PVC/MMT nanocomposites

DSC with stochastic temperature modulation study at glass transition region

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Abstract Poly(vinyl chloride) (PVC) nanocomposites with sodium montmorillonite (Na-MMT) and organically modified MMT (O-MMT) have been prepared by melt processing using mixing and extrusion techniques. The differential scanning calorimetry (DSC) with stochastic temperature modulation (TOPEMTM) results show that the glass transition temperature (T_g) of PVC is slightly higher than T_g of PVC/Na-MMT and PVC/O-MMT which would indicate that MMT plays a role of an internal plasticizer that increases the distance between the PVC macrochains. The DSC TOPEM non-reversing heat flow profiles show enthalpy relaxation effects, and the lowest value has been found for pristine PVC—the presence of MMT (both Na+ and ammonium salt modified) may generate a certain orientation level of PVC macrochains during the extrusion process. Specific heat vs temperature dependencies at different frequencies revealed that the best fit to the single profile was found for PVC/Na-MMT nanocomposite, and this observation may be related to internal stability of the composite material as confirmed by analysis of the change in the specific heat (ΔC_p).

Keywords PVC nanocomposites · DSC · TOPEM · Glass transition

Introduction

Poly(vinyl chloride) (PVC) nanocomposites with layered silicates, especially montmorillonite, have gained increased

attention in recent years due to reinforcement effects induced by inorganic filler. Improved thermal resistance, enhanced stiffness and barrier properties, as well as flame retardation have been reported [1–6].

Besides, the processing conditions for low-filled polymeric nanocomposites are similar to these of pristine resin and typical problems of microcomposites' processing, such as changes in melt viscosity or surface roughness of molded parts, do not occur. Owing to nanometric dimensions of montmorillonite particles (close to the molecular dimensions), large interphase area is achieved at low filler content [7]. Furthermore, when montmorillonite is properly modified and dispersed in the polymer matrix, effective interactions arise between organic and inorganic phases of composite material that can cause synergistic effects [8, 9].

The enhancements of the thermal properties of PVC/MMT nanomaterials were described in the literature [10–12], and it is generally accepted that the lamellar crystal structure of MMT platelets with high aspect ratio play a decisive role in restricting the molecular dynamics of the macromolecular matrix. However, plasticized PVC shows unusual elasticity due to three-dimensional network structure that consists of microdomains of around 100 Å, primary crystallites (platelet or flat needle-like lamellar structures), and secondary fringed micellar crystallites [13, 14]. It is still unclear how this complex hierarchical-type PVC morphology is affected by nanostructured MMT platelets under heating at glass transition region. More information can be obtained on those effects if temperature-modulated DSC is applied. In this technique, the heating rate changes continuously, and thus it is possible to separate the sensible (Φ_{sens}) and latent (Φ_{latent}) heat flow components. Different temperature programs (e.g., sinusoidal or saw-tooth) allow determination of the heat capacity changes and analysis of relaxation processes by measuring the frequency

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dependence of thermal processes. Useful combination of heat components separation and multi-frequency modulations is offered by a new technique—TOPEM™ DSC. In this method, a stochastic temperature modulation makes possible the analysis of dynamic behavior of material during one single measurement—without a need to make “blank” measurements. This analysis is based on the correlation between the heating rate and heat flow. It leads to the quasi-static heat capacity $c_{p,0}$, the frequency-dependent complex heat capacity, $c_p^*(\omega)$ and the non-reversing heat flow $\Phi_{\text{non-rev}}$. The second part of the heat flow—reversing component is calculated from the quasi-static heat capacity. Using sufficiently low heating rates ($0.01\text{--}2\text{ K min}^{-1}$) and small temperature perturbation δT_0 (a parameter to fulfill linearity conditions) $1\text{ mK--}0.5\text{ K}$, it is possible to obtain reversing and non-reversing heat flows identical as a sensible and latent heat flow component [15–17].

