt intercalation method was used as a promising new approach to fabricate PVC nanocomposites using polymer processing technique. The amount of nanofiller was calculated to be 5 wt. % of pure sodium montmorillonite (inorganic material) in the whole mixture. Therefore, the amount of Cloisite 30B was recalculated with respect to the amount of organic modificator. The operating temperature was from 130 to 160 °C and the screw speed 35 rpm. The conditions of mixing were same for all samples. The effect of different retention time of compounding on the morphology was investigated as well. Therefore, all compounds (PVC + nanofiller + plasticizer+ stabilizer) were compounded twice (double-pass compounding) in single screw extruder.

Characterization and Testing

The nano-phase orientation, dispersion, intercalation and exfoliation of both clays in PVC matrix were observed through four main microscopic techniques.

The degree of exfoliation and intercalation was studied using reflection mode on URD-6 Diffractometer with CuKα_1 radiation (λ = 1.54 Å). This method was used not only for PVC nanocomposites, but also for the powder form of both nanofillers.

For transmission electron microscopy (TEM, Phillips CM120) the specimens were prepared by cutting on a cryoultramicrotome equipped with a diamond knife. The cutting temperature was not same for every sample, but it was set during cutting with respect to the sample behavior, and ranged from -30°C to -5°C.

For scanning electron microscopy (SEM, JEOL JSM-35) the samples were prepared through two different techniques. In the fist one the samples were placed in liquid nitrogen and freeze-fractured, the second samples were cut at room temperature on an ultramicrotome and then plasma-etched using oxygen plasma. Plasma-etching device with the power of 10W at the frequency of 13.56 MHz was used.

The sample preparation for Atomic Force Microscopy (EXPLORER^{TM}, THERMOMICROSCOPES) was the same as the second method of SEM sample preparation using oxygen plasma etching. Plasma treatment is selective, because mineral particles of montmorillonite are inactive to the etching process, while PVC is very easily burned off.

Results and Discussion

Figure 1 shows the maxima of two nanofillers, Cloisite Na^+ (nature sodium type of montmorillonite) and Cloisite 30B (intercalated sodium type of montmorillonite). As can be seen, the former exhibits its characteristic diffraction peak at approximately 7.8°, which corresponds to basal spacing of 1.2 nm. The latter indicates its peak at 4.83°, which is equivalent to the basal spacing of 1.85 nm. This higher basal spacing compared with the value of Cloisite Na^+ is caused by intercalation of organic compound into interlayer spaces of montmorillonite.

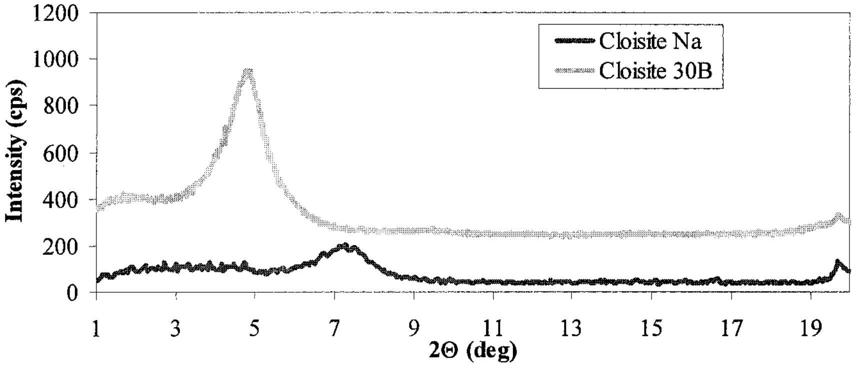

Figure 1. XRD patterns of Cloisite Na^+ and Cloisite 30B.

Our preliminary technological testing demonstrated that the polymer stability is greatly influenced by the used type of nanofiller, especially the type of organic compound utilized as an intercalating agent. Our idea was to cover the quaternary amine groups with plasticizer and therefore prevent a contact between these amine groups and active chlorine atoms. In the case of Cloisite 30B the quaternary amine groups can be the source of degradation process. Therefore, in the first step we co-intercalated the plasticizer (dioctyl phthalate) into organically modified Cloisite 30B. Gradually, these silicate nanofillers (Cloisite Na^+ and plasticizer-modified Cloisite 30B) were dispersed in polyvinylchloride matrix.

