Plasticized poly(vinyl chloride) composites: Influence of different nanofillers as antimigration agents

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ABSTRACT: In this study, plasticized poly(vinyl chloride) (PVC) composites with different nanofillers, including single-walled carbon nanotubes (SWCNTs), organoclay, TiO_2, and ZnO nanoparticles, were prepared, and their effects on plasticizer migration were investigated. Scanning electron micrographs revealed the dispersion quality of the nanofillers in the polymer matrix. It had a significant influence on the performance of the nanofillers in the process of plasticizer migration. Migration and exudation tests showed that the nanofillers could efficiently hinder plasticizer migration. On the basis of these results, we concluded that carbon nanotubes were the best antimigration agent in the plasticized system. This was ascribed to the high aspect ratio of the SWCNTs and the good interactions between them and the plasticizer. Also, TiO_2 nanoparticles showed a better performance compared to the ZnO nanoparticles. This was due to the more homogeneous dispersion of the TiO_2 in the polymer matrix and the higher surface area of the particles. The differential scanning calorimetry thermograms were in good agreement with the migration tests. The lowest change in the glass-transition temperature was observed for the composite filled with SWCNTs. This indicated that a lower amount of the plasticizer migrated from PVC. The thermogravimetric analysis curves showed that the incorporation of the nanofillers improved the thermal stability of the PVC. The results could be useful for determining the efficiency of plasticized PVC in applications. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42559.

INTRODUCTION

Poly(vinyl chloride) (PVC) is a polymer that is used in many versatile applications, such as those in the automobile industry, toys, electrical wire insulation, medicine, and pharmaceuticals. It has some advantages, including a high chemical resistance, good mechanical properties, and low cost.[1] Plasticizers are added to PVC to improve the flexibility of the polymer. On the basis of the plasticizer concentration in the formulation, the grades of the plasticized poly(vinyl chloride) (P-PVC) with different flexibilities and characteristics can be produced. The most common plasticizers are phthalate esters, particularly di(octyl phthalate) (DOP). This is due to the good plasticization performance and competitive cost of DOP.[2,3] However, because DOP and other plasticizers do not form chemical bonds with the PVC chains, they can be evaporated or migrated upon contact with liquids.[4] Some reports have indicated that DOP had adverse effects on the human body, especially for vulnerable individuals and with long-term exposure. For instance, some diseases, including deep venous thrombosis, bronchopulmonary dysplasia, and cholestasis, are outcomes of exposure to DOP.[5–8] The classification of DOP under Classification, Labeling, and Packaging regulation EC 1272/2008 is as a category 1B reproductive toxicant.[9] Also, migration causes a loss of mechanical properties and makes the PVC brittle.

Several strategies have been developed to solve DOP migration from P-PVC. One strategy is the substitution of the DOP and similar plasticizers with ones that have a lower tendency to migrate. The prevention of the DOP migration by different chemical and physical methods is another case.[3,10] Also, some polymers have been used as an alternative to PVC. These substitutions have particularly been considered in the field of medical devices.[11,12] All of these solutions have their advantages and shortcomings. Some low-molecular-weight alternative plasticizers have shown a lower degree of migration and leaching, but they included adverse effects on living organisms.[13] PVC blends containing polymeric plasticizers, such as nitrile rubber, polyesters, and polyhedral oligomeric silsesquioxane, have presented significant improvements in solving the problem of plasticizer migration. This was due to the macromolecular nature of the polymeric plasticizers, and as a result, they had no tendency to move to the surface of the PVC. The main negative aspect of these plasticizers was their lower efficiency in the processing

and plasticization of PVC compared to the low-molecular-weight plasticizers; this resulted in a higher tensile strength and stiffness and a lower elongation at break for P-PVC. Also, there was a possibility of the degradation of these polymeric plasticizers in working media, so this issue must be considered.[14–18]

The surface modification of PVC by different techniques, such as the surface coating and surface crosslinking, has its own characteristics. It was reported that surface coating by chemical vapor deposition prevented plasticizer migration, but a high cost and a loss of transparency were the main shortcomings of this method.[19] In the case of crosslinking by UV treatment, good leaching resistance for the irradiated PVC was observed, whereas a high level of the metabolite hemi-ester of DOP, that is, mono(2-ethylhexyl) phthalate, which has bad effects on organs migrated from PVC.[20,21]