Hence, the aim of this article is to analyze the influence of MMT (both non-modified and organically-treated) on the glass transition region of industrial-mode formulated PVC, including relaxation effects.

Experimental

Materials

Suspension poly(vinyl chloride) ($K = 67$, Polanvil S-67 HBD) was supplied by Zakłady Azotowe ANWIL S.A. (Poland); the commercial nanoclays: sodium montmorillonite (NaMMT) and MMT modified by benzyltrimethylammonium chloride (Nanofil® SE3010) were provided by Süd Chemie (Germany). Other additives were as follows: plasticizer—dioctyl phthalate (DOP—Zakłady Azotowe Kedzierzyn S.A., Poland); stabilizer—calcium stearate (Boryszew ERG S.A., Poland); chlorinated flame retardant—chloroparaffin (Konimpex, Poland); flame retardant—aluminum hydroxide (ATH, Alfrimal 103 from Alpha Calcit Füllstoff GmbH, Germany); and compatibilizer/plasticizer—epoxidized soybean oil (Ergoplast ES from Boryszew ERG S.A., Poland). All materials were dried before use.

Preparation of PVC/MMT nanocomposites

PVC/MMT nanocomposites were obtained by a two-step method—at the first stage, a masterbatch was prepared by mixing suspension PVC with MMT and other additives in a high-speed mixer. The second step was processing of the homogeneous mixture in a double-screw micro-extruder (HAAKE MiniLab II). The operating temperature region of

Table 1 Composition of PVC/MMT nanocomposites

Composition	wt%
PVC	100
DOP	40
Calcium stearate	2
Chloroparaffine	5
ATH	25
Epoxidized soybean oil	3
MMT	3

the micro-extruder was maintained (after a set of optimizing experiments) at ca. $140\text{ }^{\circ}\text{C}$. The operating screw's speed was maintained at 70 rpm, and the melt material has been circulated in the extruder's backflow channel. The composition of PVC/MMT nanocomposites is specified in Table 1.

Method

DSC measurements with stochastic temperature modulation have been performed using a METTLER TOLEDO 823° DSC. The following parameters were chosen: the underlying heating rate— 2 K min^{-1} , the amplitude of the temperature pulse— $\pm 0.25\text{ K}$, the switching time range (which limits the duration of the pulses)—min. 15 s and max. 30 s, and the sample weight—ca. 17 mg.

Results and discussion

TOPEM DSC profiles of plasticized PVC, PVC/Na-MMT, and PVC/O-MMT nanocomposites are shown in Fig. 1.

Glass transition temperature (T_g) of PVC ($57.4\text{ }^{\circ}\text{C}$) is slightly higher than T_g of PVC/Na-MMT ($54.7\text{ }^{\circ}\text{C}$) and PVC/O-MMT ($52.4\text{ }^{\circ}\text{C}$). These observations would indicate that the mobility of polymer chains is not restricted in the confined environment of layered silicate platelets—on the contrary, MMT acts as an internal plasticizer which increases the distance between the macrochains. In consequence, the degree of interactions between polymer chains becomes lower and T_g decreases. In general, the glass transition of polymer nanocomposites is profoundly influenced by the relative strength of the chain-particle interactions and the morphology, particularly the particle dispersion and the interparticle spacing [18]. Sufficiently, strong particle-chain enthalpic interactions lead to permanent attachment of chain segments to the nanoparticles. Under these conditions, polymer nanocomposites have been shown to exhibit two glass-transition temperatures: one associated with polymer chains far from the nanoparticles and the second associated

Fig. 1 DSC TOPEM profiles of **a** PVC, **b** PVC/Na-MMT, and **c** PVC/O-MMT

with chains in the vicinity of the nanoparticles [19, 20]. In our system under investigation, a single T_g was observed indicating that PVC–MMT enthalpic interactions are rather weak. Besides, the existence of single glass transition evidences that the plasticizer (DOP) is able to penetrate not only the intermicrodomain region of amorphous PVC but also microdomains themselves [14, 21].

