

Effects of Poly(1,2-propylene glycol adipate) and Nano-CaCO₃ on DOP Migration and Mechanical Properties of Flexible PVC

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ABSTRACT: Nano-CaCO₃ was used as nano-scale filler and poly(1,2-propylene glycol adipate) (PPA) was used as polymeric plasticizer in flexible poly(vinyl chloride) (PVC) sheets for the partial replacement of di(2-ethyl hexyl) phthalate (DOP) in this paper. The effect of PPA and nano-CaCO₃ on restraining DOP migration was evaluated via extraction tests. The results showed that the introduction of nano-CaCO₃ can decrease the extraction rate of DOP in the PVC matrix. The tensile strength and elongation at break of CaCO₃-1/PPA-20/DOP-30/PVC were similar to those of DOP-50/PVC, and CaCO₃-1/PPA-20/DOP-

30/PVC exhibited the superior suppression of DOP migration compared with DOP-50/PVC. Thermogravimetry analysis (TGA) indicated that the addition of nano-CaCO₃ effectively improved the thermal stability of the nanocomposites. Therefore, the combination of PPA and nano-CaCO₃ is an effective approach to suppress the migration of DOP. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1737–1743, 2012

Key words: PVC; DOP; nano-CaCO₃; PPA; migration

INTRODUCTION

Polyvinyl chloride (PVC) is one of the most important thermoplastics due to its excellent balance between low costs and general properties.¹ Flexible PVC is extensively used in the medical field and further used for packaging purposes. PVC is mixed with large amounts of plasticizers to obtain the desired flexibility and durability.² It is known that the plasticizer can migrate to the surface of the PVC matrix when it comes into contact with air, liquid, and an absorbent solid material.³ Plasticizer migration can reduce the functional performance of PVC, which is potentially harmful to the human body.^{4,5} The conventional plasticizer DOP, with the molecular weight of 390, is liquid and not chemically bound to the polymer. So it can escape easily from the polymer matrix during storage or get extracted to the medium while in use.^{5,6} DOP will not be substituted in many fields for an extended period as the most commonly used plasticizer for PVC. Several

approaches that refer to chemical modification or physical treatment on PVC have been developed to reduce DOP migration from flexible PVC.^{7,8} However, this study focuses attention on the polymeric plasticizer and the inorganic nano-particles to suppress DOP loss.

Under the given conditions, the permanence of a plasticizer in a flexible PVC compound depends upon three major factors which include structure, molecular weight, and polarity. Previous research showed that the bulk plasticizer with weight average molecular weight of 4060 migrated much slower than the low molecular weight species having molecular weights between 300 and 1100.⁹ It was also reported that the partial replacement of DOP with nitrile rubber (NBR), carboxylated nitrile rubber (XNBR), or epoxidized natural rubber (ENR) can suppress DOP migration.¹⁰ Plasticizer retention can be enhanced via increasing the plasticizer molecular weight, because it becomes more difficult for the plasticizer to migrate from the bulk to the surface layer.¹¹ Due to low volatility, high resistance to extraction, and low leachability offered by polymeric plasticizer, its application can alleviate the problem of plasticizer loss.¹²

Poly(1,2-propylene glycol adipate) (PPA) is a kind of polymeric plasticizer with a high molecular weight of 2000. The introduction of PPA was to reduce the migration of plasticizer DOP. Owing to

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TABLE I
Composing of PVC Samples

Sample code	Material component (phr)					
	PVC	Ca/Zn stabilizer	Stearic acid	DOP	Nano-CaCO ₃	PPA
DOP-50/PVC	100	4	0.4	50	0	0
CaCO ₃ -1/DOP-50/PVC	100	4	0.4	50	1	0
CaCO ₃ -3/DOP-50/PVC	100	4	0.4	50	3	0
CaCO ₃ -5/DOP-50/PVC	100	4	0.4	50	5	0
DOP-30/PVC	100	4	0.4	30	0	0
PPA-20/DOP-30/PVC	100	4	0.4	30	0	20
CaCO ₃ -1/PPA-20/DOP-30/PVC	100	4	0.4	30	1	20
CaCO ₃ -3/PPA-20/DOP-30/PVC	100	4	0.4	30	3	20
CaCO ₃ -5/PPA-20/DOP-30/PVC	100	4	0.4	30	5	20

ester bonds, the strong polar PPA has an affinity with DOP, so DOP cannot migrate to the surface of the PVC matrix easily.

