

MECHANICAL AND THERMAL PROPERTIES OF NANOSIZED TITANIUM DIOXIDE FILLED RIGID POLY(VINYL CHLORIDE)

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Abstract Nano-sized rod-like titanium dioxide (TiO₂) filled rigid poly(vinyl chloride) (PVC) nanocomposites were prepared by using injection-molding method. Vicat, Charpy impact and tensile tests as well as thermogravimetric and dynamic mechanical analyses were used to characterize the structure and properties of the nanocomposites. The results showed that nano-TiO₂ could improve Vicat softening temperature and also improve thermal stability of PVC during the stages of dehydrochlorination and formation of carbonaceous conjugated polyene sequences, which can be ascribed to restriction of the nanoparticles on the segmental relaxation as being evidenced by raises in glass transition and β -relaxation temperatures of PVC upon filling TiO₂. Addition of TiO₂ nanoparticles less than 40 phr (parts per hundreds of resin) could significantly improve impact strength of the composites while the TiO₂ agglomeration at high contents leads to a reduction in impact toughness.

Keywords: Poly(vinyl chloride) (PVC); Titanium dioxide (TiO₂); Thermal property; Mechanical property; Impact strength.

INTRODUCTION

Poly(vinyl chloride) (PVC) represents an important polymer worldwide due to its outstanding properties and versatility. However, it exhibits low toughness and poor processing stability. Extensive studies have been focused on PVC composites with enhanced material performance and cost advantages. The use of fillers has been a common practice to enhance performance of thermoplastics such as heat distortion temperature, hardness, toughness, dimensional stability, stiffness and mold shrinkage.

Recently, various nanosized fillers such as montmorillonite (MMT), silicon dioxide (SiO₂) and calcium carbonate (CaCO₃) have been extensively reported to enhance toughness, stiffness and heat resistance of polymers^[1–20]. Mechanical and thermal properties are of importance for polymeric composites used as structural materials, which are greatly dependent on the characteristics of the filler, and the interaction between the filler and the matrix. Chen *et al.*^[19] modified nano-SiO₂ to mediate the interfacial interaction with PVC and found that high energy vibromilling modified SiO₂ particles can improve mechanical properties of PVC composites remarkably. Nano-CaCO₃ can promote fusion of PVC more than micro-CaCO₃^[20]. More than 5 phr (parts per hundreds of resin) well dispersed nano-CaCO₃ could improve impact strength, heat stability and weathering resistance simultaneously^[21]. Titanate-treated CaCO₃ with smaller particle sizes can greatly improve tensile and impact strengths of PVC composites due to improved interfacial adhesion^[8]. MMT could improve mechanical properties of PVC depending on the preparation methods. The nanocomposites prepared *via* solution blending followed by melt compounding exhibit thermal properties superior to those by solution blending^[13].

Nanosized titanium dioxide (TiO₂) with a high screen effect over the whole UV range is one of the most

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common fillers used in nanocomposites. TiO_2 may act as a UV absorber preventing penetration of UV light beyond a depth of 50–100 μm and protecting PVC from degradation^[22–24]. A small fraction of TiO_2 is usually used to improve photostability of PVC due to its screen effect on photooxidation of polyene (photobleaching). It may also be activated by UV in the presence of water and oxygen, therefore accelerating PVC degradation^[25–28]. Nano- TiO_2 has been used as a filler to improve mechanical properties of polymers. Hussain *et al.*^[29] investigated influence of coupling agents on mechanical properties of TiO_2 particulates filled epoxy composites and found that titanate coupling agent could improve Young's modulus and flexural strength more significantly than silanes. Ng *et al.*^[30] synthesized nano- TiO_2 /epoxy composites exhibiting tougher and higher scratch resistance than the traditional filled composites. A low concentration of nano- TiO_2 could improve essential work notably while lower plastic work fairly for polyamide 66 at room temperature^[31]. However, little attention has been paid to influence of nano- TiO_2 on mechanical and thermal properties of PVC nanocomposites. In this work, we prepared rigid PVC/ TiO_2 nanocomposites by melt blending and injection molding. Influence of nano- TiO_2 on thermal and mechanical properties of the rigid nanocomposites was studied.

