POLYMER/CLAY NANOCOMPOSITES: INTERCALATES BASED ON DIOLS

Alena KALENDOVÁ[a], Lucie KOVÁŘOVÁ [a]

[a] *Department of Polymer Engineering, Faculty of Technology, Tomas Bata University in Zlín, Nám. TGM 275, 762 72 Zlín, Czech Republic, E-mail: kalendova@ft.utb.cz*

Abstract

This work discusses the problem of intercalates preparation and their suitability for polymer/clay nanocomposites. The most common intercalating agents and polymers are shown. Two types of montmorillonite modification with polyethylene glycol and with ethylene glycol-diacetate including the XRD patterns are demonstrated in this study. The influence of concentration and temperature to the intercalation process was studied. From the XRD analysis resulted that both of the intercalants show successful intercalation and they can be used into polymer/clay nanocomposites.

1. INTRODUCTION

Polymer nanocomposites are broadly studied throughout the world till now. One of the most investigated fillers, as a source of nanofillers, is montmorillonite (MMT). It is a layered silicate with natural nanometer structure[1] and it becomes to the phylosilicates. This clay has sandwich-type structure with one octahedral Al sheet and two tetrahedral Si sheets. There are many types of phylosilicates, including kaolinite, montmorillonite (MMT), hectorite, saponite, and mica.[2]

The dispersion of the multilayer silicate particles into discrete monolayers is hindered by the incompatibility between hydrophilic layered silicate and polymers. Therefore, the surface of the inorganic components is organically modified before the inorganic/polymer nanocomposite are prepared to enhance the compatibility between the inorganic and organic phases.

One of the ways of modifying the galleries of the layered silicates to make the silicates more organophilic is cation exchange method. It is based on the MMT ability to sorb some types of cations and to keep them in the change state.[3, 4] The next suitable method is an ion-dipole modification of clay galleries. That one is based on ion-dipole interaction of organic intercalant and interlayer cation.

In summary, the organic modification of the inorganic components is the most important process before polymer/clay nanocomposites are prepared. Therefore this work focuses on the intercalation process especially to the influence of intercalant concentration and temperature of intercalate preparation.

2. EXPERIMENTAL

Unmodified montmorillonite, Na^+ MMT, with a cationic exchange capacity of 92.6 meq/100 g, was obtained from Southern Clay Products. The intercalation process was based on ion-dipole method. Polyethylene glycol 6000 (PEG) and ethylene glycol-diacetate (EGDAC) were chosen to play the role of intercalant. The organic matters based on glycol were selected due to the fact, that PEG is polymer plasticizer. The powder diffraction data of investigated intercalates were collected in 2□ range using the RTG HZG 4 powder diffractometer in reflection mode.

2.1 Intercalates preparation

All intercalates were prepared in Thermomix by 2 000 rpm. The conditions of preparation are given in the Table 1.

Tab.1 Intercalates preparation conditions

Sample	$w_1:w_2$ (g/g)	$T_{intercalation}$ (°C)	t (hour)	**Sample**	$w_1:w_2$ (g/g)	$T_{intercalation}$ (°C)	t (hour)
Na^+ MMT	-	-	-	Na^+ MMT	-	-	-
PEG1	1:0,3	80	24	EGDAC1	1:0,3	80	24
PEG2	1:0,5	80	24	EGDAC2	1:0,5	80	24
PEG3a	1:1	25	192	EGDAC3a	1:1	25	192
PEG3b	1:1	80	24	EGDAC3b	1:1	80	24
PEG3c	1:1	150	6	EGDAC3c	1:1	150	6
PEG4	1:1,5	80	24	EGDAC4	1:1,5	80	24
PEG5	1:3	80	24	EGDAC5	1:3	80	24

w_1 – Na^+ MMT weight, w_2 – intercalant weight

The intercalation process was proceed for 4 days by room temperature and then heated.

3. RESULTS

3.1 Review of intercalants

The first compatibilizing agents used in the synthesis of nanocomposites (polyamide 6-clay hybrids) were amino acids.[5] Numerous other kinds of compatibilizing agents have been used in the synthesis of nanocomposites today´s. The overview of the most popular is given below.

Alkylammonium ions are one of the most famous because they can be exchanged easily with the ions situated between the clay layers. The most used alkylammonium ions are according to Okamoto: dimethyl dioctadecyl ammonium cation (Ditallow), Benzyl dimethyl octadecyl ammonium cation (BMC), Bis(2-hydroxy-ethyl) octadecyl amonium cation (HET), Dimethyl, 2-ethyl hexyl octadecyl ammonium cation (MHTL).[6]

Next intercalant group is presented with neutral polar molecules such as octadecylamine, dodecylamine [7, 8], octadecylamine [8, 9], dioctylphthalate [10], etc. Neutral molecules are used especially in ion-dipole intercalation process. Silanes have been also used because of their ability to react with the hydroxyl groups situated at the surface and at the edges of the clay layers.[11] In the literature the substances as hexadecyl- and cetyl-pyridinium cation [12, 13], rhodamine B [14] appears as well.

3.2 Concentration and temperature influence on the intercalate structure

This study is focussed on the influence of intercalant concentration and temperature. Therefore intercalates based on PEG and EGDAC with different weight ration were prepared. The XRD diffraction was used to find out the d-spacing changes. The value of d was recalculated in accordance with the Bragg equation. The results are shown in Table 2.

Tab.2 XRD study: interlayer distance d

Sample	**w_1:w_2** g/g)	**d** (nm)	**Change to Na^+MMT** (%)	**Sample**	**w_1:w_2** g/g)	**d** (nm)	**Change to Na^+MMT** (%)
Na^+ MMT	-	**1,2**	**-**	Na^+ MMT	-	**1,2**	**-**
PEG1	1:0,3	**1,7**	41,7	EGDAC1	1:0,3	**1,4**	16,7
PEG2	1:0,5	**1,7**	41,7	EGDAC2	1:0,5	**1,4**	16,7
PEG3a	1:1	**1,7**	41,7	EGDAC3a	1:1	**1,5**	25,0
PEG3b	1:1	**1,7**	41,7	EGDAC3b	1:1	**1,4**	16,7
PEG3c	1:1	**1,7**	41,7	EGDAC3c	1:1	**1,3**	8,3
PEG4	1:1,5	**1,7**	41,7	EGDAC4	1:1,5	**1,4**	16,7
PEG5	1:3	**1,7**	41,7	EGDAC5	1:3	**1,5**	25,0

It can be seen that Na^+ MMT was intercalated by both of the intercalants. The better results gives PEG (d = 1.7 nm). The temperature and concentration do not influence the PEG intercalates. This fact confirms the assumption of prof. Loyense, that temperature does not influence the intercalation process at room temperature in inert atmosphere.[15] It should be point out that prof. Loyense hypothesis hold true only for some substances as resulted from the EGDAC intercalates. It can be also said that the oxidative environment does not play important role in case of PEG intercalates.

The d-spacing is stepwise changed with the growing concentration of EGDAC intercalant. The change was marked at the weight ratio 1:3 (increase from 1.4 to 1.5 nm). The temperature influences the d-spacing as show the tab. 2. The best results was obtained for intercalate prepared at 25 °C and with increasing temperature the interlayer distance decreased.

4. CONCLUSION

One of the most important factors in the process of polymer/clay nanocomposites preparation is modification of clay with suitable compatibilizer. Both of the intercalants, PEG and EGDAC, intercalate the sodium type of MMT. The temperature influenced the process of intercalation only in case of EGDAC. Larger distance was observed for PEG intercalates. Next the influence of time to the d-spacing of Na^+ MMT will be tested

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