Various nano-scale fillers, including montmorillonite, silica, calcium carbonate, and aluminum oxide, are reported to improve the properties of polymers such as toughness, stiffness, and heat resistance.¹⁰ Spherical nano-particles, which have low aspect ratio and large surface area, can result in strong interfacial interactions between the filler and the polymer matrix. Nano-CaCO₃ is one of the most common spherical nano-scale fillers for preparation of nanocomposites. Baohong Yang et al. have reported that inorganic nano-particles such as nano-CaCO₃ with high surface area effectively reduced plasticizer migration of flexible PVC.¹⁵

Little attention was paid to the combination of polymeric plasticizer and nano-scale particles to reduce DOP leaching. Thus in this paper, PPA and nano-CaCO₃ together were employed to enhance the resistance of DOP migration and improve the mechanical properties of the PVC matrix. Thermal stability and morphology of PVC composites with PPA and nano-CaCO₃ were also discussed in this paper.

EXPERIMENTAL

Materials

PVC resin (trade name SG-3, k-value 72–71, 1350–1250) was supplied by Tianjin Chemical Plant, China. Nano-CaCO₃ (density 2.5–2.6 g/m³; mean grain size 15–40 nm; shape of particle, cubic) was supplied by Shandong Haina Nanometre New Material Co. Ltd, China. DOP (analytically pure) was supplied by Tianjin Letai Chemical Supermarket. Both Ca/Zn stabilizer and stearic acid were supplied by Tianjin Worldlang International Trading Co. Ltd. PPA (viscosity, 3500–4500; density, 1.07–1.10.) was supplied by Lanxi Wanshengda Chemical Co. Ltd., China.

Sample preparation

Nano-CaCO₃ was dried at 60°C for 12 h in a vacuum oven before usage. PVC resin and required amounts of fillers are shown in Table I according to the formulation. All components were blended for 5 min by using a high-speed mixer (SK-106B). Mixing was carried out in two steps: (1) PPA or DOP was fully absorbed by the PVC resin. (2) Plasticized PVC was mixed with other powder (such as Ca/Zn stabilizer, stearic acid, and nano-CaCO₃). The mixture obtained was further melt blended using a two-roll mixer at 165°C for 5 min to give composite films of 1 mm thickness.

Migration of DOP

The experiments of DOP extraction from the solvent were conducted as follows: 2.000 g of composite film was introduced into stoppered erlenmeyer flasks (100 mL) and extracted at room temperature with 20 mL of hexane without shaking. The content of plasticizer leached from PVC samples was measured by High Performance Liquid Chromatography (HPLC). HPLC analysis was performed using Varian Prostar 210 LC pump operating at room temperature with a C₁₈ column (150 mm × 4.6 mm, 5.0 μm). The injected volume was 20 μL and the eluent was monitored at 224 nm with a Varian Prostar 325 LC Detector. Before injection, the liquor for determination was diluted with hexane into a suitable concentration. Separation was performed with a mobile phase consisting of a methanol/water mixture (9 : 1 v/v), pumped at a flow rate of 1.0 mL min⁻¹. The migration rate of the samples was calculated using the formula:

$$\text{migration rate (\%)} = W_1/W_2 \times 100 \quad (1)$$

where W_1 is the weight of the extracted DOP tested by HPLC; W_2 , initial weight of the test specimen.

Thermal stability

The thermal decomposition characteristics of the samples were determined using a thermogravimetric analyzer (Q500). The weight loss against temperature was measured at a heating rate of $20^{\circ}\text{C min}^{-1}$ from 20 to 600°C in nitrogen environment.

Tensile properties

The tensile properties were performed with a universal testing machine (CMT4503) in compliance with ISO 527.3 : 1995. All the tests were done at room temperature, at a testing speed of 100 mm min^{-1} . The sheets were cut into dumbbell-shaped specimens. Five specimens from each sample type were tested and the average value was reported.

Morphology

A scanning electron microscope (JSM-6380) was employed to study and record the fracture surface after tensile tests of the samples. The fractured specimen surfaces were coated with a thin layer (10–20 nm) of gold palladium. The coating was carried out by placing the specimen in a high vacuum evaporator and vaporizing the metal held in a heated tungsten basket.

RESULTS AND DISCUSSION

Migration of DOP

PVC plasticizers can be released from flexible PVC in different ways: (1) volatilization from the PVC surface to the air, (2) extraction from PVC to a liquid in contact with it, (3) migration from PVC to a solid or semisolid in contact with it, (4) exudation under pressure.^{13,15} According to the literature, hexane has been widely used in migration test for phthalates in plasticized PVC samples and for the evaluation of migration stability. It was preferred to obtain a fast preliminary indication to other media such as distilled water and mineral oil. So hexane was used as the extraction medium in the evaluation of DOP extraction.¹⁴

