POLYVINYL CHLORIDE/ MONTMORILLONITE NANOCOMPOSITES
Glass transition temperature and mechanical properties

W. B. Xu[1,2] *, Z. F. Zhou[1], M. L. Ge[1] and W.-P. Pan[2]

[1]Department of Polymer Science and Engineering, Hefei University of Technology, Hefei, 230009 Anhui, China
[2]Department of Chemistry, Materials Characterization Center, Western Kentucky, Bowling Green, KY, 42101, USA

Abstract

Polyvinyl chloride (PVC)/organic-montmorillonite composites were prepared by melt intercalation. Their structures and properties were investigated with X-ray diffraction (XRD), differential scanning calorimetry (DSC) and mechanical testing. The results showed that PVC chains could be intercalated into the gallery of organically modified montmorillonite to form exfoliated PVC/organic-montmorillonite nanocomposites, and the glass transition temperatures of PVC/organic-montmorillonite composites were lower than that of neat PVC. However, the tensile strength, and both the Izod type and Charpy notched impact strengths of PVC/organic-montmorillonite nanocomposites were fitted with the linear expressions: $\tau = 535.07 - 6.39 T_g$, $\sigma_I = 378.76 - 4.59 T_g$ and $\sigma_C = 276.29 - 3.59 T_g$, respectively.

Keywords: DSC, glass transition temperature, melt intercalation, montmorillonite, nanocomposite, polyvinyl chloride

Introduction

Polymer/clay nanocomposites are a class of hybrid materials composed of organic polymer matrix in which inorganic particles with nanoscale dimension are embodied [1–4]. At this scale, the inorganic fillers improve dramatically the properties of polymer even though their amount is small. These nanocomposites exhibit improved modulus, lower thermal expansion coefficient and gas permeability, higher swelling resistance and enhanced ionic conductivity compared to the pristine polymers presumably due to the nanoscale structure of the hybrids and the synergism between the polymer and the silicate [5–6]. Preparing nanocomposites by intercalating layered silicates has proved to be a versatile approach to diminish the length scale of component phase. MMT belongs to the dioctahedral smectite group [7]. Consisting of silicate layers of approximately 200 nm in length and 1 nm in thickness, and the interlayer spacing between stacked layers is also approximately 1 nm. Since MMT is

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environmentally friendly, naturally abundant and economic, it has been applied in numerous industrial fields due to its good performance-cost ratio. The outstanding feature of MMT is that the silicate layers can be expanded and even delaminated by organic molecules under proper conditions. Thus, during the processing of polymer/MMT nanocomposites, the nanoscale silicate layers can be dispersed in the polymer matrix and the reinforcement phase forms in situ on the molecular level, which is very different from conventional filled composites. Moreover, it has been found that the polymer/MMT nanocomposites can be prepared by conventional processing techniques, such as extrusion and injection methods [8, 9]. Therefore, fabricating such nanocomposites is efficient and cost effective, which has drawn increasing attention in recent years, since montmorillonite reinforced nylon nanocomposites with excellent mechanic properties were developed by Toyota group, much attention has been devoted to smectite as a reinforcement material for polymers [10–14], e.g. polystyrene, polyamide, poly(ethylene oxide).