EXPERIMENTAL

Materials

One hundred phr PVC (S-700, Qilu Petrochem. Co., Shandong, China) and 0–80 phr silane modified rutile TiO_2 nanoparticles (Hangzhou Wanjing New Material Co., Zhejiang, China) were used to prepare the PVC nanocomposites. The additives used were 2 phr organictin (HTM-2010, Haipudun Chem. Co. Ltd., Zhejiang, China), 3 phr glyceryl monostearate (GMS), 3 phr acrylic processing aid (ACR) (401, Hangzhou Chuanhua Co. Ltd., Zhejiang, China) and 0.5 phr dioctyl phthalate (DOP) (Hangzhou Chuanhua Co. Ltd., Zhejiang, China).

Sample Preparation

All additives were mixed into PVC powders using a high-speed mixer (10 L, Wuhan Yiyang Plastics Machinery Co. Ltd., Hubei, China). The mixture was melt blended in a conical twin-screw extruder (Wuhan Yiyang Plastics Machinery Co. Ltd., Hubei, China). Temperature of the extruder was maintained at 157°C, 167°C, 175°C and 170°C, respectively, from the hopper to the die. The extrudate was pelletized by hot cutting and the pellets were injection molded into dumbbell tensile specimens according to GB16421-1996 using an injection molding machine (Boy 55, Boy, Germany) in the temperature range from 155°C to 170°C with a mold temperature of 35°C.

Characterization

The specimens were placed in a thermostatic container (MT3065, Guangzhou ESPEC Environmental Equipment Co. Ltd., China) to equilibrate at prescribed temperatures, and were then taken out quickly. Charpy impact tests were carried out using a pendulum impact testing machine (ZBC 1400-2, MTS Systems Co. Ltd., China). At least ten specimens were tested for each set of samples.

Tensile tests were performed using a universal testing machine (CMT4202, Shenzhen SANS Test Machine Co. Ltd., China) according to GB16421-1996 in a tensile velocity of 50 mm/min at room temperature (15°C). At least eight specimens were tested for each set of samples.

Ultrathin sections of 15–20 nm were cut from the injection-molded bars using a microtome (LKB-5, LKB Co., Switzerland). Dispersion of nano- TiO_2 in the matrix was examined using TEM (JEM-1230, JEOL Ltd., Japan) with an accelerating voltage of 120 kV.

SEM (S-4800, Hitachi Co., Japan) observation was performed to study morphology of the nanocomposites. Micrographs were taken from the fracture surfaces of the specimens after being coated with gold.

DMA was performed on a DMA 242 thermal analyzer (NETZSCH-Gerätebau GmbH, Germany) using a single cantilever geometry. Specimens with a size of 4 mm × 10 mm × 40 mm were submitted to sinusoidal deformation of 0.2 mm amplitude at frequency 1 Hz in the temperature range from –120°C to 180°C with a heating rate of 3 K/min.

Vicat softening test was carried out on a Vicat softening tester (CEAST Scientific Instruments Co., Italy) at

a weight of 10 N and a heating rate of 50 K/h. Vicat softening temperature (T_v) was recorded at which the needle penetrated 1 mm.

TGA was conducted on a thermogravimetric analyzer (SDT Q600, TA, USA) at a heating rate of 5 K/min from ambient temperature to 700°C under nitrogen atmosphere.