It seems that in the highly plasticized systems in which the presence of a plasticizer eases the motion of macrochains, the extent of this effect is larger than effect of constraints induced by nanoadditive-MMT. Although there are numerous evidences for constraining the polymer chain motions on the nanometer scale by layered silicates (“nanoconfinement effects”) which may occur both in the intragallery space and at or near the MMT surface [22], it is still a subject of debate in regard to plasticized blends which effect prevails. Since the enhanced interchain interactions

correlate with increases in the activation energy of the glass transition, it would be advisable to perform relaxation kinetic analysis for PVC/MMT systems—such studies are in progress.

The non-reversing heat flow curves made it possible to determine the enthalpy relaxation effects, and the lowest value has been found for PVC (0.41 J g^{-1}) in comparison to PVC/Na-MMT (0.68 J g^{-1}) and PVC/O-MMT (0.58 J g^{-1}). The presence of MMT (both Na⁺ and ammonium salt modified) may generate a certain orientation level of PVC macrochains during the extrusion process. Then the cooling rate is too fast to allow macromolecules to rearrange in a thermodynamical equilibrium configuration, and they remain in an ‘out of equilibrium’ glassy state with internal stresses unrelaxed.

Specific heat vs temperature dependencies for measurements of pristine PVC, PVC/Na-MMT, and PVC/O-MMT

Fig. 2 Specific heat vs temperature plots at different frequencies for **a** PVC, **b** PVC/Na-MMT and **c** PVC/O-MMT

nanocomposites at different frequencies are displayed in Fig. 2.

Interestingly, the best fit to the single profile was found for PVC/Na-MMT nanocomposite, and this observation may be related to internal stability of the composite material—the less prone the specific heat is to changes in temperature frequencies in the dynamic TOPEM DSC experiment, the more robust the structure of the tested material is. This effect was confirmed by analysis of the change in the specific heat (Δc_p) with the lowest value for PVC/Na-MMT blend. Since the size of the step change in the specific heat at the glass transition temperature is a measure of the increase in number of rotational modes of the main chain segments which become active at the transition, the

lowest value for PVC/Na-MMT nanocomposite indicates its relative stability. The PVC/Na-MMT nanocomposite does not contain organic modifier of MMT (benzyltrimethylammonium chloride) which may either undergo degradation during processing or disadvantageously interact with the components of industrial PVC formulation.

Conclusions

DSC with stochastic temperature modulation proved to be an efficient method to distinguish reversing and non-reversing heat flow components in the glass transition region for PVC/MMT nanocomposites. Based on TOPEM

DSC data, it has been found that the glass transition temperature (T_g) of PVC (57.4 °C) is slightly higher than T_g of PVC/Na-MMT (54.7 °C) and PVC/O-MMT (52.4 °C). It proves that MMT is not restricting the mobility of polymer chains through formation of a confined environment, but it acting as an internal plasticizer which increases the distance between the macrochains. It causes that the interactions between polymer chains become weaker and T_g value decreases. A single T_g was observed indicating that PVC-MMT enthalpic interactions are rather weak. Besides, the existence of single glass transition evidences that the plasticizer (DOP) is able to penetrate not only the inter-microdomain region of amorphous PVC but also microdomains themselves. Non-reversing DSC TOPEM heat flow curves show enthalpy relaxation effects, and the lowest value has been found for PVC in comparison to PVC/Na-MMT and PVC/O-MMT. The possible explanation could be that the presence of MMT (both Na⁺ and ammonium salt modified) may generate a certain orientation level of PVC macrochains during the extrusion process, and some internal stresses remain unrelaxed. Analysis of the specific heat vs temperature dependencies at different frequencies revealed that the best fit to the single profile was found for PVC/Na-MMT nanocomposite, and this observation may be related to internal stability of the composite material as confirmed by analysis of the change in the specific heat (ΔC_p).

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