Polyvinyl chloride (PVC), as an important commercial polymer, has been studied and used widely in industrial fields for many years. However, due to its inherent disadvantages, such as low thermal stability and brittleness, PVC and its composites are subject to some limitations in certain applications [15]. Therefore, it is necessary to develop new PVC products with altered properties in order to broaden PVC applications. Recently, the development of PVC/layered silicate nanocomposites presents a new way to prepare high performance PVC composites. Wang [16, 17] reported the preparation and characterization of PVC-clay nanocomposites formed by both melt and solution blending. The effects of the clay loading level, the presence and amount of plasticizer, melt blending time and annealing time, etc., on the structure of the nanocomposite and the thermal and mechanical properties have also been investigated. Trilica *et al.* [18] took dioctylphthalate (DOP) as cointercalater for organic MMT and PVC because they found alkylammonium salts between the interlayers of organic MMT, could catalyze PVC degradation. Although DOP prevented the degradation of PVC, the MMT only acted as a plasticizer carrier and the mechanical properties of the composites were not enhanced significantly. Du [19] reported more information concerning the thermal degradation and charring of PVC/MMT nanocomposite in the presence of DOP by the use of X-ray photoelectron spectroscopy and the acquisition of the carbon (C1s), chlorine (Cl2p), and oxygen (O1s) spectra. For PVC–clay nanocomposites the surface at high temperatures is dominated by carbon, and not the oxygen of the clay. The presence of the clay does retard the chain-stripping degradation of the PVC and the enhanced char formation accounts for the observation of enrichment of carbon. Zhang [20] investigated the effect of silicate modification and MMT content on the morphology development, relaxation behavior, optical clarity and mechanical properties of the PVC/MMT nanocomposites. All of the previous studies mainly discussed the effect of DOP on the structure, thermal stability and mechanical property of the PVC/organic MMT nanocomposites, and PVC/MMT nanocomposites were belong to intercalated nanocomposites.

In this paper, the effect of Org-MMT content on the glass transition temperature and mechanical properties of the PVC/Org-MMT nanocomposites was investigated.

The PVC/Org-MMT exfoliated nanocomposites with different Org-MMT content were prepared by melt blending PVC with organically modified MMT, the glass transition temperature was measured by differential scanning calorimeter (DSC), mechanical properties including the tensile strength, notched Izod impact strength and notched Charpy impact strength were also tested, and the relationship between glass transition temperature and mechanical properties of PVC/Org-MMT are discussed in this paper.

Experimental

Materials

PVC used was purchased from Xuzhou Chemical Factory (brand SG-5) and used without any treatment. Na^+-montmorillonite was available from Lin'an Chemistry Agent Factory (China), and organic-montmorillonite (Org-MMT) was synthesized in our own laboratory according to [16]. Various processing additives for PVC, such as heat stabilizer, lubricant (paraffin) were industrial grade products.

Preparation of PVC/Org-MMT nanocomposite

PVC, Org-MMT and various processing additives were put into high-speed mixing machine (Model GH-10A), the rotor speed was 1000 rpm, mixing time was 1 min, then the mixture was melt mixed in a roller mill (Model SK 160B) at 175–180°C for 10 min. The resulting sheet was compression molded using a vulcanization machine (Model QLB400-400-2) at a temperature of 180°C for 20 min into a plate with thickness of 4 mm. The sheets were prepared for structure characterization and physical properties measurements.

Measurements

X-ray diffraction (XRD) analysis was carried out in order to confirm whether the PVC/Org-MMT nanocomposites were formed. D/max-γB diffractometer was employed with CuK_α radiation at room temperature by using graphite-filter. The XRD patterns were scanned in 2θ ranges from 1.2 to 10° at a rate of $1°\ min^{-1}$. The interlayer distance of Org-MMT in composite was calculated from the (001) peak by using the Bragg equation, $2d\sin\theta=n\lambda$.

A Perkin Elmer DSC-2C apparatus was used for measuring glass transition temperature of PVC and PVC/Org-MMT systems. The temperature and energy readings were calibrated with indium at scanning rate of $10°C\ min^{-1}$ employed in the measurements. All measurements were carried out in nitrogen atmosphere. The raw sample was heated to 180°C and held isothermally for 5 min to eliminate previous thermal history. The sample was cooled at constant rate of $10°C\ min^{-1}$, then was heated to 165°C at a heating rate of $10°C\ min^{-1}$, and the heat flow curve was recorded as a function of temperature.

The tensile test was carried out with a Model LJ-1000 testing machine at a crosshead speed of $10\ mm\ min^{-1}$ at room temperature, the notched Charpy type im-

pact test was examined with a Model XCJ-500 impact testing machine at room temperature, and the notched Izod type impact test was investigated on a Model UJ-4 impact testing machine at room temperature according to GB1040-1996, GB1042-1996 and GB1843-1996, respectively.

