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Enhancement of the thermal stability, mechanical properties and morphologies of recycled PVC/clay nanocomposites

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Summary

Recycled PVC/clay nanocomposites were prepared by melt mixing of recycled PVCs and modified clays. Characterization of the nanostructure of the nanocomposites was carried out using wide angle X-ray diffraction (WAXD) and transmission electron microscopy(TEM). In case of 10wt.%, the characteristic peak of modified clay was perfectly disappeared, because of aids of plasticizers as co-intercalator. Thermal stability was evaluated from the thermal decomposition behaviors and linear dimension changes by TGA and TMA system. Coefficients of thermal expansion of the nanocomposites were also observed from TMA analysis. Dynamic mechanical properties were evaluated using DMA system. The thermal and mechanical properties of the nanocomposites were improved simultaneously for varied clay loadings, 1,3,5,10wt.%, compared to recycled PVC. Especially, the storage modulus of the nanocomposites with 10wt.% clay loading was increased 11 times compared to that of recycled PVC.

Introduction

In recent years, the study of polymer-clay nanocomposite has attracted intense interest from academic and industrial researchers in the past decade[1-8]. The primary goal of fabricating nanocomposites is to enhance the strength, toughness and thermal stability of polymeric components using molecular or nanoscale reinforcements[9]. In addition to various fibres and mineral particles, such as montmorillonite (MMT) have played an important role as effective reinforcement components in developing new nanocomposites[10,11].

The nanocomposite is generally comprised of an organically modified clay and some polymer. The clay that is most commonly used is MMT as mentioned above, which is an aluminosilicate mineral with sodium ions present between the clay layers. This space between the clay layers is referred as the clay gallery. To make this clay compatible with organic polymers, the sodium ions are usually ion-exchanged with an organic ammonium or phosphonium salt to convert this material into a hydrophobic clay. The nanocomposites may be prepared by melt blending, solution blending and *in-situ* polymerization process[12]. Based on same concepts, various polymer-clay nanocomposites were reported, such as polyamide 6/clay nanocomposites[13,14], epoxy/clay nanocomposites[15,16], acrylic polymer/clay nanocomposites[17] and polystyrene/clay nanocomposite[18,19]. For instance, compared to polyamide 6, the tensile strength of polyamide 6-clay nanocomposites at 5 wt.% clay loading level was 49% higher, the tensile modulus was 68% higher, and heat distortion temperature was 87°C higher, while the impact strength was almost unchanged[20].

Poly (vinyl chloride) (PVC) is nowadays, together with polyethylenes, the thermoplastic with the widest range of applications. The reason is, undoubtedly, its excellent mechanical properties, high compatibility with additives, processability and low cost[21]. However, thermal stability is still serious problem. The thermal degradation of PVC leads the evolution of hydrogen chloride gas, extensive discoloration of PVC and lowering of physical and mechanical properties[22]. These problems become more serious in case of using recycled PVC, which is matrix material we were interested. The estimated annual PVC world production is at present 22 million tons. In addition to the PVC homopolymer, PVC products consist of metal stabilizers, plasticizers and fillers. Most of the PVC production waste is recycled mechanically[23]. But, the thermal and mechanical properties of recycled PVC products drop considerably. Recycled PVC and its compounds are subject to some limitations in certain applications. Therefore, it is necessary to develop recycled PVC products with high quality and good properties in order to yield high added values and broaden recycled PVC applications[24].

Recently, PVC/clay nanocomposites started receiving attention to many researchers. But, there are only few reports about PVC/clay nanocomposites[25]. Trilica et al. took dioctylphthalate (DOP) as co-intercalator for modified clay and PVC[26]. Wang et al. prepared intercalated PVC/clay nanocomposites with improved thermal stability more or less[27].

In this study, we reported about the preparation of PVC/clay nanocomposites. The effects of clay contents on nanocomposite structures and the thermal and mechanical properties were investigated.