RESULTS AND DISCUSSION

Figure 1 shows toughness of PVC nanocomposites as a function of TiO_2 content. Filling improves impact strength from 2.7 kJ/m² of rigid PVC to a maximum of 6.1 kJ/m² at 40 phr TiO_2 . Further increasing particle loading gives rise to lower impact energy due to aggregation effect of the nanoparticles in the matrix. PVC/ CaCO_3 nanocomposites prepared by *in situ* polymerization is tougher than pure PVC and Charpy impact energy reaches a maximum of 5.25 kJ/m² at 5 wt% nano- CaCO_3 ^[6]. Xie *et al.*^[32] prepared *in situ* PMMA modified nanosized antimony trioxide to fill PVC and found that Charpy notched impact strength of the nanocomposite with 2.5 wt% nanoparticle increases to a maximum of 5.85 kJ/m² from 3.09 kJ/m² of PVC. Xie *et al.*^[7] also prepared PVC composites filled with 20 wt% of PMMA-coated-talc and found an improvement of impact strength from 3.20 kJ/m² of pure PVC to 3.37–4.05 kJ/m². It is rather surprising that TiO_2 at a loading as high as 40 phr could improve the Charpy impact strength more effectively than other nanosized fillers. Probably, the well dispersed TiO_2 particle could absorb impact energy *via* interfacial debonding^[33].

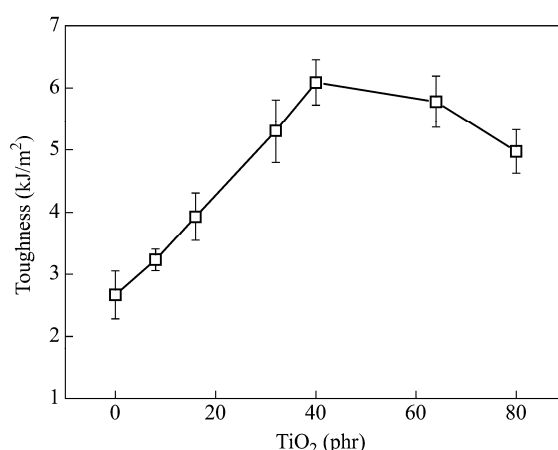


Fig. 1 Influence of TiO_2 content on impact toughness of PVC nanocomposites

Figure 2 shows SEM micrographs taken from impact-fractured surfaces of the nanocomposites. Rigid PVC exhibits brittle failure characteristic. The nanocomposite at 8 phr TiO_2 shows some ductile characteristics with appearance of delamination and corrugation. A few elliptical voids due to interfacial debonding can be observed around TiO_2 nanoparticles, which is in agreement with the cavitation mechanism of micro-sized rigid particles reported by Xie *et al.*^[6] and Zuiderduin *et al.*^[33] TiO_2 at 40 phr forms aggregates of about 0.4 μm and the fracture surface of the composite forms a great many of microvoid responsible for the improved impact strength. Large agglomerates of more than 0.6 μm appear in the composite with 64 phr TiO_2 , which act as the origin of failure thus reduce the impact strength.

Figure 3 shows TEM micrographs of PVC nanocomposites. The nano- TiO_2 particles are rod-shaped with a short axis of about 30 nm and an aspect ratio of about 3 but they form prolate aggregates even at 16 phr content. The nanocomposite with 40 phr contains well dispersed rod-shaped particles and also aggregates. Nano- TiO_2 at high contents above 40 phr aggregates seriously, accounting for the reduced toughness.

