

EFFECT OF THE CLAY MODIFICATION ON THE THERMAL PROPERTIES OF PVC

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Abstract. The intercalation of organic compound is necessary to functionalize the montmorillonite surface. So, the intercalation of diethylene glycol and polyethylene glycol and the influence of plasticizer, namely tricresyl phosphate and isodecyldiphenyl phosphate as co-intercalating agents were studied. For the PVC/clay nanocomposites the suspension type of PVC was used and the compound was prepared by the melt intercalation method. Two kinds of MMT (Cloisite®Na⁺, Cloisite®30B) and laboratory modified MMT by intercalation (diethylene glycol, polyethylene glycol) and co-intercalation (tricresyl phosphate and isodecildiphenyl phosphate) agents were used for the set of nanocomposite samples. The thermal stability of nanocomposite specimens was tested using of thermo gravimetric analysis, DMA and pH method.

Keywords: PVC, montmorillonite, thermal stability

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INTRODUCTION

Polymer composites belong to the most dynamically development materials in the 21st century. Because, these materials are able to offered many advantages and due to the optimal ration of polymer and filler could bring materials whose have exactly corresponding properties of the specific PVC product.

Polyvinyl chloride (PVC) is one of the most widespread thermoplastic materials in the world owing to its valuable properties, wide applications, high chemical resistance, barrier properties and low cost [1,2]. On the other hand, thermal stability and processibility of PVC is inferior compared with common polymers, for example polyethylene, polypropylene, polyamide. The poorer thermal stability is close-knit with the manufacturing properties and reduction of usage time of the products. Therefore, it is necessary to search PVC with a good thermal stability [3,4].

Preparing PVC/clay nanocomposites can be one of the effective ways to improve PVC final properties. For the preparation of polymer/clay nanocomposites, modification of layered silicate is very important factor due to achievement of polymer/clay exfoliated structure. During modification of the clay the metal ions on basal surfaces of the layered clay must be exchanged to organic cations that change polarity of the gallery environment and the forces between platelets are decreased and hence the compatibility of polymer-clay is improved [5,6,7]. Melt intercalation is the most widely used method for preparation of nanocomposite materials, but this process requires high temperatures. If this temperature is higher than the thermal stability of the applied organic agent, the decomposition of this agent occurs [7-10].

In this paper, the effect of modification of MMT on the thermal stability of PVC/MMT nanocomposites is investigated. Two kinds of MMT were used and for the modification of MMT, various kinds of intercalation and co-intercalation agents were applied. Then, thermal stability was measured.

EXPERIMENTAL

Materials

In this work, suspension polyvinyl chloride (Neralit 652) was supplied by Spolana a.s., Czech Republic. Two different types of montmorillonite (MMT) were obtained from Southern Clay Products, Inc. Texas USA: natural unmodified MMT Cloisite Na⁺, which has cation exchange capacity of 92.6 mequiv./100g, and MMT organically modified by alkyl quaternary ammonium salt Cloisite 30B, which has cation exchange capacity of 90 mequiv./100g. Finally, intercalation agents (diethylene glycol (DEG) and polyethylene glycol (PEG)), and co-

intercalation agents (tricresyl phosphate (TCP) and isodecyl diphenyl phosphate (IDDP)) were utilized as modifiers of montmorillonite.

The first aim of this research was to prepare modified fillers from two types of MMT: MMT Cloisite Na⁺ and Cloisite 30B. The ion–dipole method was employed for the modification of nanofillers by intercalation and co-intercalation agents at 85 °C in laboratory mixer.

Nanocomposite materials were prepared by mixing montmorillonite with suspension type of PVC on Buss KO-kneader MKS 30. The operating temperature ranged from 130 to 150 °C and the screw speed was 70 rpm.

Methods

pH method was used for determination of the tendency of PVC compounds to evolving hydrogen chloride and any other acidic products. A sample in a test tube was heated in nitrogen atmosphere at 200°C until a predetermined change in the pH of absorbing solution was obtained, required for a certain amount of hydrogen chloride. Times required for pH change to 3.8 were measured and named the stability times.

Dynamic mechanical analysis (DMA) of unfilled PVC and PVC/clay nanocomposite samples was carried out in tensile mode at 30 °C, a constant frequency of 1 Hz and force amplitude of 1N.

Thermo gravimetric analysis (TGA) was carried out using TGAQ500 analyser. The mass loss vs. temperature was measured at a heating rate of 20 °C/min in inert atmosphere from laboratory temperature to 600°C.