Alternative polymers, such as polysiloxanes, polyurethanes, and polyolefins, do not require a plasticizer and show good flexibility without it,[11,12,22,23] but migration of antioxidants and other additives is a major concern. These additives are added to maintain the properties of the polymer during processing and end use. Furthermore, these polymers are not cost competitive with P-PVC.[24–27]

With respect to the aforementioned reasons, it appears that a new approach with nanofillers in PVC can help with the DOP migration issue. Yang et al.[28] reported a decrease in plasticizer migration through the addition of $CaCO_3$ and SiO_2. They showed that with the addition of 20 wt % fillers, the migration of the diisononyl phthalate and trioctyl trimellitate could be decreased up to 20% compared to the pure PVC. In the aforementioned report, they used plasticizers other than DOP, and the amount of added nanofillers for achieving a relatively good result was high.

In this study, P-PVC and its composites filled with different nanofillers, including organoclay, TiO_2, and ZnO nanoparticles, and single-walled carbon nanotubes (SWCNT) were fabricated. The aim of this research was to investigate the effect of a low content (5 wt %) of the nanofillers on the migration and exudation of the most common plasticizer, that is, DOP. We present the relationships among the chemical nature, dispersion quality of the nanofillers in the polymer matrix, and interactions between the nanofillers and DOP with efficiency in hindering the DOP migration, as observed with scanning electron microscopy (SEM) observations, differential scanning calorimetry (DSC) curves, Fourier transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD) spectroscopy.

EXPERIMENTAL

Materials

The emulsion PVC resin (K-value = 74) was provided from European Vinyls Corp. (EVC group of companies). DOP was supplied by Arak Petrochemicals. A barium cadmium stabilizer from Shetab Shimi was used as a thermal stabilizer. The TiO_2 nanoparticles, organoclay under the trademark Cloisite 30B, and SWCNTs were purchased from Titan PE Technology (Shanghai), Inc., Southern Clay Products, and Oil Industry Institute (Iran), respectively. The nanotubes had a diameter of

$$ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2 + Na_2SO_4$$

$$Zn(OH)_2 \longrightarrow ZnO + H_2O$$
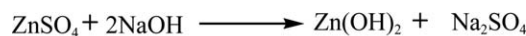
Figure 1. Chemical reactions for the synthesis of the ZnO nanoparticles.

about 2 nm, a length of some micrometers, and a carbon purity greater than 95%. Other materials, including activated carbon, zinc sulfate dehydrate, and NaOH, were obtained from Merck.

Preparation of the ZnO Nanoparticles

In this study, the ZnO nanoparticles were synthesized according to procedure reported elsewhere.[29] Chemical reactions for the synthesis of ZnO are shown in Figure 1.

Preparation of P-PVC

P-PVC was prepared by the mixture of the PVC powder (100 phr), DOP (60 phr), and Ba–Cd heat stabilizer (0.2 phr) in a mixer for 15 min at ambient temperature. Then, the blend was evacuated to eliminate air bubbles. Finally, PVC plastisol was placed onto an aluminum mold and cured in an oven for 8 min at 180°C.

Preparation of the P-PVC Composites

For the fabrication of the PVC composites, a mixture of the DOP (60 phr), Ba-Cd heat stabilizer (0.2 phr), and one of the nanofillers (organoclay, TiO_2 and ZnO nanoparticles, and SWCNTs; 5 phr) were sonicated for 45 min at 60°C. In the next stage, the PVC powder was added to the suspension, and plastisol was stirred for 15 min at room temperature. Eventually, the mixture was molded and cured for 8 min at 180°C. In this study, NCPM, NCPZ, NCPT, and NCPN were PVC composites filled with organoclay (modified montmorillonite), ZnO, TiO_2, and nanotubes (SWCNTs), respectively.

Migration Study

To investigate the migration of DOP in the prepared samples, a migration test according to ASTM D 1203-94 was carried out. Samples with dimensions of 10 × 10 mm^2 with 0.5 mm thickness were placed in activated carbon and heated in an oven for a week at 70°C. After every 24 h during the week, the samples were cleaned, and their weights were recorded. The difference between the initial and final weights indicated the amount of DOP migration. The weight loss percentage was calculated from following equation:

$$\text{Weight loss} = \frac{W_0 - W_i}{W_0} \times 100$$

where W_0 and W_i are the initial weight and the weight at time i, respectively.