Experimental

Materials

The recycled PVC scraps known as decoration sheets were supplied by GreenPol Co.. The scraps were washed and granulated into flakes through 3~5mm screen. Organically modified clays, MT2EtOH (M: methyl; T: tallow with ~65% C18, ~30% C16 and ~5% C14; EtOH: bis-2-hydroxyethyl), also known as Cloisite® 30B were purchased from Southern Clay Product, Inc.

Preparation of recycled PVC/clay nanocomposites

Recycled PVC/clay nanocomposites were prepared by melt mixing recycled PVCs and clays in the internal mixer of a Haake Rheomix 600. The mixing temperature was fixed at 170°C, the rotor speed was 60 rpm, and the mixing time was 5mins. The nanocomposite samples were compression molded into sheets of 1 mm in thickness by hot pressing at 170°C and 20 MPa for 2mins, followed by cooling to room temperature at the same pressure. The molded sheets were cut and designed to use for each measurements. To have the same thermal history, recycled PVCs and nanocomposites with 0~10 wt.% were thermally processed at the same conditions.

Wide angle X-ray diffraction (WAXD)

Wide angle X-ray diffraction measurements were accomplished using Rigaku D/MAX-2000 X-ray diffractometer with Cu K_α radiation ($\lambda = 0.154$nm) and a scanning rate of 1°/min. Bragg's law, $\lambda = 2d\sin\theta$, was used to calculate the crystallographic spacing, d.

Differential Scanning Calorimetry(DSC)

Differential Scanning Calorimetry was carried out using DSC Q1000 system of TA instruments at heating rate of 10°C/min under a flowing nitrogen atmosphere. The temperature was changed from 25 to 200°C.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using TGA Q500 system of TA instruments at heating rate of 20°C/min under a flowing nitrogen atmosphere. The temperature was changed from 25 to 800°C.

Rheometrics Dynamic Spectrometer (RDS)

Rheological analysis was carried out using RDS system of Rhometric Co. at 150~220°C under a flowing nitrogen atmosphere. The strain amplitude and the frequency were constant at 10% and 1rad/sec, respectively.

Thermomechanical analysis (TMA)

Thermomechanical analysis was performed using TMA Q400 system of TA instruments at heating rate of 5°C/min under 0.05N static force. The temperature was changed from 30 to 55°C.

Dynamic mechanical analysis (DMA)

Dynamic mechanical properties were measured using DMA Q800 system of TA instruments at heating rate of 5°C/min under a flowing nitrogen atmosphere, the amplitude was 20μm, and the frequency was 1 Hz.

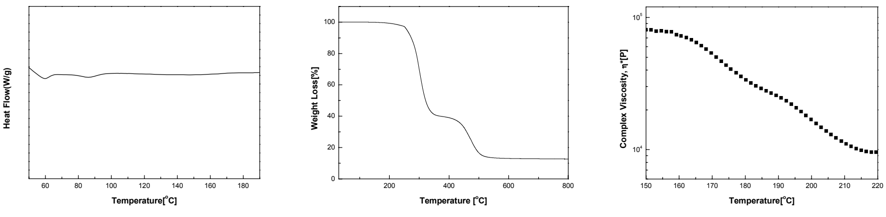
Transmission electron microscopy (TEM)

The nanocomposite samples for TEM were prepared ultrathin-sectioned by ultra cryogenic microtome equipped with a diamond knife. Ultrathin-sectioned samples were collected and placed on a 200 mesh copper grid. The TEM micrographs were obtained with a Carl Zeiss-EM 912 Omega apparatus running at an acceleration voltage of 80kV.

Results and discussion

Pristine properties of recycled PVC scraps

One of the most important factors in polymer recycling is that we should collect the uniform recycled polymer scraps and acquire the original properties. Pristine thermal, mechanical and rheological properties were shown in Figure 1. In Figure 1 (a), DSC thermogram shows that the glass transition temperature of recycled PVC is 60~70°C. It means that the recycled PVC scraps contain the considerable amounts of plasticizers. And the relatively broad peak at 80~90°C seems to be due to the various unknown additives. From TGA curves in Figure 1 (b), it is known that the first degradation happens under 300°C because hydrochloric acid gas starts to generate at this step. Melt viscosity changes are shown in Figure 1 (c). Melt viscosities of recycled PVC were decreased considerably as the temperature increased. And the thermal degradation did not happen even at 220°C.



