Mechanical Properties and Fracture Behavior of PVC-Bentonite Nanocomposites

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1. Abstract

The nanostructure, mechanical properties and fracture behavior of polyvinyl chloride (PVC)-bentonite nanocomposites have been investigated. Nanocomposites with 5wt % concentration of bentonite were prepared by melt extrusion followed by two-roll-milled processing. X-ray scattering was utilized to study the micro and nanostructure of the two-roll-milled sheets. The nanocomposites were compounded with two types of coupling agents, KZTPP® and Tamol 2001®. Optical microscopy showed that the materials remained optically transparent, i.e., they did not show evidence of nanoclay agglomeration. The WAXS patterns of PVC-bentonite-KZTPP nanocomposite were anisotropic, suggesting flow-induced preferred orientation of the nanoplates. Moreover, the *001* reflection of the bentonite was shifted towards smaller angles, suggesting that the nanoplates were intercalated by the macromolecules. On the other hand, the WAXS patterns of PVC-bentonite-Tamol 2001 nanocomposite remained isotropic and did not show evidence of bentonite, suggesting exfoliation of the nanoplates. The nanocomposites showed an increase in glass transition temperature T_g, with the sequence $T_{g,\mathrm{PVC}} < T_{g,\mathrm{KZTPP}} < T_{g,\mathrm{Tamol\ 2001}}$. Tensile fracture toughness was investigated; the tests revealed that the Young's modulus and yield stress are enhanced for the intercalated nanocomposite. Strikingly, the exfoliated nanocomposite showed similar tensile deformation as the neat polymer.

2. Introduction

Polyvinyl chloride (PVC) is one of the major thermoplastics used today (world-wide production is considered in 36 million tons per year). 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. Preparing PVC/clay nanocomposites may be one of the effective ways to improve this material's performance. For example, the PVC/MMT nanocomposites produced by melt compounding with organically modified MMT appeared to exhibit better performance than those produced with untreated clays [1-5]. It was reported that they showed an improvement in mechanical and thermal properties [3-5], better dispersion [5], enhancement of stiffness, higher impact strength and good optical properties [1]. Organically modified MMT by ammonium cations had a great influence on the hybrids prepared by melt compounding, while they had not obvious effect on the PVC/MMT nanocomposites produced via in situ polymerization [5]. In the present work PVC-bentonite nanoclay was compounded with two different processing additives. The thermal and mechanical properties and microstructure are investigated.

3. Experimental

3.1 Materials

The as-received extruded and rolled-milled sheets of about 3.25 mm thickness consist of PVC with $\overline{M}_w \approx 70{,}000$ g/mol (Rohm & Haas Co.). Nanocomposites were prepared by adding 5 wt % bentonite and 0.5 wt % of KZTPP®, a flame retardant, cyclo[dineopentyl (diallyl)] pyrophosphate dineopentyl (diallyl) zirconate (Kenrich Petrochemicals Inc.,Bayonne, N.J., USA); and Tamol 2001®, a hydrophobic high-performance pigment dispersant (Rohm and Haas Co, Philadelphia PA, USA). The samples are listed in Table 1.

Table 1 Thermal and mechanical properties of PVC nanocomposites

Sample	T_g (°C) 1st heat	*E'* (MPa) 110 °C	E_a (KJ/mol)	*E* (GPa)	UTS (MPa)
PVC	78.7	13.3	856	4	59
PVC + 5 % Bentonite + 0.5 % KZTPP	80.5	16.9	861	6	86
PVC + 5 % Bentonite + 0.5 % Tamol 2001	81.2	19.1	870	4	60

3.2 Mechanical properties

The samples were mechanically tested in accordance with the ASTM D638 standard [6]. Tension tests were carried out at room temperature on the universal testing machine Instron 4206 using a crosshead speed of 1 mm/min.

3.3 Microscopy

Optical micrographs of as-molded and fractured samples were obtained in reflection mode and under white light conditions. Photomicrographs were acquired using a Moticam 100 digital camera manufactured by Motic Inc. Image analyses were carried out using ImageTool software, v3.0 (UTHSCSA, Texas, USA).

3.4 Synchrotron X-ray scattering

The X-ray scattering data were collected at the Advanced Photon Source, Argonne National Laboratory (Argonne, Illinois, USA) on the DND-CAT beam line 5. The samples were investigated in transmission mode, the patterns were collected using the CCD Mar 165 and exposure time of 60 seconds. The sample-to-detector distance was 782 mm, calibrated using silver behenate.