Exudation Study

To monitor the exudation of DOP from P-PVC into the unplasticized poly(vinyl chloride) (U-PVC), the method described in ASTM D 2199-82 was used. The samples were cut into pieces with dimensions of 20 × 20 mm^2 with 0.5 mm thickness and then placed between two U-PVC sheets (with the same dimensions) and pressed by 0.110 MPa in an oven for a week at 60°C (Figure 2). Similar to the previous experiments, the weight of the samples was measured, and the weight loss due to the exudation was determined.
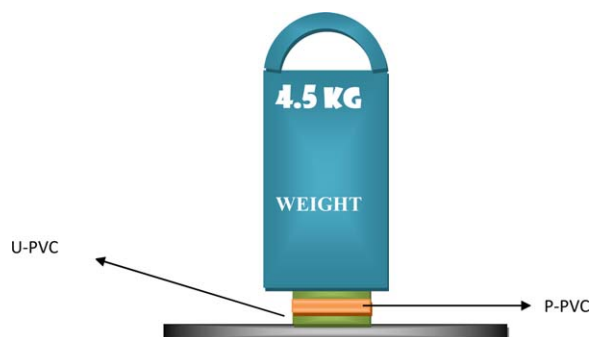
Figure 2. Schematic for the exudation of the plasticizer into the contacting polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. XRD Data Obtained for the ZnO and TiO$_2$ Particles

Nanoparticle	b	2θ (°)	Particle size (Å)
ZnO	0.32	31.77	255.83
	0.29	34.43	289.93
	0.33	36.28	253.43
TiO$_2$	1.08	25.50	75.10
	1.09	48.09	79.77
	1.18	62.79	78.63

performed with a Mettler TA4000 at a heating rate of 10°C/min under an N$_2$ atmosphere.
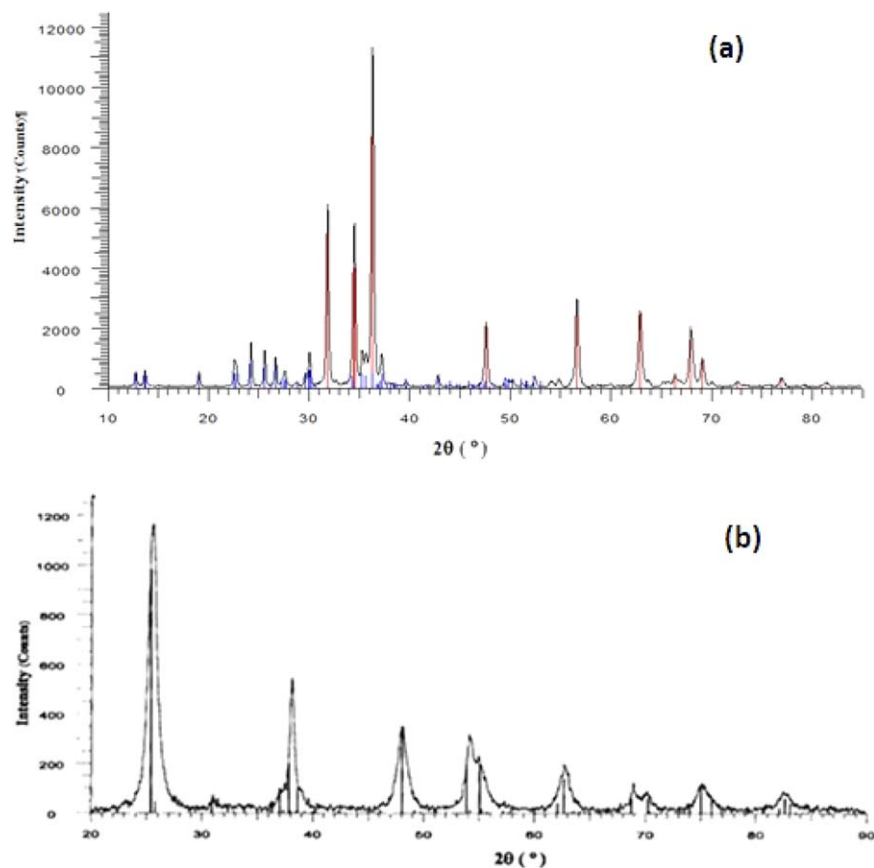
RESULTS AND DISCUSSION