(a) (b) (c)

Figure 1. Basic properties of recycled PVC: (a) DSC thermogram, (b) Thermal decomposition behaviors from TGA, (c) Complex viscosity from RDS

Intercalated/exfoliated structure of recycled PVC/clay nanocomposites

X-ray diffraction patterns of organically modified clay and recycled PVC/clay nanocomposites with different clay content were shown in Figure 2. From Figure 2, it is obvious that at the overall clay loading level, 1~10 wt.%, the specific peak of clay is disappeared and the corresponding gallery spacing is widened to exfoliation level. It can be thought that the plasticizers in recycled PVC can be located in the gallery space of clay because it is considerably lower molecular weight materials and has greater mobilities than recycled PVC. Moreover, as mentioned above, it is thought that the plasticizers acts as co-intercalator between clays and recycled PVCs. This effect made it possible to fabricate the exfoliated recycled PVC/clay nanocomposite even with 10 wt.% clay contents.

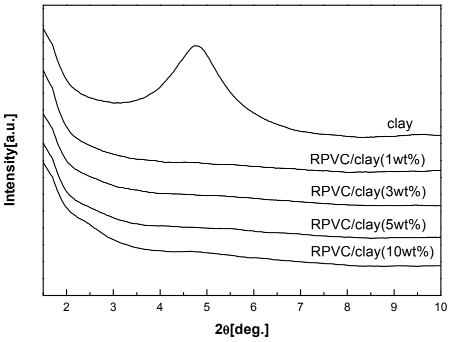


Figure 2. X-ray diffraction patterns of the nanocomposites

Thermal decomposition behavior of the nanocomposites

Thermal stability of recycled PVC/clay nanocomposites is enhanced relative to that of recycled PVC and this is shown in Figure 3. This table includes the temperature at which 10% degradation starts as a measure of the onset of the degradation, the temperature at which 50% degradation occurs as a measure of the mid-point of the degradation and the residue of non-volatile at 800°C, char. From the table and figure, it is obvious that the degradation of the nanocomposites is retarded as the contents of clay increase.

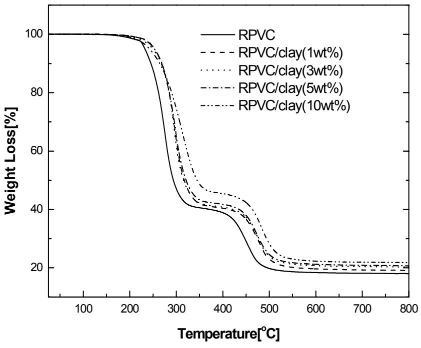


Figure 3. Thermal decomposition behaviors of the nanocomposites

Measurement of dimensional changes and coefficient of thermal expansion (CTE)

Linear dimension changes of recycled PVC/clay nanocomposites are shown in Figure 4. It is known that the dimensional changes of the nanocomposites over 30~55°C are highly decreased with the increments of clay loading. This result means that the thermal stability of the nanocomposites is highly improved compared to recycled PVC. Coefficients of thermal expansion of the nanocomposites from TMA analysis are presented in table 1. CTE values are decreased considerably with increasing the clay contents.

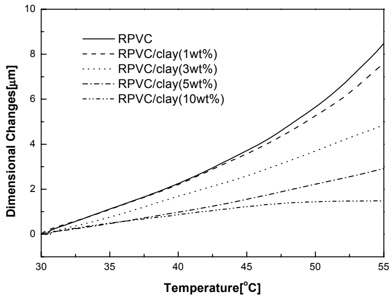


Figure 4. Measurement of linear dimensional changes of the nanocomposites

clay contents [wt.%]	Coefficient of thermal expansion [μm/m·°C]
None	360.0
1	319.8
3	195.0
5	104.6
10	64.6