The migration rate is plotted against the extraction time as shown in Figure 1. After 24 h extraction by hexane CaCO_3 -1/DOP-50/PVC had the lowest migration rate (23.25%) among the CaCO_3 -n/DOP-50/PVC composite series [Fig. 1(a)]. Probably, nano- CaCO_3 can enhance the resistance of extraction of DOP due to its high surface energy and unsaturated bond of atoms.¹⁵ Leached DOP from PPA-20/DOP-30/PVC was less than that from DOP-30/PVC, which indicated that the introduction of PPA lowered the extraction rate of DOP. Moreover, the combination of 1 phr nano- CaCO_3 and 20 phr PPA

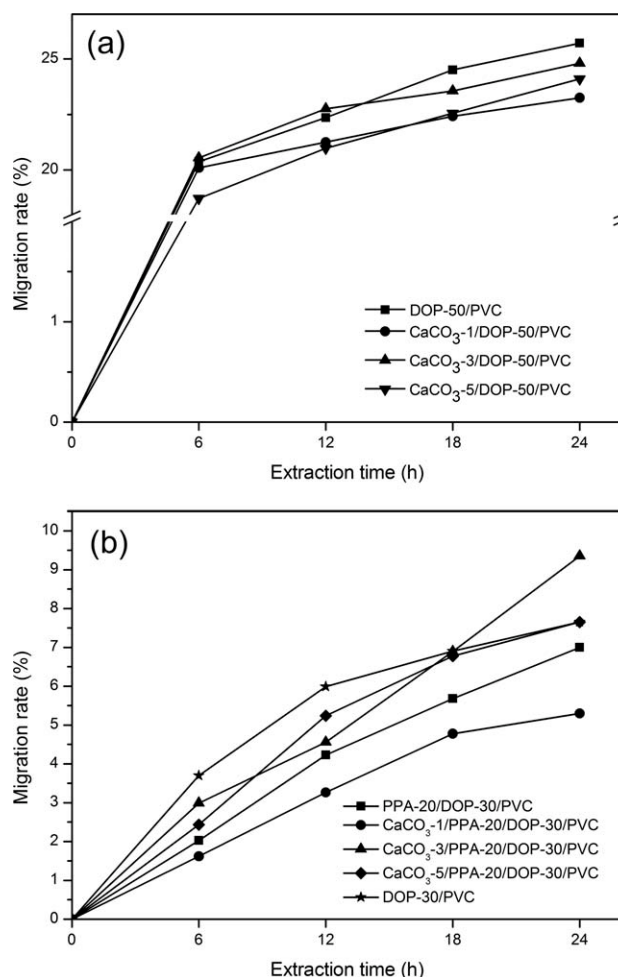


Figure 1 (a) Migration rate plotted against extraction time for CaCO_3 -n/DOP-50/PVC composites; (b) Migration rate plotted against extraction time for CaCO_3 -n/PPA-20/DOP-30/PVC composites.

together decreased the migration rate (5.30%, 24 h) of DOP by 30.7% compared with DOP-30/PVC (7.65%, 24 h) [Fig. 1(b)]. It is obvious that more time could increase the loss of plasticizers from the PVC samples. The increasing rate of migrated DOP from the CaCO_3 -n/DOP-50/PVC samples became slower after extraction time of 12 h, suggesting that DOP migration was close to the equilibrium state, whereas DOP in CaCO_3 -n/PPA-20/DOP-30/PVC composite films migrated more slowly. The molecular size of DOP is small enough to penetrate into the PVC polymer structure, so extraction of the plasticizer occurs. Conversely, the molecular size of PPA is too large to penetrate the PVC polymer structure. And at the same time, the ester bonds of PPA have an affinity with DOP due to its strong polarity. So the dissolution of DOP in hexane became more difficulty.

The DOP migration rates of PVC samples containing different amount of nano- CaCO_3 are shown in Figure 2. The addition of nano- CaCO_3 suppressed