Characterization of the Nanoparticles

The prepared ZnO and commercial TiO$_2$ nanoparticles were studied with XRD technique. To calculate the average size of the particles, the Scherrer formula[30] was used:

$$\text{Size of the particles} = \frac{0.9\lambda}{b\cos\theta}$$

where λ (wavelength) is 1.541 Å. Figure 3 shows the XRD patterns of the nanoparticles. Also, in Table I, the XRD data, including the peak width at half-maximum height (b) and the

Characterization

The morphology of the prepared ZnO nanoparticles and different composites was evaluated with an AIS-2100 model 550 SERON Technology scanning electron microscope. The FTIR spectra for characterization of the nanoparticles were recorded by a Jasco FTIR-6300 spectrometer. The XRD patterns were obtained on a Bruker, D8 Avance X-ray diffractometer. DSC measurements were carried out by a Mettler TA4000 under a nitrogen atmosphere at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) of the P-PVC and composites were

Figure 3. XRD patterns for (a) ZnO and (b) TiO$_2$ particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
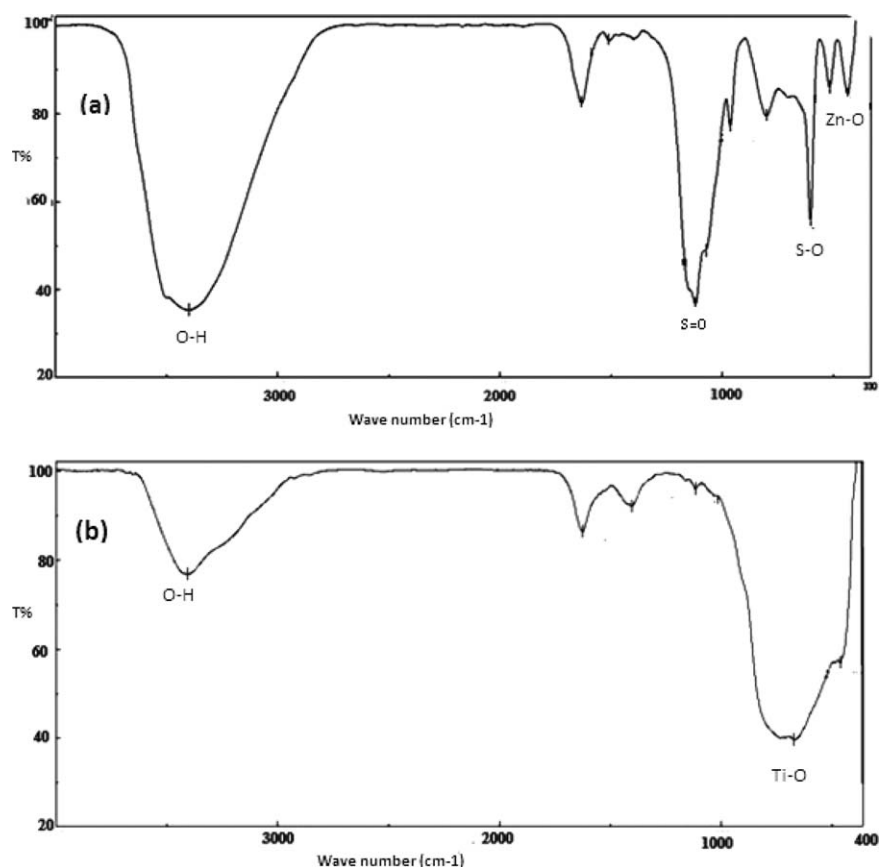
Figure 4. FTIR spectra for the (a) ZnO and (b) TiO$_2$ nanoparticles.

particle size, are presented. According to the results, the average sizes of the ZnO and TiO$_2$ particles were about 26.5 and 8 nm, respectively.