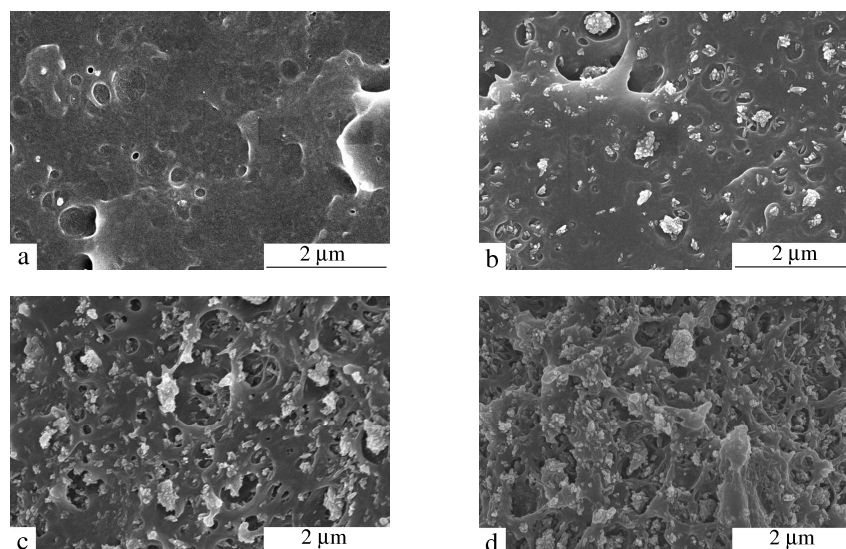


Fig. 2 SEM micrographs of PVC nanocomposites with 0 phr (a), 8 phr (b), 40 phr (c) and 64 phr TiO₂ (d)

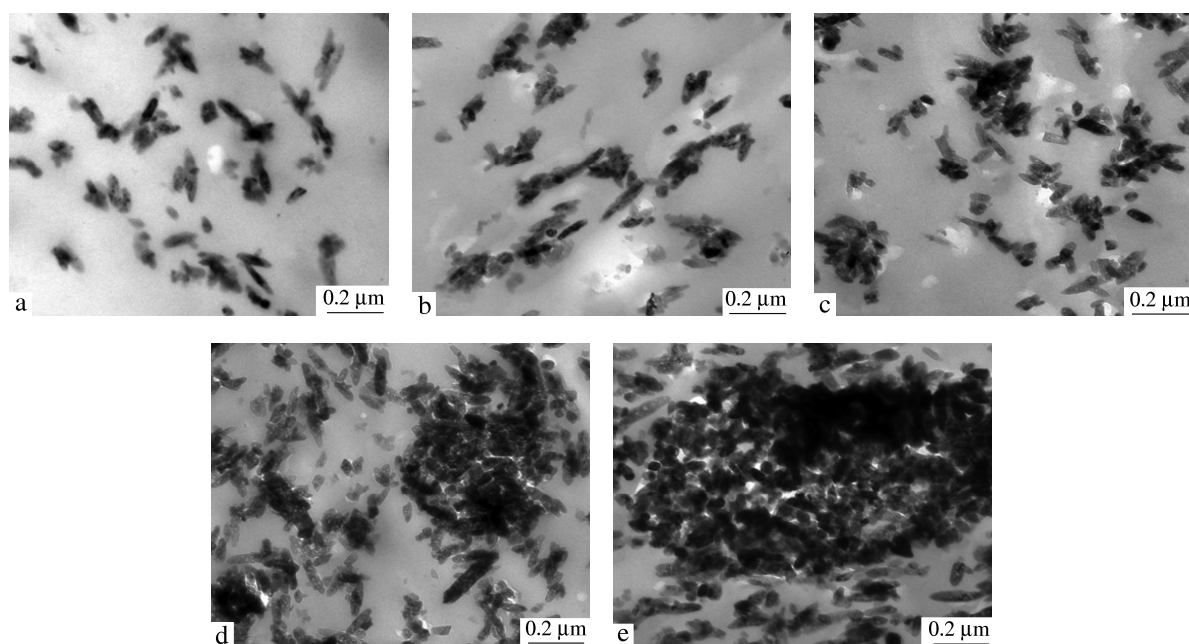


Fig. 3 TEM micrographs of PVC nanocomposites with 16 phr (a), 32 phr (b), 40 phr (c), 64 phr (d) and 80 phr TiO₂ (e)

Figure 4 shows engineering stress-strain (σ - ϵ) curves of PVC nanocomposites. PVC fractures at break strain $\epsilon_b = 23\%$ immediately after yielding, and the yielding strain $\epsilon_y = 15\%$ and yielding stress $\sigma_y = 69.6$ MPa. Both ϵ_y and σ_y of nanocomposites reduce gradually with increasing TiO₂ content. The rigid PVC breaks during the strain softening following the yielding while the strain softening is gradually depressed with increasing TiO₂ loading. Table 1 shows σ_y , ϵ_y , Young's modulus E , stress at break σ_b and strain at break ϵ_b of the nanocomposites. PVC and its nanocomposites at TiO₂ loading below 64 phr break at a narrow ϵ_b range from 21.7% to 23.8%. The nanocomposite with 80 phr TiO₂ breaks at a low ϵ_b of 16.5% due to the great filler agglomeration. In comparison, σ_y of the nanocomposites is significantly higher than that of 28 phr nano-CaCO₃ filled PVC/acrylonitrile-butadiene-styrene resin (100/20) blend^[34].