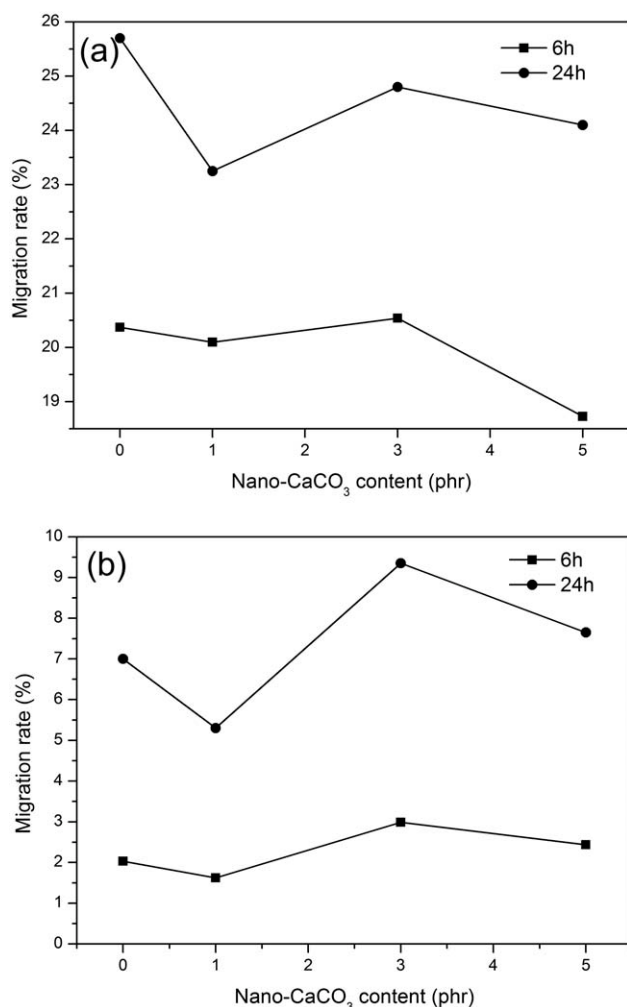


Figure 2 (a) Migration rate plotted against nano-CaCO₃ content for CaCO₃-n/DOP-50/PVC composites; (b) Migration rate plotted against nano-CaCO₃ content for CaCO₃-n/PPA-20/DOP-30/PVC composites.

DOP migration slightly in CaCO₃/DOP-50/PVC system as compared with DOP-50/PVC [Fig. 2(a)]. Contrary to what was expected, the increase of nano-CaCO₃ content did not lead to better barrier properties for DOP migration owing to the poor dispersion of nano-particles in the PVC matrix. For nano-CaCO₃, it is more easy to disperse in the DOP/PVC system than in the PPA/DOP/PVC system due to the high viscosity of PPA. The migration rate (after 6 h extraction) of CaCO₃-3/PPA-20/DOP-30/PVC (2.99%) and CaCO₃-5/PPA-20/DOP-30/PVC (2.44%) are slightly higher than that of PPA-20/DOP-30/PVC (2.03%) as shown in Figure 2(b). But all the DOP migration rates of CaCO₃-n/DOP-50/PVC are lower than that of DOP-50/PVC.

Tensile properties

The tensile strength and elongation at break of CaCO₃-n/PPA-20/DOP-30/PVC composites at vari-

ous nano-CaCO₃ contents are presented in Figure 3. All the mechanical properties of PVC films are summarized in Table II.

From Figure 3(a), it is obvious that DOP-30/PVC exhibited the highest tensile strength (22.20 MPa), while the tensile strength of PPA-20/DOP-30/PVC (11.88 MPa) was the lowest. It indicates that the introduction of 20 phr PPA decreased the tensile strength of PVC by 46.5%. After the addition of nano-CaCO₃, all the tensile strength of CaCO₃-n/PPA-20/DOP-30/PVC (16.21, 16.16, 15.06 MPa) were increased as compared with that of PPA-20/DOP-30/PVC (11.88 MPa). But there was no significant difference among the values of tensile strength for all the CaCO₃-n/PPA-20/DOP-30/PVC composite films. The elongation at break of CaCO₃-n/DOP-50/PVC decreases with the increasing nano-CaCO₃ content as shown in Figure 3(b). However, CaCO₃-1/PPA-20/DOP-30/PVC displayed the highest elon-