The FTIR spectra of the ZnO and TiO$_2$ nanoparticles are shown in Figure 4. As shown in Figure 4(a), the stretching and bending vibrations of the O—H functional group appeared in 3400 and 470 cm^{-1}, respectively. The peak at 434 cm^{-1} corresponded to the stretching vibrations of the Zn—O bond. On the other hand, symmetric and asymmetric stretching vibrations of the S=O were observed at 1073, 1120, and 1200 cm^{-1}, respectively. Also, the FTIR spectrum showed an absorption peak for S—O at 600 cm^{-1}.[31,32] The XRD and FTIR curves demonstrated that the prepared nanoparticles contained Zn$_3$O(SO$_4$)$_2$ (8.7 wt %) in addition to ZnO (91.3 wt %). As shown in Figure 4(b), the absorption peaks for Ti—O and O—H appeared at 420–800 and 3100–3500 cm^{-1}, respectively. The weak band at 1625 cm^{-1} was attributed to the bending vibrations of coordinated H$_2$O.[33,34]

Through a comparison of the absorption intensity and peak area for O—H stretching vibrations, we understood that the concentration of hydroxyl groups on the surface of the ZnO particles was higher than that of the TiO$_2$ particles.

Morphological Properties
Figure 5 shows the SEM micrograph of the prepared ZnO nanoparticles. This image indicates that the synthesized nanoparticles were in plane and flake form. Also, SEM images from the

surfaces of the pure PVC and prepared nanocomposites are shown in Figure 6. Figure 6(b) shows that the ZnO nanoparticles were in agglomerated form in some regions; this originated from differences in the polarity between the nanoparticles and PVC chain. The SEM micrograph for the sample containing TiO$_2$ shows that the TiO$_2$ nanoparticles dispersed more homogeneously than the ZnO nanoparticles in the PVC matrix. This was attributed to the higher concentration of the hydroxyl groups on the surface of the ZnO particles compared to that on the TiO$_2$ particles. As a result, the ZnO particles were more
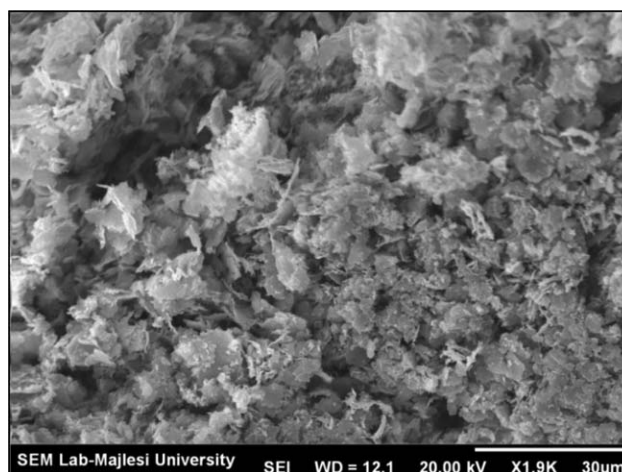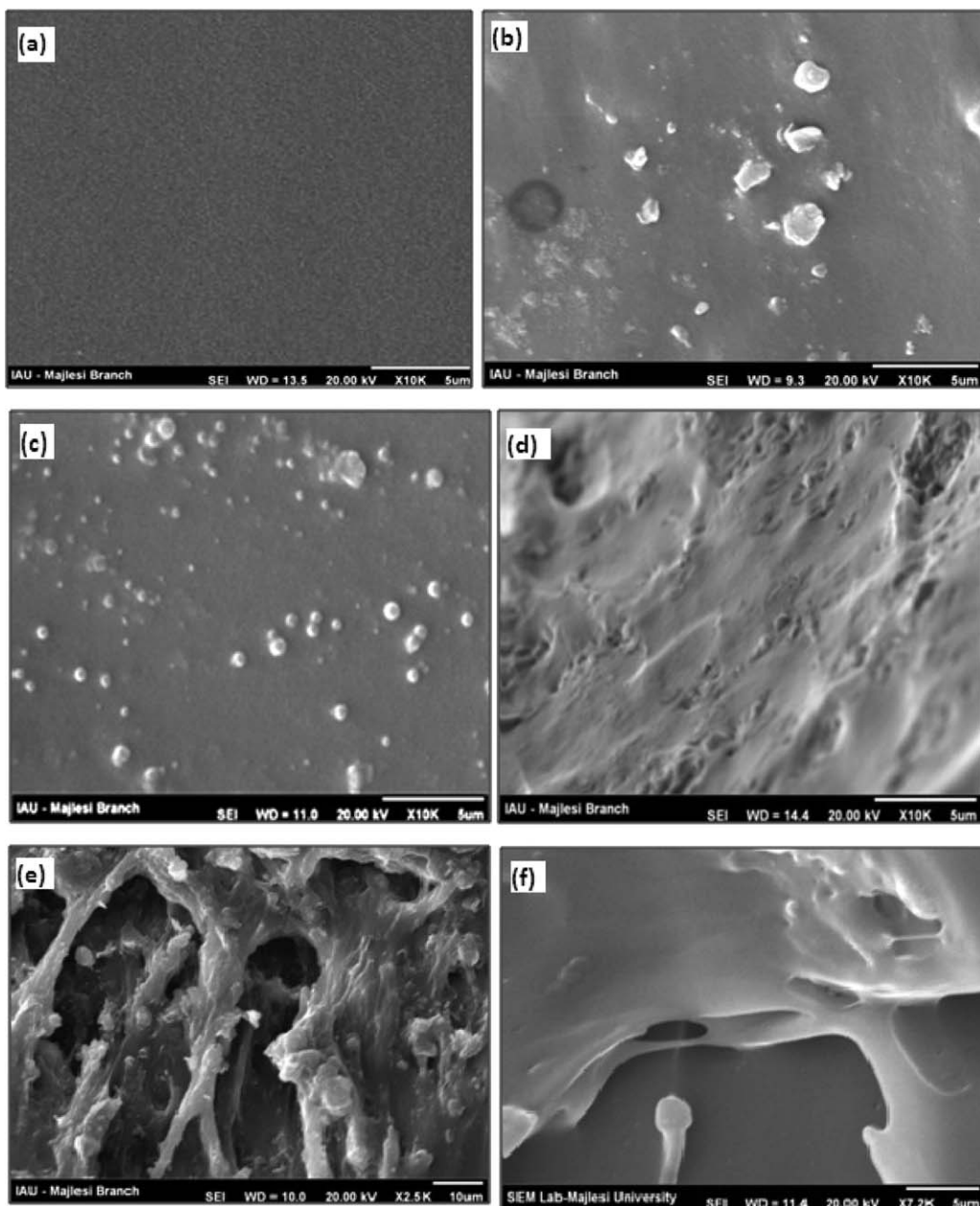