4. Results and discussion

The microstructure was investigated via X-ray scattering [7]. Figure 1 shows X-ray patterns for PVC and the nanocomposites. PVC (1a) shows two crystalline (weak) reflections superposed on a broad amorphous halo, the KZTPP nanocomposite (1b) shows small-angle equatorial reflections corresponding to d-spacing of 1.51 nm ($d_{bentonite}$=1.206 nm). This indicates that the macromolecules have intercalated the nanoclay. Finally, the Tamol 2001 nanocomposite does not show evidence of bentonite suggesting that the nanoclay has been exfoliated. The glass transition temperature, tensile modulus and activation energies, T_g, E', E_a, were determined by dynamic mechanical analysis (DMA) using temperature-frequency sweeps [7], see Table 1. T_g, E' and E_a increased slightly relative to the neat PVC. There is a greater increase of these properties for the exfoliated nanocomposite.

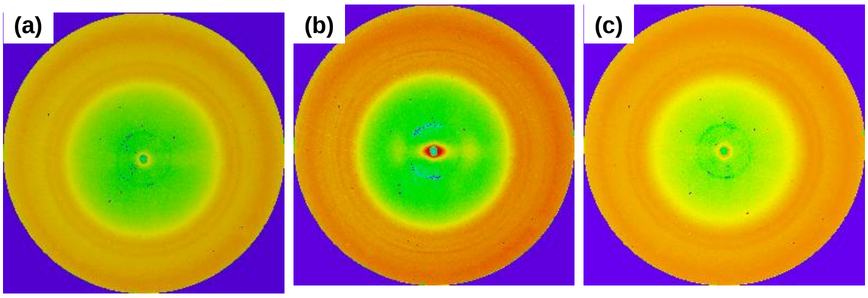

Figure 1. X-ray scattering pattern of PVC-bentonite nanocomposites. (a) neat PVC, (b) PVC-KZTPP, and (c) PVC-Tamol 2001. Extrusion direction is vertical.

Figure 2 shows strain-stress curves for PVC and the nanocomposites. PVC shows a pronounced yield stress, followed by a cold drawing plateau and a strain hardening region before reaching the strain at failure. PVC-Tamol 2001 nanocomposite shows very similar behavior to the neat PVC except that the strain at failure is greatly reduced. Finally, PVC-KZTPP nanocomposite showed a significant increase in yield stress (UTS), higher Young's modulus and slight reduction of strain at failure. The micrographs of the fractured surfaces show that neat PVC suffers slight plastic deformation before final fracture (micrographs a and b). The nanocomposite PVC-bentonite-KZTPP (2c) shows no plastic deformation at the fractured surface. Finally, the fractured surface of the nanocomposite PVC-bentonite-Tamol (2d) show plastic deformation and slight fibrillation indicating a failure by decohesion.

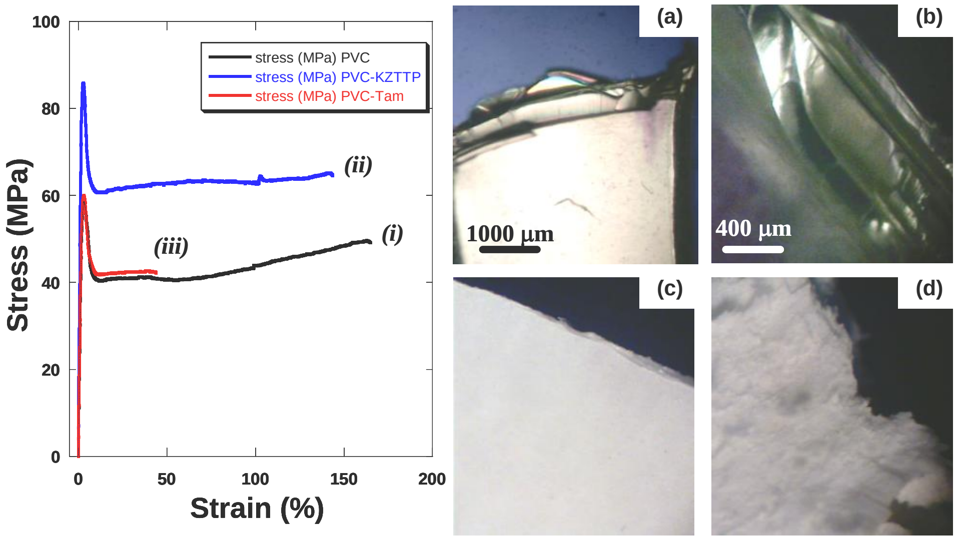

Figure 2. Stress-strain curves for PVC nanocomposites (i) neat PVC, (ii) PVC-KZTPP and (iii) PVC-Tamol 2001. Optical micrographs of fractured regions: (a) neat PVC under POM, (b) neat PVC, (c) PVC-KZTPP and (d) PVC-Tamol 2001.

5. Conclusions

The nanostructure, glass transition temperature, UTS, strain at failure and Young's modulus were influenced by the sort of additive added to PVC-bentonite nanocomposites. KZTPP promoted intercalation of the nanoclay whereas Tamol2001 produced nanoclay exfoliation. The intercalated nanocomposite showed better tensile mechanic properties.

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6. References

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