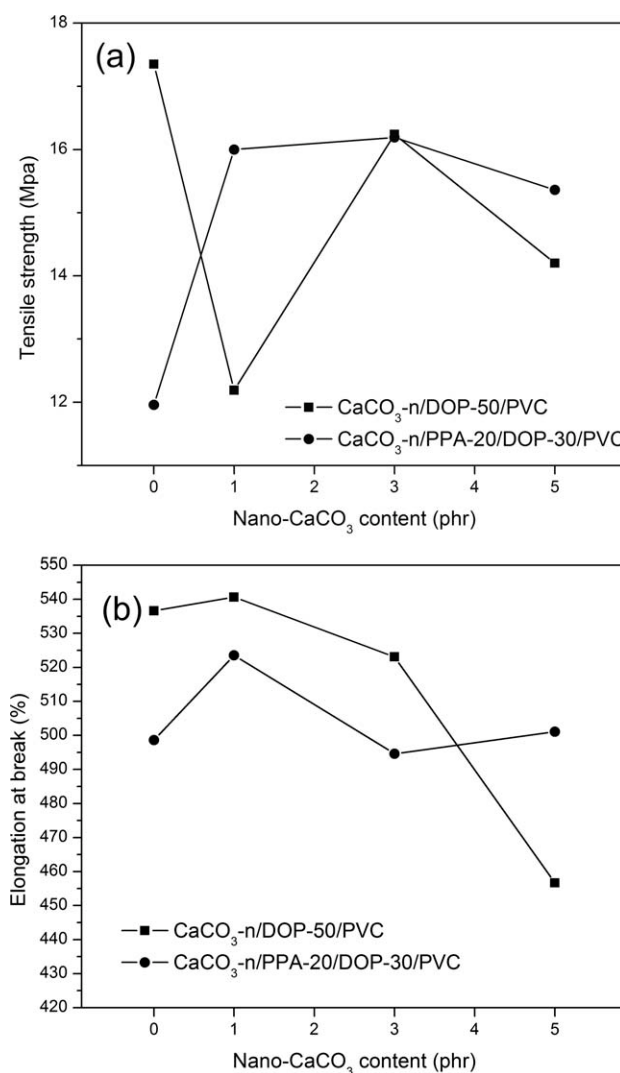


Figure 3 (a) Tensile strength of the samples versus nano-CaCO₃ content; (b) Elongation at break of the samples versus nano-CaCO₃ content.

TABLE II
Mechanical Properties of PVC Films

Sample	Tensile strength (MPa)	Elongation at break (%)
DOP-50/PVC	17.35	536.64
CaCO ₃ -1/DOP-50/PVC	11.94	540.64
CaCO ₃ -3/DOP-50/PVC	16.22	523.08
CaCO ₃ -5/DOP-50/PVC	14.37	456.65
DOP-30/PVC	22.20	360.42
PPA-20/DOP-30/PVC	11.88	498.64
CaCO ₃ -1/PPA-20/DOP-30/PVC	16.21	523.53
CaCO ₃ -3/PPA-20/DOP-30/PVC	16.16	494.63
CaCO ₃ -5/PPA-20/DOP-30/PVC	15.06	501.08

gation at break and tensile strength among the CaCO₃-n/PPA-20/DOP-30/PVC samples. Some researchers reckoned that the low nano-particles could effectively increase the strength of the composite.¹⁶ However, nano-CaCO₃ with high surface energy was easy to aggregate and the poor dispersion of nano-CaCO₃ will lead to the large difference between the real values and the theoretical values.

Typical stress-strain curves for the samples with various contents of plasticizers are shown in Figure 4. It is obvious that the Young's modulus of DOP-50/PVC was lower than that of DOP-30/PVC but higher than that of PPA-20/DOP-30/PVC. It can be explained that DOP migration from PVC matrix is more difficult than PPA with the time and the migration of DOP, resulting in the loss of effect of plasticization. Thus, PPA-20/DOP-30/PVC's plasticization effect can be maintained for a longer time. So, it is very possible that the PVC matrix with plasticizer PPA shows the lower Young's modulus than that of PVC matrix with plasticizer DOP. As expected, DOP-50/PVC showed the highest value of elongation at break (536.64%), while the elongation value of DOP-30/PVC (360.42%) was the lowest. DOP-30/PVC exhibited the highest tensile strength (22.20 MPa) and that of PPA-20/DOP-30/PVC (11.88 MPa) was the lowest.

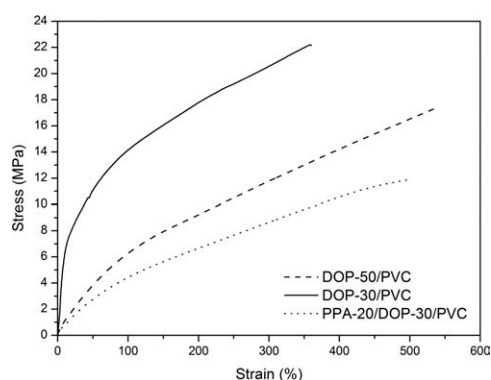


Figure 4 Stress-strain curves of the three plasticized samples.

Morphology

SEM was employed to examine the fracture surface in the films. DOP-30/PVC exhibits smooth fracture surface while DOP-50/PVC shows ductile characteristics with a rough fracture surface compared with DOP-30/PVC as shown in Figure 5. For PPA-20/DOP-30/PVC [Fig. 5(c)], the roughness concentration of fracture surface is between that of DOP-30/PVC [Fig. 5(a)] and that of DOP-50/PVC [Fig. 5(b)]. These results were consistent with the tensile behaviors of