Table 1. Coefficient of thermal expansions of recycled PVC/clay nanocomposites

Dynamic mechanical analysis of the nanocomposites

Figure 5 shows the storage modulus of the nanocomposites as a function of temperature. As shown in Figure 5, the storage moduli (G′) of the nanocomposites are all higher than that of recycled PVC. The nanocomposites of the highest content of clay show the highest storage modulus. Especially, the nanocomposite with 10 wt.% clay loading shows the noteworthy increased storage modulus compared to the nanocomposite with 1, 3 and 5 wt.% clay loadings. To clarify this result more precisely, the storage modulus of the nanocomposites relative to that of recycled PVC is shown in Figure 6. The relative storage modulus of the nanocomposites below the glass transition temperature was relatively small. However, above the glass transition temperature they drastically increased up to the peak tops at about 50~60°C and then decreased. For instance, at 55°C, the storage modulus of the nanocomposite with 10 wt.% clay loading is 11 times compared to recycled PVC. It was thought that the polymer chain mobility was confined near T_g by the rigid clays so that the relative storage modulus was increased.

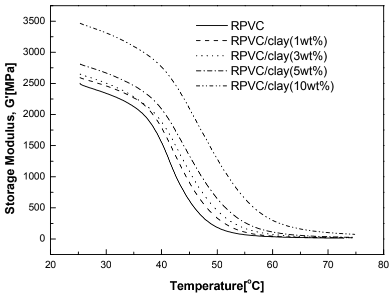


Figure 5. Measurement of the storage modulus of the nanocomposites

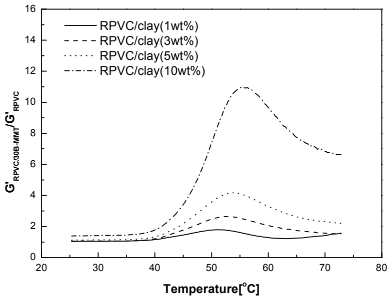
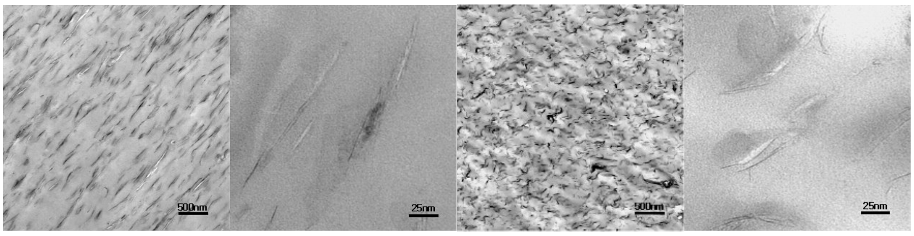


Figure 6. Measurement of the relative storage modulus of the nanocomposites

Transmission electron microscopy

Figure 7 shows the TEM images of the nanocomposites. It is clear from Figure 7(a) and (c) that the clay is dispersed uniformly throughout the recycled PVC matrix. Still, some of small black spots may be an indication of some poorly dispersed clay aggregates. The higher magnification images in Figure 7(b) and (d), however, show the fully exfoliated individual clay layers. It is obvious that the nanocomposites have exfoliated structures rather than intercalated structures, in which the stacked layers are exfoliated to individual silicate layers. From the TEM images, it is confirmed that the presence of a primarily exfoliated structure along with some intercalated structure.



(a) (b) (c) (d)

Figure 7. TEM micrographs of nanocomposites: (a) clay 5wt.%(x 20,000), (b) clay 5wt.%(x 400,000), (c) clay 10wt.%(x 20,000), (d) clay 10wt.%(x 400,000)

Conclusions

Recycled PVC/clay nanocomposites with exfoliated dispersions were obtained via melt mixing of recycled PVC and clay. The plasticizers act as a co-intercalator between recycled PVC and clay and make it feasible to achieve the exfoliated structure. Thermal decomposition behaviors and linear dimensional changes of the nanocomposites are improved compared to recycled PVC and the degree of the improvement of properties is proportional to the contents of clays. The coefficients of thermal expansion are decreased with addition of clays. The storage moduli of the nanocomposites are also increased compared to recycled PVC. At 55°C, the storage modulus of the nanocomposite with 10wt.% clay content was 11 time higher than that of recycled PVC.

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