As can be seen from Figure 2, which shows XRD patterns of PVC composites containing Cloisite Na^+, there is a shift of peaks maximum towards the lower 2Θ value in the case of longer retention time. It means that the larger basal spacing (silicate layer plus interlayer space) corresponding to the lower value of the peaks maximum can be induced by the longer time of mixing in Buss KO-kneader. It can support the transport of polymer chains from the bulk melt into the interlayer space of layered silicates. On the other hand, PVC composites with Cloisite Na^+ did not show remarkable changes in the peaks maxima compared with the data of pure Cloisite Na^+ powder in Figure 1. It signifies that a structure containing agglomerates of the nanoparticles was obtained.

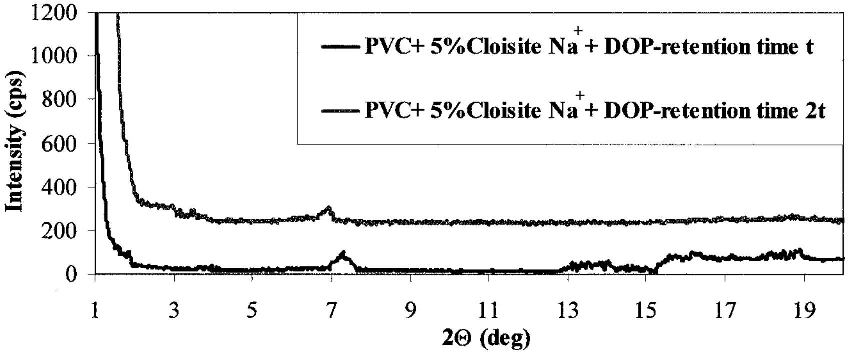

Figure 2. XRD scans of PVC/Na+ MMT composites with different time of mixing in Buss KO-kneader.

In order to get a more precise interpretation, the morphology of PVC/clay nanocomposites was also examined by TEM technique. Figures 3 and 4 illustrate the structure of these samples. The dispersion of clay particles (Na^+ MMT) in PVC matrix has resulted in the formation of clay tactoides with the layers aggregated in an unintercalated face-face form. The longer retention time has caused better dispersion of clay tactoides in PVC matrix. However, it does not significantly effect the intercalation and exfoliation of the clay particles.

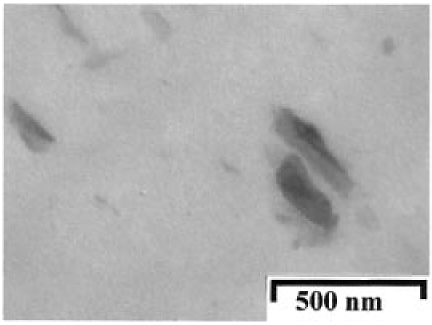

Figure 3. TEM micrograph of intercalated PVC/Na^+ MMT nanocomposite (retention time t).

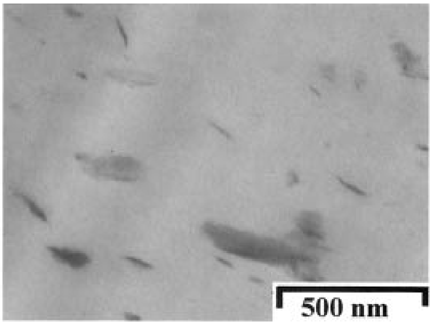

Figure 4. TEM micrograph of intercalated PVC/Na+ MMT nanocomposite (retention time 2t).

As revealed the Figure 5, the peaks maxima of PVC + Cloisite 30B + DOP are almost the same for two samples containing Cloisite 30B. They show two characteristic peaks at 2Θ values of 2.1 and 4.64°, corresponding to basal spacing of 4.3 and 1.9 nm, respectively. As can be seen from a comparison of the peaks maxima for Cloisite 30B in Figure 1 (powder form of Cloisite 30B) and 5 (PVC composites containing Cloisite 30B), there are new peaks corresponding to higher basal spacing in the case of Cloisite 30B dispersed in PVC matrix. The finite expansion of gallery height (basal spacing) is probably associated with the intercalation of organic compound and also polymer chains into clay interlayer since the larger distance of montmorillonite layers obviously demonstrates the advantage of the intercalation or co-intercalation process, the better dispersion of clay in polymer matrix or the higher level of exfoliation.

