

## INFLUENCE OF INTERCALATION AGENTS ON THE THERMAL STABILITY OF PVC/CLAY NANOCOMPOSITES

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### Abstract

Polyvinyl chloride (PVC)/montmorillonite (MMT) nanocomposites were prepared via melt-intercalation method. Two kinds of MMT (Cloisite®Na<sup>+</sup>, 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 and pH methods.

### 1. INTRODUCTION

Polymers are a very important factor in our lives. There is virtually no industry where products of polymerization are not used. 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 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 good thermal stability [3,4].

PVC/clay nanocomposite materials are one of the ways for development of effective PVC products. These nanocomposites have improved properties compared with the virgin polymers. For the preparation of polymer/clay nanocomposites, modification of layered silicate is very important, because clay is hydrophilic and polymer is hydrophobic, so the compatibility of these materials is poor. Organic modifiers, namely ammonium, imidazolium and phosphonium compounds are used to increase the compatibility. Melt intercalation is the most widely used method for preparation of nanocomposite materials, but this process needs high temperatures. If this temperature is higher than the thermal stability of the applied organic agent, the decomposition of this agent occurs [5,6,7].

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

### 2. EXPERIMENTAL

#### 2.1 Materials

In this work, suspension polyvinyl chloride (Neralit 652) was supplied by Spolana a.s., Czech Republic. Two different types of MMT were obtained from Southern Clay Products, Inc. Texas USA: natural unmodified MMT Cloisite®Na<sup>+</sup>, 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, intercalated agents (diethylen glycol (DEG) and polyethylene glycol (PEG)), and co-intercalated agents (tricresyl phosphate (TCP) and isodecildifenyl phosphate (IDDP)) were utilized as modifiers of montmorillonite.

The first aim of this research was prepared modified fillers from two types of MMT: Cloisite®Na<sup>+</sup> and Cloisite®30B. The ion-dipole intercalation method was employed for the modification of nanofillers with the help of intercalation and co-intercalation by various agents at 85 °C in laboratory mixer for 60 minutes.

Nanocomposites were prepared mixing of unmodified and modified MMT 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.

## 2.2 Methods

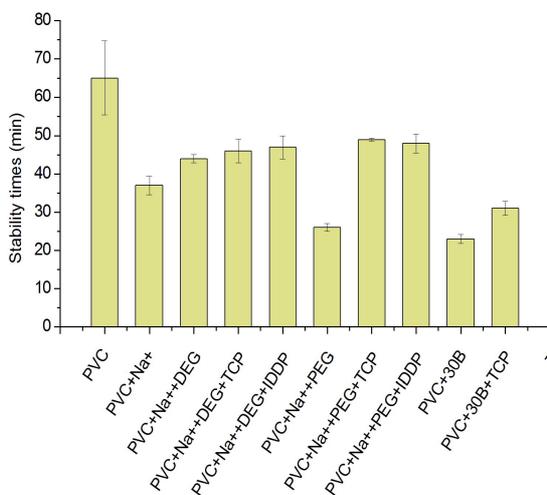
*pH method* was used for determination of the tendency of PVC compounds to evolving hydrogen chloride and any other acidic products. A sample in a test tube was heated in nitrogen atmosphere at 200°C until a predetermined change in the pH of absorbing solution was obtained, required for a certain amount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

*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 500 °C.

## 3. RESULTS AND DISCUSSION

It is known that basic quaternary amine group is a source of the degradation processes. Therefore, diethylen glycol, polyethylene glycol and plasticizers (TCP, IDDP) are used as intercalation and co-intercalation agents to prevent a contact between amine and active chloride atom.

For the determination of the tendency of unfilled PVC and the 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



**Fig. 1.** The stability times of unfilled PVC and

nanocomposite materials are specified in Fig. 1. As can be seen, the PVC without clay was possessed the longest stability time (65 min) from all PVC samples. On the other hand, all of the laboratory intercalated nanocomposite samples had longer stability times than PVC filled by Cloisite ®30B (commercial intercalated clay). In this case, the stability time for the nanocomposite sample containing Cloisite ®30B was 23 min. PVC/MMT intercalated by DEG had about 59 % higher stability time than the PVC/MMT/PEG. PVC/MMT intercalated by PEG and co-intercalated by TCP or IDDP had about 57% higher the stability times

(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 can be suitable for improving thermal stability of PVC/clay nanocomposite, because phosphate has function as a flame retardant.

#### PVC/MMT nanocomposites

Table 1 summarises the results from TGA. The surprise was that all nanocomposite samples containing organically modified MMT recorded three peaks compared to unfilled PVC or PVC/unmodified MMT. This difference could be explained by presence of intercalation and co-intercalation agents, which could initiated thermal degradation of PVC. For each TG steps the weight lost onset temperature ( $T_{\text{onset}}$ ) and the temperature of the maximum mass loss ( $T_{\text{max}}$ ) were characterised. In generally,  $T_{\text{onset}}$  and  $T_{\text{max}}$  of the first thermal degradation step was decreased almost for all nanocomposites. However, PVC/MMT modified by PEG and TCP have comparable thermal properties with pure PVC. It means that phosphate intercalation agents, especially TCP could improve thermal stability of PVC/MMT than PVC/MMT modified by quaternary ammonium salts (sample: PVC+30B), which could accelerate the thermal degradation of PVC. On the other hand, PVC/unmodified MMT had about 20 °C lower  $T_{\text{onset}}$  than unfilled PVC. Further; unmodified MMT is not plays important role for improving PVC degradation. But the addition intercalation and co-intercalation agents (DEG, DEG+TCP, PEG+TCP) to MMT the thermal degradation of PVC/clay could be improve. Though  $T_{\text{onset}}$  of the second degradation step was reduced almost for all nanocomposite specimens compared to unfilled PVC,  $T_{\text{max}}$  is enhanced, especially for PVC+MMT+DEG+IDDP, PVC+MMT+PEG and PVC+MMT+PEG+IDDP ( $T_{\text{max}}$  for the second stage was about 10 °C higher than  $T_{\text{max}}$  of unfilled PVC). It can be indicated than nanocomposite could slightly improve thermal degradation at high temperature.

**Table 1** The results of TGA analysis

Samples	First step			Second step	
	$T_{\text{onset}}$ (°C)	$T_{\text{max}1}$ (°C)	$T_{\text{max}2}$ (°C)	$T_{\text{onset}}$ (°C)	$T_{\text{max}}$ (°C)
PVC	246	-	277	426	440
PVC+Na <sup>+</sup>	241	-	270	411	420
PVC+Na <sup>+</sup> +DEG	244	228	263	416	427
PVC+Na <sup>+</sup> +DEG+TCP	245	240	267	432	442
PVC+Na <sup>+</sup> +DEG+IDDP	236	234	265	422	450
PVC+Na <sup>+</sup> +PEG	235	230	268	417	461
PVC+Na <sup>+</sup> +PEG+TCP	246	232	278	427	445
PVC+Na <sup>+</sup> +PEG+IDDP	237	230	271	425	449
PVC+30B	236	227	263	426	423
PVC+30B+TCP	241	228	265	429	445

#### 4. CONCLUSION

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

#### ACKNOWLEDGEMENTS

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