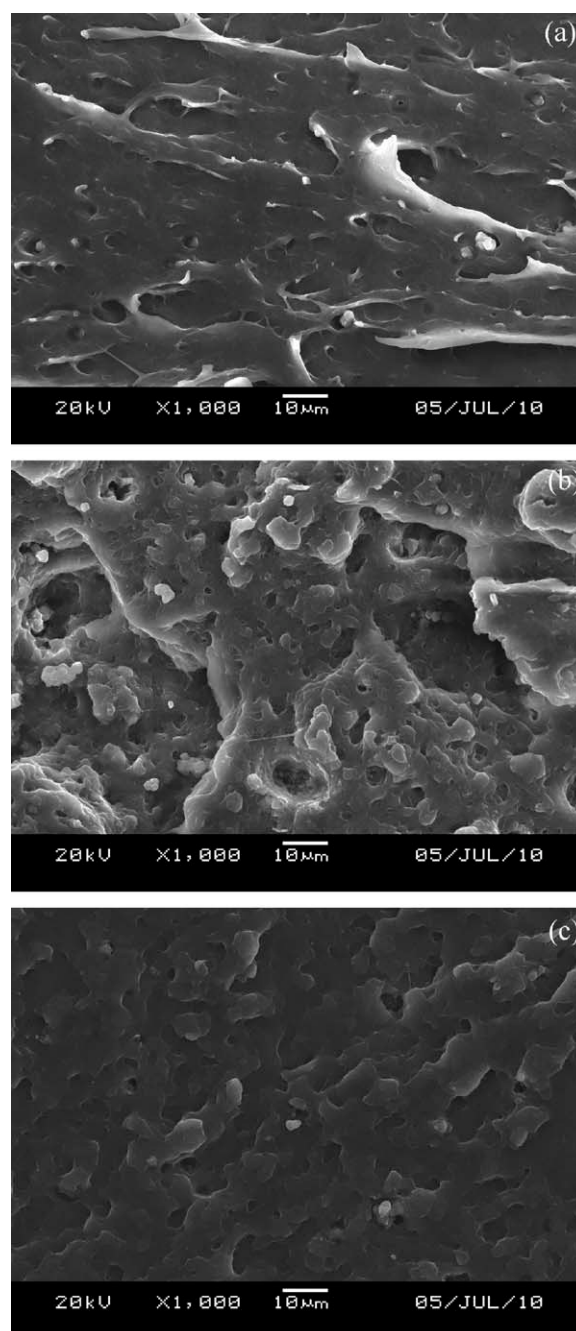


Figure 5 The micrographs of the fracture surfaces of PVC films after tensile tests: (a) DOP-30/PVC; (b) DOP-50/PVC; (c) PPA-20/DOP-30/PVC.