This interpretation can be evidenced by TEM technique in Figures 6 and 7. Individual clay platelets are clearly visible. These two pictures demonstrate that many silicate layers are exfoliated into nanometer layers. It is very probable that the longer time of mixing in Buss KO-kneader causes regular dispersion and orientation of the nanoparticles in the PVC matrix via melt-intercalation process.

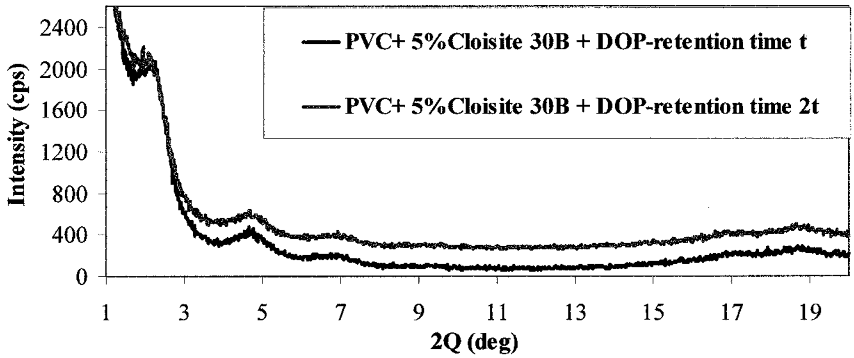

Figure 5. XRD scans of PVC/Cloisite 30B nanocomposites with different time of mixing in Buss KO-kneader.

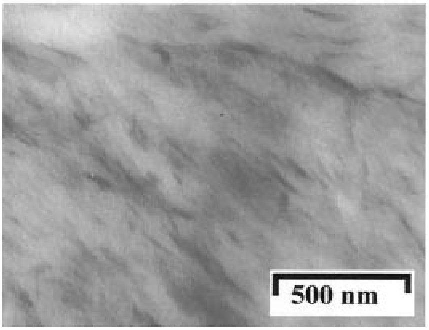

Figure 6. TEM micrograph of PVC/Cloisite 30B nanocomposite (retention time t).

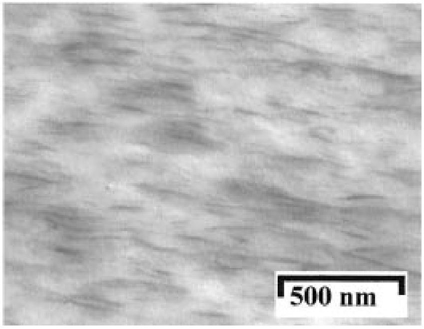

Figure 7. TEM micrograph of PVC/Cloisite 30B nanocomposite (retention time 2t).

Figures 8 and 9 show PVC/Cloisite 30B nanocomposite (retention time t) obtained by scanning electron microscopy for comparison with transmission electron microscopy. They differ in the method of sample preparation. In the first case the common technique was used, where the sample was placed in liquid nitrogen and then freeze fractured. The second sample, however, was cut using an ultramicrotome at room temperature and then plasma-etched using oxygen. The sample prepared only by cutting (on ultramicrotome) was not suitable for SEM, because individual clay particles were not distinguished from polymer (PVC) matrix. The results given in both figures support the idea that very good dispersion and intercalation of clay particles in PVC matrix was received. The silicate layers are better visible in Figure 9, where polymer matrix was burned due to the oxygen plasma. On the other hand, there might have been a lot of other structures or artefacts, in other words significant morphological changes, caused by burning away the polymer.

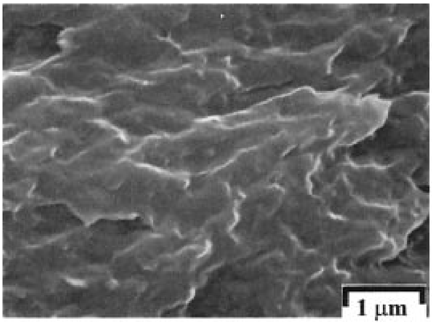

Figure 8. SEM micrograph of PVC/Cloisite 30B nanocomposite – retention time t (the samples were placed in liquid nitrogen and freeze-fractured).