Result and discussion

For the determination of tendency of unfilled PVC and nanocomposite samples to evolve hydrogen chloride and any other acid product at 200 °C, pH method was used. The results of the stability tests of the nanocomposite materials are specified in Table 1. As can be seen, the PVC without clay possesses the longest stability time from all PVC samples (65 min). On the other hand, all of the laboratory intercalated nanocomposite samples had longer stability times (37 – 49 min) than PVC filled by the commercially intercalated MMT (Cloisite 30B) (23 min). When PVC samples filled by MMT modified by DEG or PEG were compared, the PVC/MMT/DEG had about 59 % higher stability time than PVC/MMT/PEG. If the half amount of intercalation agent was replaced by co-intercalation agents (TCP, IDDP), extremely rise of the stability occurred. PVC/MMT intercalated by PEG and co-intercalated by TCP or IDDP had about 57 % higher stability time (49 and 48 min) in comparison with PVC/MMT intercalated only by PEG (26 min), in particular. It could be said that the phosphate co-intercalation agents could be suitable for improving thermal stability of PVC/clay nanocomposites.

TABLE 1. Stability times of PVC measured by pH method

Samples	Time to degradation (min)	Temperature(°C)	Ratio*
PVC	65	200	-
PVC+Na ⁺	37	200	1 : 0.5
PVC+Na ⁺ +DEG	44	200	1 : 0.25 : 0.25
PVC+Na ⁺ +DEG+TCP	46	200	1 : 0.25 : 0.25
PVC+Na ⁺ +DEG+IDDP	47	200	1 : 0.25 : 0.25
PVC+Na ⁺ +PEG	26	200	1 : 0.25 : 0.25
PVC+Na ⁺ +PEG+TCP	49	200	1 : 0.25 : 0.25
PVC+Na ⁺ +PEG+IDDP	48	200	1 : 0.25 : 0.25
PVC+30B	23	200	1 : 0.5
PVC+30B+TCP	31	200	1 : 0.25 : 0.25

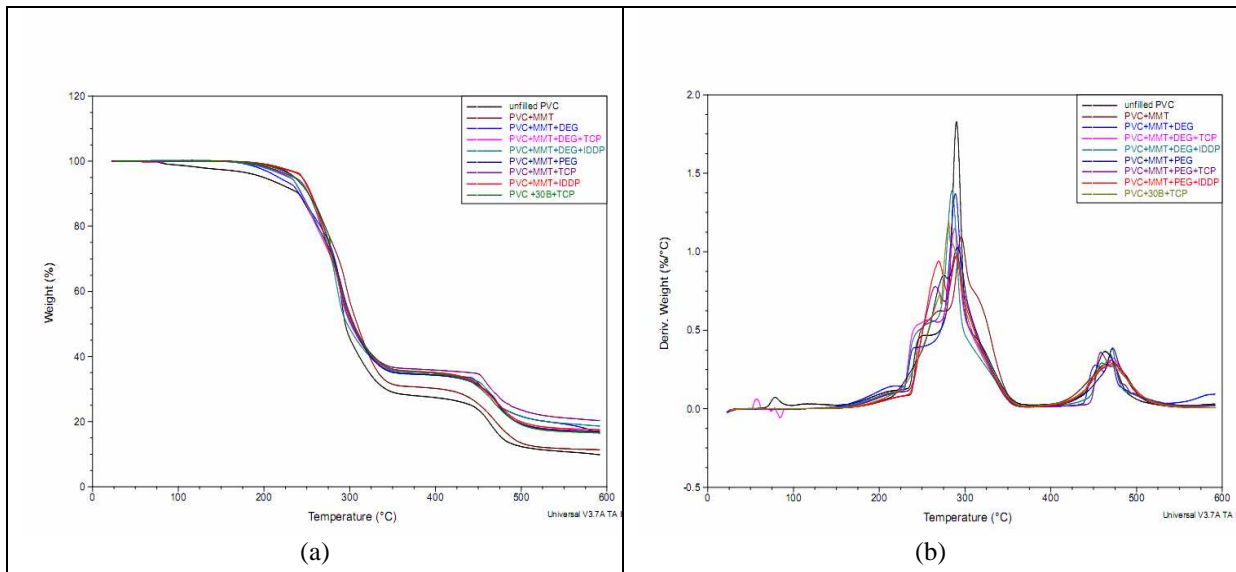
* It means ratio among nanofiller, intercalation and co-intercalation agents, respectively.