Results and discussion

X-ray diffraction analysis

The X-ray diffraction patterns of PVC/Org-MMT nanocomposite with different Org-MMT content are shown in Fig. 1. As can be seen from Fig. 1, the (001) plane diffraction peak of Org-MMT appears around $2\theta \sim 3.82°$, corresponding to the interlayer distance of 3.21 nm calculated from the Bragg law, $2d\sin\theta = n\lambda$. For PVC/Org-MMT composites, no diffraction peak appears at the testing scale, that is, from 1.2 to 10°, implying that the interlayer distance was larger than 7.35 nm during direct melt process. This clearly indicates that macromolecule chains had intercalated into the galleries of Org-MMT and exfoliated the layer of montmorillonite. This may be the result of the strong interaction between polar PVC molecule and the silicate layer. PVC can penetrate the silicate particle and intercalated into the galleries. As a result, exfoliated PVC/Org-MMT nanocomposites were produced.
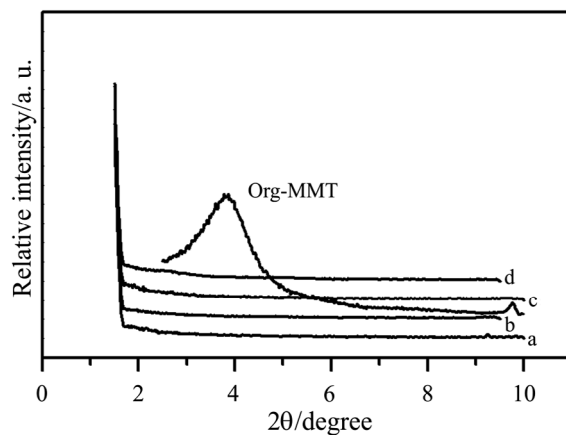
Fig. 1 XRD scans for PVC/Org-MMT nanocomposite. Org-MMT content (phr):
a – 3; b – 5; c – 7; d – 10

Glass transition temperature of PVC/Org-MMT nanocomposite

An overlay of DSC curves of virgin PVC and PVC/Org-MMT nanocomposites with Org-MMT loading of 3, 5, 7, 10 parts per hundred resin (phr) is presented in Fig. 2. According to Fig. 2, a plot of glass transition temperature *vs*. content of Org-MMT is obtained, as shown in Fig. 3. It can be found that the glass transition temperature of PVC/Org-MMT are slightly lower than that of virgin PVC.
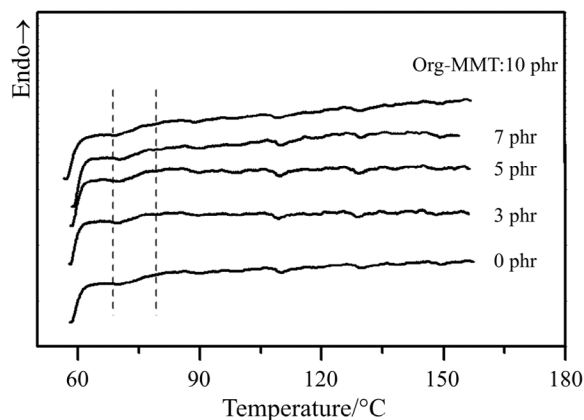
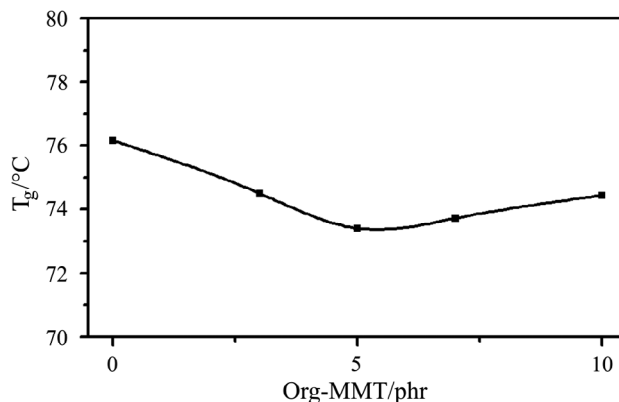**Fig. 2** DSC heating scans of PVC/Org-MMT nanocomposites