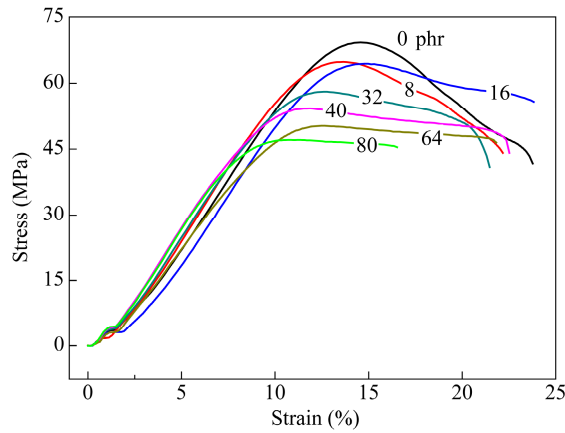


Fig. 4 Stress-strain (σ - ϵ) curves of PVC nanocomposites with different TiO_2 contents as indicated

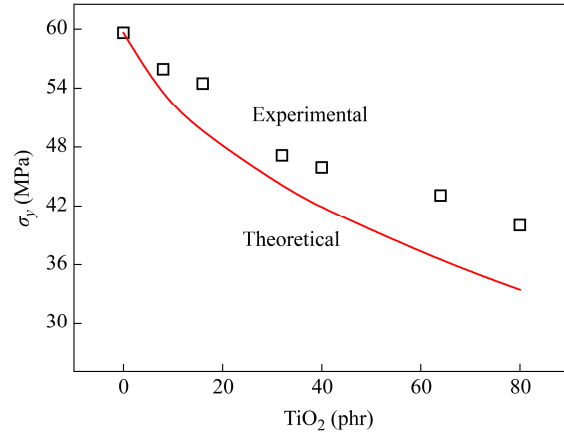


Fig. 5 Variation of yielding stress σ_y with TiO_2 content for PVC nanocomposites

As shown in Fig. 5, σ_y of the nanocomposites decreases with increasing TiO_2 content, which could be ascribed to the nano- TiO_2 promoting local yielding in the interstitial matrix between the particles^[35]. σ_y of filled composites can be predicted by Nicolais-Narkis theory^[36]

$$\sigma_y = \sigma_{ym} (1 - 1.21\phi^{2/3}) \quad (1)$$

where σ_{ym} is yielding strength of the matrix and ϕ is volume fraction of filler. The experimental σ_y values are higher than the Nicolais-Narkis theory prediction, which can be readily assigned to the interfacial interaction that restricts the molecular motion of the PVC matrix.

Table 1. Mechanical properties of the nanocomposites

TiO_2 content (phr)	E (MPa)	σ_y (MPa)	ϵ_y (%)	σ_b (MPa)	ϵ_b (%)
0	655.5	69.8	14.7	43.7	23.6
8	679.6	65.0	13.4	45.2	22.0
16	644.7	65.0	14.7	55.8	23.8
32	666.3	57.8	12.2	49.8	20.5
40	680.2	54.5	11.6	47.8	22.2
64	687.0	50.7	12.1	47.0	21.7
80	757.6	46.7	10.0	45.4	16.5