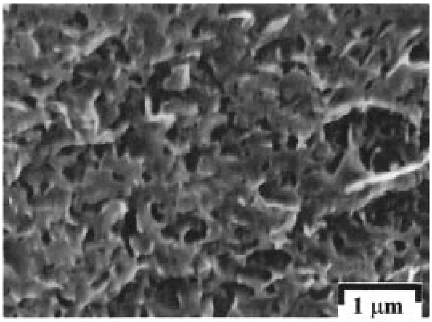

Figure 9. SEM micrograph of PVC/Cloisite 30B nanocomposite – retention time t (the sample was cut on an ultramicrotome and then plasma etched).

Scanning Electron Microscopy in Transmission Mode can provide very similar micrograph compared with TEM technique; this is shown in Figure 10 of PVC/Cloisite 30B nanocomposite (retention time 2t) prepared by cutting on an ultramicrotome at room temperature. There is a slight possibility that in the case of cutting at room temperature larger-scale deformation of thin clay particles originated compared with cutting at low temperature (freeze cutting). However, this room temperature cutting is easier and cheaper. Figure 11 shows AFM micrograph of PVC/Cloisite 30B nanocomposite (retention time 2t) obtained in the non-contact mode. The lack of detectability between individual clay particles and polymer matrix in the case of using only cutting at room temperature resulted in utilizing oxygen plasma etching. So, sample preparation was the same as the second sample for SEM.

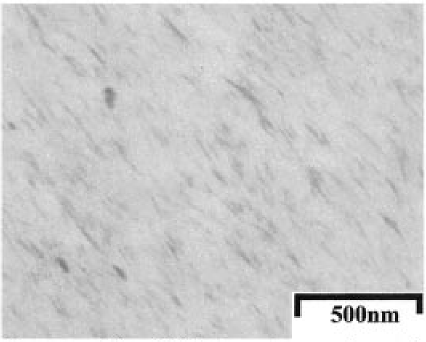

Figure 10. STEM micrograph of PVC/Cloisite 30B nanocomposite – retention time 2t (the sample was cut on an ultramicrotome).

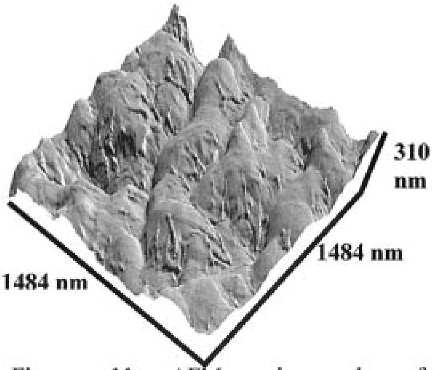

Figure 11. AFM micrograph of PVC/Cloisite 30B nanocomposite (the sample was cut on an ultramicrotome and then plasma-etched).

Conclusions

The objective of this study was to compare different types of methods to explore morphology of PVC nanocomposites. TEM, SEM, AFM and X-ray diffraction were the basic methods used. Partially intercalated and disordered PVC nanocomposites were obtained by melt compounding of PVC with sodium type of montmorillonite (Cloisite Na^+) in the presence of DOP. However, the same process resulted in intercalated and partially exfoliated structures of PVC nanocomposites with organically modified montmorillonite (Cloisite 30B). It was found that the longer retention time (time of sample mixing) in Buss KO-kneader can induce the better dispersion and orientation of silicate nanoparticles in PVC matrix. On the other hand, it is highly improbable that the longer time of compounding noticeably affects the exfoliation process without previous intercalation of montmorillonite. It should be noted that this study has examined only morphology of PVC nanocomposites. Hence, further detailed studies on the determination of mechanical, thermal and rheological properties of PVC nanocomposites were done and will be published in our next article. Unfortunately, we are unable to say if the sample preparation in each microscopic method can be suitable for other polymers to obtain good results (clear micrograph).

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