**Fig. 3** Plot of T_g *vs*. Org-MMT content of PVC/Org-MMT nanocomposite

Giannelis *et al*. [22] reported that intercalated PS-organosilicates do not show the characteristic bulk glass transition for PS. Wan [20] presented that the glass transition peak of intercalated PVC/MMT nanocomposites shifted to higher temperatures compared to that of pristine PVC by dynamic mechanical thermal analysis (DMTA), and was explained by the confined environment which restricts the mobility of polymer chains within the interlayer. In the PVC/Org-MMT nanocomposites studied here, XRD results indicate that exfoliated structures dominate. In this case, the PVC blocks are physically linked to the clay plates. This effect limits the movement of the PVC segments increasing the glass transition temperature of the PVC; on the other hand, the interlayer of MMT may take the role of a plasticizer, increasing the distance between PVC chains resulting in decreases of the interaction force between PVC molecules and lead to the lower glass transition temperature of PVC/Org-MMT.

Relationship between glass transition temperature and mechanical properties

Figure 4 shows the plot of tensile strength *vs*. glass transition temperature of PVC/Org-MMT nanocomposites. After linear fit, the relationship between glass transition temperature and tensile strength yields the following equation,

$$\tau = 533.07 - 6.39T_g \qquad (1)$$

where τ refers to the tensile strength, and T_g refers to the glass transition temperature of PVC. It can be found that the tensile strength decreases with the increase of the glass transition temperature for PVC/Org-MMT nanocomposite.
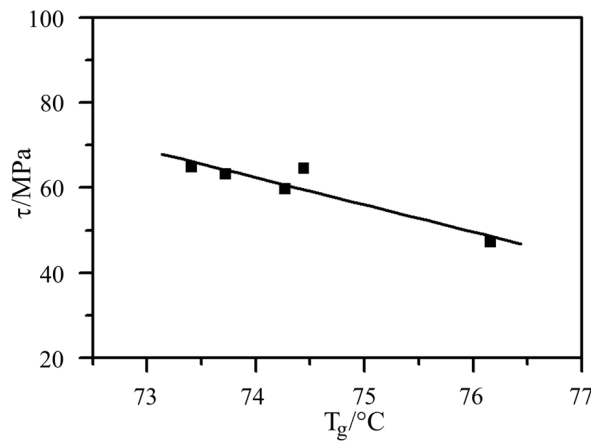
Fig. 4 Plot of tensile strength *vs*. T_g of PVC/Org-MMT nanocomposite

Figure 5 shows the plot of notched Izod type impact strength *vs*. glass transition temperature of PVC/Org-MMT nanocomposites, again a plot of the notched Izod type impact strength *vs*. the glass transition temperature yields a linear relationship:

$$\sigma_I = 378.76 - 4.59T_g \qquad (2)$$

where σ_I refers to the notched Izod type impact strength, and T_g refers to the glass transition temperature of PVC. It can be found that the notched Izod type impact strength decrease with the increase of the glass transition temperature for PVC/Org-MMT nanocomposite.

Figure 6 shows the plot of notched Charpy type impact strength *vs*. glass transition temperature of PVC/Org-MMT nanocomposites. Similarly, a linear relationship is found:

$$\sigma_C = 276.29 - 3.59T_g \qquad (3)$$

where σ_C refers to the notched Charpy type impact strength, and T_g refers to the glass transition temperature of PVC. It can be found that the notched Charpy type impact strength decreases with the increase of the glass transition temperature for PVC/Org-MMT nanocomposite.
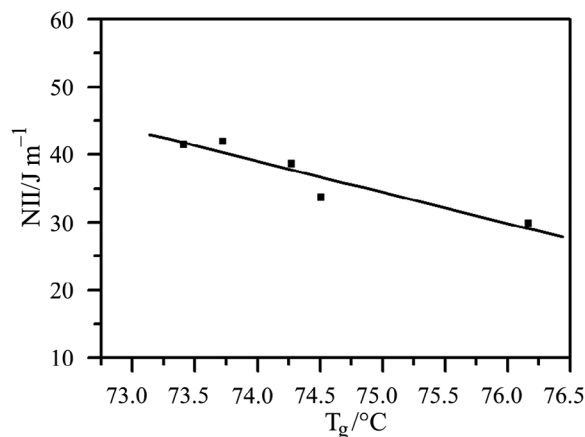
Fig. 5 Plot of notched impact strength *vs. T*$_g$ of PVC/Org-MMT nanocomposite
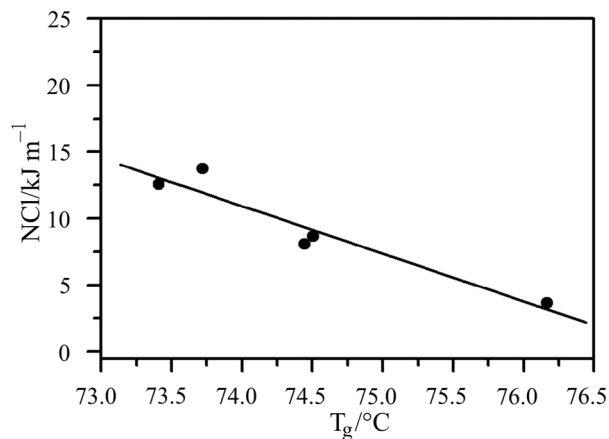

Fig. 6 Plot of Charpy impact strength *vs. T*$_g$ of PVC/Org-MMT nanocomposite

Although the notched impact strength, either Izod type or Charpy type, decreases with the increase of the glass transition temperature, the decreasing relationship for the Izod type is more pronounced than the Charpy type as shown by the slopes of Eqs 2 and 3. This result is related to the shape of notch in each case being different. The tip of Izod type is sharper than that of the Charpy type.

Figure 7 shows the structure model of PVC/Org-MMT nanocomposite, which can illustrate the change of mechanical property of PVC/Org-MMT nanocomposite. As shown in Fig. 7, the exfoliated layer of MMT is homogenous dispersed in PVC matrix, and when the nanocomposite was loaded with tensile stress, the tensile strength will increase as a result of the orientation of MMT layer. When the impact loading is added, MMT layers can take a role to transfer and confuse impact energy as physical crosslinking points.
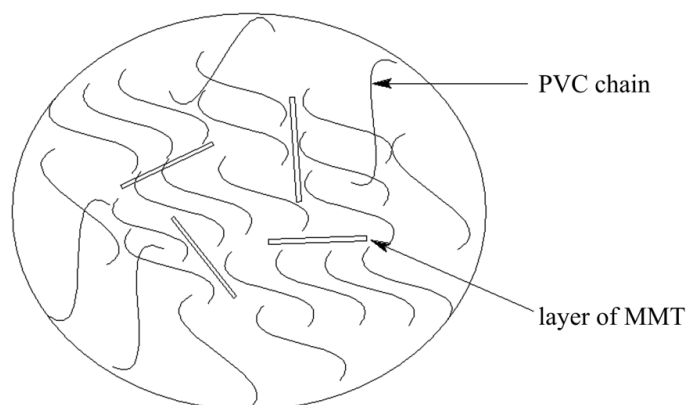
Fig. 7 Schematic illustration of PVC/Org-MMT nanocomposite

Conclusions

PVC/organic-montmorillonite composites were prepared by melt intercalation. XRD results show that PVC chains can be intercalated in organically modified montmorillonite to form exfoliated PVC/organic-montmorillonite nanocomposites, and it was found that the glass transition temperatures of PVC/organic-montmorillonite composites were lower than that of neat PVC by DSC, this is a competitive result than the increase in the glass transition temperature by PVC chain linkage to the clay plates whereas a decrease in glass temperature can be explained by decreases in the interaction force between PVC chains as the MMT plates act as a plasticizer. The tensile strength, Izod type notched impact strength and Charpy type notched impact strength of PVC/organic-montmorillonite nanocomposites were fitted with the linear expressions: $\tau=535.07-6.39T_g$, $\sigma_I=378.76-4.59T_g$ and $\sigma_C=276.29-3.59T_g$, respectively.

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