Dynamic mechanical properties of filled polymers are greatly affected by interfacial interaction between the inorganic particles and the matrix. DMA is helpful for determining the interaction between different components at molecular level^[37]. Figure 6 shows the storage modulus E' and loss factor $\tan\delta$ as a function of temperature T for the nanocomposites at 1 Hz. PVC experiences the β -transition from -102°C to 24°C ascribed to the localized conformational transitions^[38, 39], as a broad transition peak appeared in the $\tan\delta$ curves. At the α -transition, E' drops sharply by two orders of magnitude. According to the peak temperatures of the loss modulus curve, the β - and the α -transition (glass transition) temperatures (T_β and T_g) of pure PVC are determined at -56.1°C and 87°C , respectively. Increasing TiO_2 content causes an improvement of E' in the glassy state and E' reaches maximum at 64 phr TiO_2 . Table 2 shows T_β and T_g of the nanocomposites. It is seen that both T_β and T_g increase with increasing TiO_2 content and T_β varies more significantly than T_g , which is ascribed to strong interfacial interaction between PVC matrix and the nano- TiO_2 particles^[6, 40]. In comparison, filling PVC with less than 5 wt% micro- or nano- CaCO_3 by melt compounding^[11] or by *in situ* polymerization does not cause marked changes of T_g . The DMA result confirms that nano- TiO_2 particles stiffen the nanocomposites by restricting the localized conformational transitions and the segmental motion of the PVC matrix.

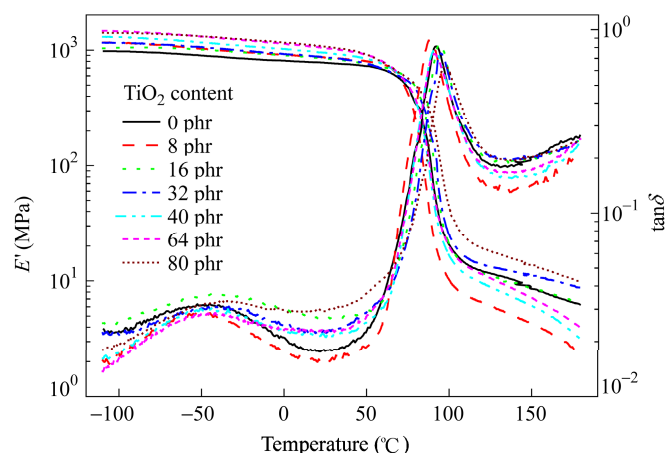


Fig. 6 Storage modulus E' and loss tangent $\tan\delta$ against temperature T for the nanocomposites

Table 2. β - and α -transition temperatures of the nanocomposites

TiO ₂ content (phr)	0	8	16	32	40	64	80
T_{β} (°C)	-56.1	-51.5	-47.0	-43.5	-42.9	-41.9	-39.2
T_{α} (°C)	87.0	88.2	88.7	88.8	89.3	90.6	91.8

Figure 7 shows the influence of TiO₂ content on Vicat softening temperature T_v of PVC nanocomposites. T_v increases tremendously with increasing TiO₂ content, from 78°C of PVC to 101°C for the nanocomposite containing 80 phr TiO₂, which could be related to the TiO₂ nanoparticles creating a protective shielding layer on the surface^[17]. Pan *et al.*^[41] found that T_v of PVC/Na⁺-MMT nanocomposites prepared *via* emulsion polymerization increases progressively from 77°C to 92°C with MMT loading varying from 0 to 6.0 wt%. However, Madaleno *et al.*^[13] found that direct blending PVC with Na⁺-MMT or organically modified MMT results in a drastic decrease in T_v especially for PVC containing 2–5 phr nanoclay. They suggested that MMT layers dispersed in PVC matrix may act as a plasticizer increasing the distance between PVC chains and thus decreasing the intermolecular interaction between PVC chains.