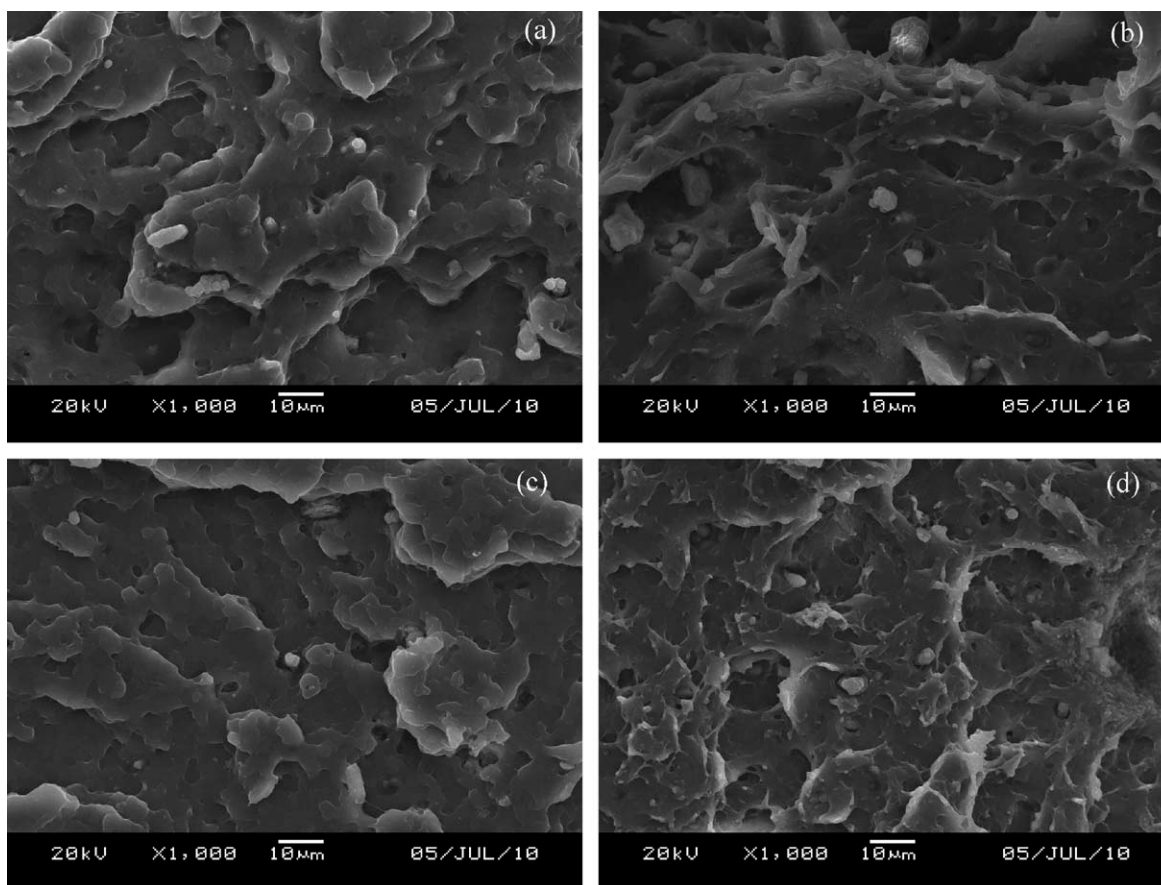


Figure 6 The micrographs of the fracture surfaces of PVC films after tensile tests: (a) CaCO_3 -1/DOP-50/PVC; (b) CaCO_3 -5/DOP-50/PVC; (c) CaCO_3 -1/PPA-20/DOP-30/PVC; (d) CaCO_3 -5/PPA-20/DOP-30/PVC.

the samples. The number of particles with approximately 1–5 μm in diameter increased with the increasing content of nano- CaCO_3 as shown in Figure 6. The effects of aggregation on the properties of composites are detrimental, which results in a decrease of polymer antimigration and tensile properties. There exists a large number of voids on the fracture surface of composites, which was clearly caused by matrix cavitations due to the addition of the nano- CaCO_3 particles.¹⁷ The relative high content of nano- CaCO_3 [Fig. 6(b) CaCO_3 -5/DOP-50/PVC; Fig. 6(d) CaCO_3 -5/PPA-20/DOP-30/PVC] led to more voids and rough fractures compared with the low nano- CaCO_3 content samples [Fig. 6(a) CaCO_3 -1/DOP-50/PVC; Fig. 6(c) CaCO_3 -1/PPA-20/DOP-30/PVC]. The SEM micrographs revealed that the interface between CaCO_3 particles and the matrix is clear, suggesting that the interfacial adhesion between the two phases is poor.¹⁸

Thermogravimetry analysis (TGA)

The TGA curves of the samples are shown in Figure 7 and correlative values of decomposed temperature for the samples are listed in Table III. Similar to

DOP-50/PVC, the nanocomposites revealed two-stage degradation: the first stage attributes to the volatilization of hydrogen chloride molecules

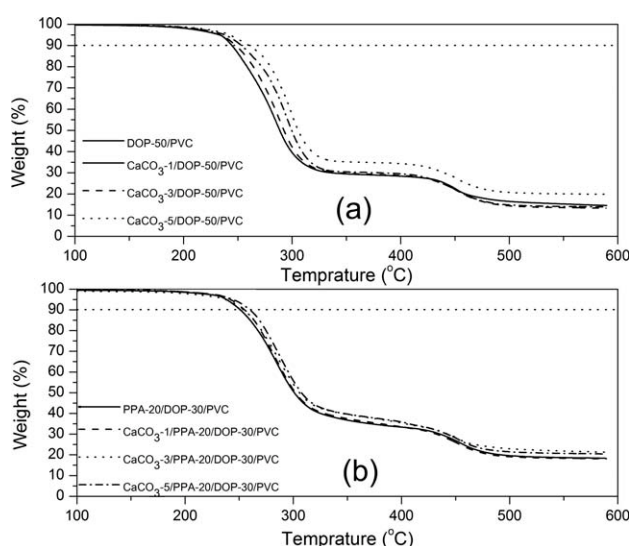


Figure 7 TGA curves for the CaCO_3 -n/DOP-50/PVC nanocomposites and CaCO_3 -n/PPA-20/DOP-30/PVC nanocomposites.