The next part of the study investigated the polymer-filler interaction using DMA. Table 2 illustrates the modulus obtained by DMA analysis of un-filled PVC and PVC/MMT nanocomposite samples at 30 °C. It was found that the storage and loss moduli increased about 22 % when a small amount of MMT was introduced to PVC. Furthermore, it could be concluded that PVC samples filled by MMT modified by intercalation and co-intercalation agents exhibit improvement of moduli. This increase may be attributed to the better dispersion of MMT in PVC matrix and storage interaction between MMT and PVC.

TABLE 2. The results of DMA analysis at 30 °C

Samples	Storage modulus (MPa)	Loss modulus (MPa)
PVC	169	68
PVC+Na ⁺	229	87
PVC+Na ⁺ +DEG	279	94
PVC+Na ⁺ +DEG+TCP	309	104
PVC+Na ⁺ +DEG+IDDP	320	108
PVC+Na ⁺ +PEG	311	103
PVC+Na ⁺ +PEG+TCP	353	111
PVC+Na ⁺ +PEG+IDDP	379	114
PVC+30B	451	132

Figure 1a and 1b represent thermo gravimetric (TG) and differential thermo gravimetric (DTG) curves of unmodified PVC and PVC/clay nanocomposites, and the corresponding data are summarized in Table 3. The curves reveal two degradation steps of un-filled PVC and PVC/MMT nanocomposite samples. The first step can be attributed to dehydrochlorination of PVC, and the second step corresponds with condensation and fragmentation phases. For each degradation steps, the weight lost onset temperature (T_{onset}), which indicated 20 wt. % mass loss, and the temperature of the maximum mass loss (T_{max}) were characterised. Generally, T_{onset} of the first thermal degradation step decreased for all nanocomposites. However, T_{max} of the first thermal degradation step slightly increased when PVC was filled by unmodified MMT. PVC/MMT modified by PEG and TCP or IDDP had comparable T_{max} with un-filled PVC. Furthermore, T_{onset} of the second degradation step was also reduced for almost all nanocomposite specimens compared to unfilled PVC. Though, PVC filled by MMT modified by DEG and IDDP had the highest T_{onset} of the second degradation step (454 °C) and the lowest T_{onset} had nanocomposites PVC/MMT and PVC/30B (439 °C) when compared it to unfilled PVC (445 °C). It means that phosphate intercalation agent, especially TCP, could improve thermal stability of PVC. T_{max} of the second degradation step was increased for almost all nanocomposite samples.

**FIGURE 1.** a) TGA and b) DTGA curves for unfilled PVC and PVC nanocomposite samples**TABLE 3.** The results of TGA analysis

Samples	First step		Second step	
	T_{onset} (°C)	T_{max} (°C)	T_{onset} (°C)	T_{max} (°C)
PVC	268	290	445	464
PVC+Na ⁺	257	295	439	471
PVC+Na ⁺ +DEG	259	288	449	469
PVC+Na ⁺ +DEG+TCP	252	287	445	473
PVC+Na ⁺ +DEG+IDDP	256	285	454	471
PVC+Na ⁺ +PEG	251	291	452	472
PVC+Na ⁺ +PEG+TCP	248	290	450	458
PVC+Na ⁺ +PEG+IDDP	245	290	442	472
PVC+30B	243	280	439	463
PVC+30B+TCP	255	282	441	467

CONCLUSION

PVC is one of the most useful plastics in the world due to its wide application and low cost. However, during processing thermal degradation of PVC is usually evolved. Therefore, there is one way for the reduction of this problem, which is formation of PVC/clay nanocomposites. The aims of this research were to prepare organoclay using ion-dipole method with intercalation agents (diethylene glycol, polyethylene glycol), and co-intercalation agents (trycresyl phosphate, isodecyldiphenyl phosphate) and also the preparation of PVC/clay nanocomposites using melt intercalation method. Finally, the influence of laboratory modified MMT on thermal properties of PVC were studied and compared to PVC/clay modified by quaternary ammonium salt and un-filled PVC.

From the results of DMA it was shown that the moduli of PVC nanocomposites increase with using intercalation and co-intercalation agents. A possible explanation could be that clay modified by intercalation and co-intercalation agents is more polar than the clay modified only by the intercalation surfactant, and hence it is more compatible with the polymer matrix. However, the moduli of PVC/MMT laboratory modified are still lower than PVC/MMT commercially modified. It means that PVC/MMT commercially modified had the best exfoliation structure.

The thermal stability of PVC/MMT nanocomposites prepared by melt intercalation method was lower than unfilled PVC. The low thermal stability is supposedly because of the presence of metals, free and interlayer water in MMT. On the other hand, almost all PVC/MMT laboratory modified nanocomposites had enhanced thermal stability compared to PVC/clay commercially intercalated by quaternary ammonium salts.

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