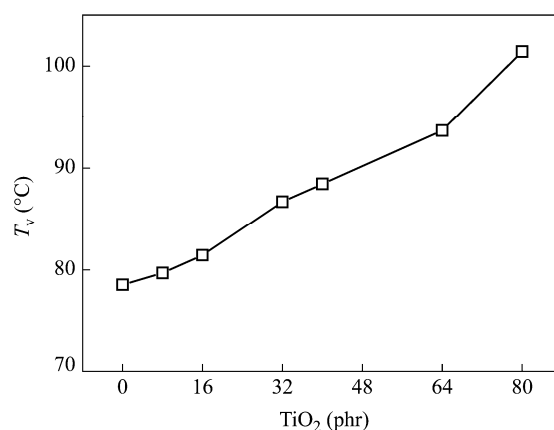


Fig. 7 T_v as a function of TiO₂ content for PVC nanocomposites

Figure 8 shows TGA and derivative thermogravimetric (DTA) curves of the nanocomposites in nitrogen atmosphere. The nanocomposites exhibit a two-stage degradation^[17, 42]. The first one is attributed to dehydrochlorination of PVC, leaving conjugated polyene sequences^[43]. The second decomposition above 400°C corresponds to thermal cracking of the carbonaceous conjugated polyene sequences, resulting in volatile

products of benzene, toluene, naphthalene, methylnaphthalenes and further polyaromatic hydrocarbons. The formation of aromatic products undergoes *via* intramolecular cyclic reactions^[44]. The temperature at 5 wt% weight loss is located at 263°C for PVC and it is shifted to 265–271°C in the nanocomposites. The nanocomposites demonstrate a marked reduction in the decomposition rate during the stage of dehydrochlorination. There are two decomposition peaks as shown in the DTA curves during PVC decomposition. The temperature at maximum weight loss rate is 289°C for PVC while it is shifted to 310°C upon adding 8 phr TiO₂. The temperature at maximum weight loss rate is lowered upon further loading TiO₂, to 290°C in the nanocomposite containing 80 phr TiO₂. The second DTA peak temperature of pure PVC located at 451°C is shifted to 466°C for the nanocomposite. TiO₂ could form chlorides with HCl, which depresses the HCl and benzene formation^[45]. The results show that the well dispersed TiO₂ particles can improve the thermal stability of PVC.

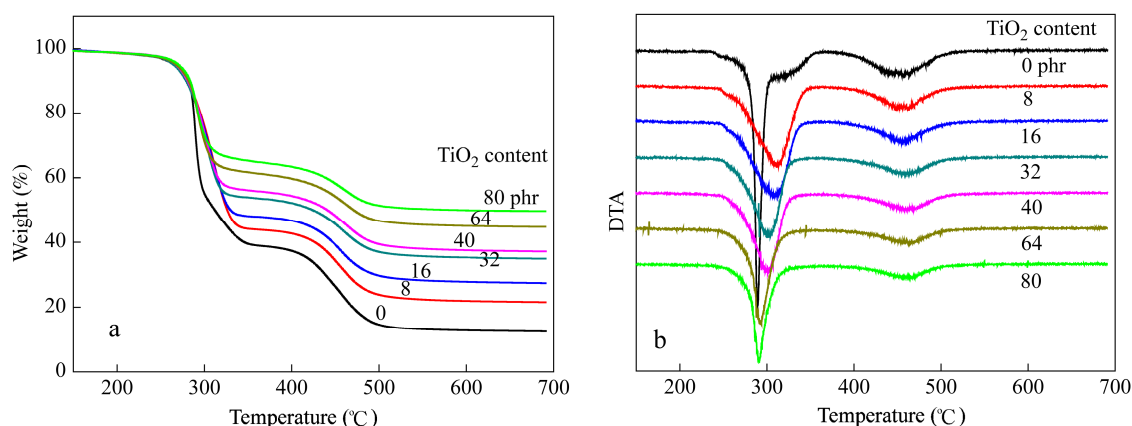


Fig. 8 TGA (a) and DTA (b) curves of PVC nanocomposites in nitrogen atmosphere

CONCLUSIONS

Rod-shaped TiO₂ nanoparticles act as effective filler for improving performance of injection molded rigid PVC nanocomposites. Incorporation of nano-TiO₂ could significantly improve thermal stability of rigid PVC, which is accompanied with shift of the β -relaxation and the glass transition of PVC to high temperatures. The nanoparticles well dispersed in PVC could improve impact strength of the composites.

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