TABLE III
Initial Decomposition Temperatures (T_d , °C) of Nanocomposites
Determined by TGA Analysis

Sample	T_d (°C)	Sample	T_d (°C)
DOP-50/PVC	244.44	DOP-30/PVC	249.27
CaCO ₃ -1/DOP-50/PVC	248.21	PPA-20/DOP-30/PVC	251.06
CaCO ₃ -3/DOP-50/PVC	253.30	CaCO ₃ -1/PPA-20/DOP-30/PVC	252.79
CaCO ₃ -5/DOP-50/PVC	260.39	CaCO ₃ -3/PPA-20/DOP-30/PVC	254.24
		CaCO ₃ -5/PPA-20/DOP-30/PVC	260.01

followed by the formation of the conjugated polyene sequences, while the second stage corresponds to the thermal cracking of the carbonaceous conjugated polyene sequences.¹⁹ Previous studies indicated that the nanoscale compounding of the nano-CaCO₃ particles can improve the thermal stability of nanocomposites.²⁰ Decomposition temperature (T_d , at weight loss of 10 wt %) of CaCO₃-5/DOP-50/PVC (260.39°C) is higher than that of DOP-50/PVC (244.44°C) by about 15°C; and T_d of CaCO₃-5/PPA-20/DOP-30/PVC (260.01°C) is higher than that of PPA-20/DOP-30/PVC (251.06°C) by approximately 10°C. According to the TGA analysis, at high temperature, the enhancement of the formation of residue indicates that the nano-CaCO₃ improves the thermal stability of the nanocomposites. The presence of nano-CaCO₃ can enhance the formation of char and hinder diffusion of volatile decomposition products within the nanocomposites.

CONCLUSIONS

The introduction of inorganic nano-CaCO₃ and PPA has a synergistic effect on the suppression of DOP migrating from flexible PVC. From DOP extraction test, the addition of nano-CaCO₃ can reduce the migration rate of plasticizer in the CaCO₃-n/DOP-50/PVC system. The DOP extraction rate of PPA-20/DOP-30/PVC was reduced compared with that of DOP-30/PVC. The combination of nano-CaCO₃ and PPA decreased the tensile strength and elongation at break of PVC composite samples. CaCO₃-1/PPA-20/DOP-30/PVC exhibited the best performance among all the samples. The worsening mechanical properties of the PVC composite system with the increasing content of nano-CaCO₃ was attributed to the poor dispersion of nano-CaCO₃. The disper-

sion of nano-particles plays a key role in the composite system, which affects the performance of the PVC specimen. The combination of PPA and nano-CaCO₃ is an effective approach to resist the migration of DOP from flexible PVC.

References

- Lederer, B. J Vinyl Addit Technol 1998, 4, 90.
- Navarro, R.; Perrino, M. P.; Tardajos, M. G.; Reinecke, H. Macromolecules 2010, 43, 2377.
- Mercer, A.; Castle, L.; Conyw, J.; Gilbert, J. Food Addit Contam 1990, 7, 497.
- Lan, O. W.; Wong, S. K. J Chromatogr A 1996, 737, 338.
- Huber, W. W.; Grasl-Kraupp, B.; Schulte-Herman, R. Crit Rev Toxicol 1996, 26, 365.
- Latini, G.; De Felice, C.; Verrotti, A. Reprod Toxicol 2004, 19, 27.
- Jayakrishnan, A.; Lakshmi, S. Nature 1998, 396, 638.
- Duvis, T.; Karles, G.; Papaspyrides, C. D. J Appl Polym Sci 1991, 42, 191.
- Stark, T. D.; Choi, H.; Diebel, P. W. In 57th Canadian Geotechnical Conference/5th Joint CGS&IAH-CNC Conference, 2004.
- Sunny, M. C.; Ramesh, P.; George, K. E. J Elast Plast 2004, 36, 19.
- Svoboda, R. D. J Vinyl Tech 1991, 13, 130.
- Hakkarainen, M. Adv Polym Sci 2008, 211, 159.
- Marcilla, A.; Garcia, S.; Garcia-Quesada, J. C. J. Anal. Appl. Pyrolysis 2004, 71, 458.
- Messori, M.; Toselli, M.; Pilati, F.; Fabbri, P.; Pasquali, L.; Nannaronea, S. Polymer 2004, 45, 805.
- Yang, B.; Bai, Y.; Cao, Y. J Appl Polym Sci 2010, 115, 2178.
- Wu, D.; Wang, X.; Song, Y. Jin, R. J Appl Polym Sci 2004, 92, 2714.
- Yang, K.; Yang, Q.; Li, G.; Sun, Y.; Feng, D. Polym Compos 2006, 27, 445.
- Sterky, K.; Jacobsen, H.; Jakubowicz, I.; Yarahmadi, N.; Hjertberg, T. Eur Polym Mater 2010, 46, 1203.
- Shah, B. L.; Shertukde, V. V. J Appl Polym Sci 2003, 90, 3278.
- Patil, C. B.; Kapadi, U. R.; Hundiwale, D. G.; Mahulika, P. P. J Mater Sci 2009, 44, 3118.