Figure 5. SEM micrograph of the prepared ZnO nanoparticles.

Figure 6. SEM micrographs of the (a) pure PVC and composites filled with (b) ZnO, (c) TiO$_2$, (d,e) organoclay (surface and cross-section views), and (f) carbon nanotubes.

hydrophilic, and there was less interfacial adhesion between them and the organic polymer matrix.

In Figure 6(d,e), the SEM micrographs from the surface and cross section of the PVC/organoclay composite are presented. Because of the layered structure of the montmorillonite (MMT), the surface of this composite was rougher than the other ones. As shown, there were many cavities in the composite. This resulted from the fact that organic modifier within the layered silicates acted as an internal lubricant and reduced the friction between PVC chains.[35] The SEM image for the PVC/SWCNT showed that the carbon nanotubes generated bridges in cracks and, consequently, improved the mechanical and thermal properties of the composite. This has been reported in our previous works.[36–38] These bridges could act as an obstacle for plasticizer migration.

Migration and Exudation of the Plasticizer
In the test, the plasticizer molecules migrated to the surface and consequently to the activated carbon. This trend resulted from two phenomena: 1) weak van der Waal's interactions between the polymer chains and plasticizer molecules (no chemical bonds) that allowed the plasticizer to diffuse through the matrix and 2) the concentration gradient between the PVC matrix and the external environment. This created a competition between the PVC chains and the activated carbon for absorbing plasticizer molecules.
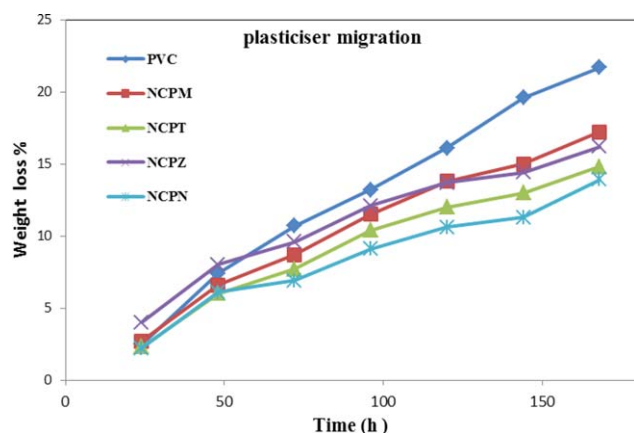
Figure 7. Weight loss (plasticizer migration) in the pure PVC and different composites versus the time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. Weight loss (plasticizer exudation) in the pure PVC and different composites versus time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The weight losses of the samples due to the plasticizer migration are shown in Figure 7. This revealed that different nanofillers restrained the migration of DOP and reduced its degree and rate. As shown in Figure 7, with the addition of SWCNTs to PVC, the degree of migration decreased to 13.9% (a decrease of 36% compared to PVC). The composite containing TiO_2 nanoparticles exhibited a 32% decrease in migration. A decrease in the plasticizer migration for the composites compared to that of the pure PVC is summarized in Table II. On the basis of the results, we present the following trend for the efficiency of the additives in preventing plasticizer from migrating:

$$SWCNT > TiO_2 \text{ nanoparticles} > ZnO \text{ nanoparticles} > Organoclay$$

The plasticizer molecules could migrate (exudate) into the polymer in contact with PVC. Figure 8 shows the exudation of DOP into the adjacent polymer for the prepared composites as a function of time. The results follow the same trend as the previous test; that is, all additives were successful in reducing the degree of exudation. Also, the weight loss of P-PVC decreased dramatically (ca. 34%) through the incorporation of the SWCNTs into the polymer matrix (Table II). So, on the basis of these two tests, the carbon nanotubes could act as an antimigration agent very efficiently. This was due to several reasons: The first one was the high aspect ratio of the SWCNTs and π–π interactions between their graphitic wall and benzene rings of the plasticizer; this allowed the SWCNTs to absorb a higher amount of the plasticizer and lower the rate of the migration.

Table II. Decreases in the Migration and Exudation of the Plasticizer for Composites Filled with Different Nanofillers versus the Pure PVC

Sample	Decrease in migration (%)	Decrease in exudation (%)
NCPZ	25	14
NCPM	21	11
NCPT	32	19
NCPN	36	34
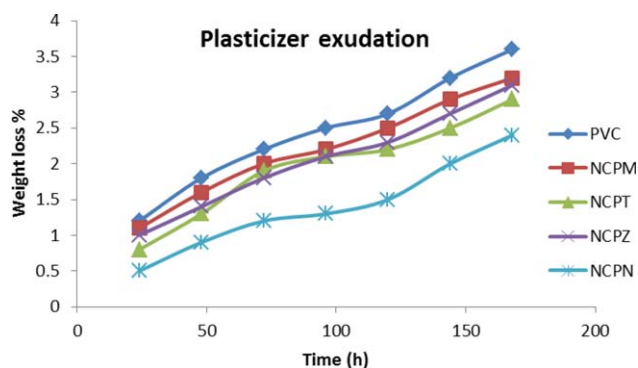
Another explanation may be that the carbon nanotubes created a tortuous pathway for the plasticizer molecules to pass, so migration become more difficult. In other words, the SWCNTs reduced the mobility of the PVC chains and, hence, hindered the diffusion of the plasticizer through the polymer matrix.[39,40]

On the basis of the results, the TiO_2 nanoparticles were better than the ZnO ones in hindering migration and exudation of the plasticizer. As shown in the SEM micrographs and XRD data, the TiO_2 nanoparticles had a lower size, higher surface area, and better dispersion in the PVC matrix compared to the ZnO nanoparticles; this helped them interact with the plasticizer molecules and prevented the migration more effectively.

The previous findings show that the nanofillers used in this study had significant effects on the prevention of the plasticizer from migration. Therefore, the incorporation of these nanofillers into the artificial leather and other products made of PVC and where P-PVC is in the vicinity of other polymers increases their lifetime and performance.

Investigation of the Migration by DSC

With the addition of the plasticizers to the polymer matrix, glass-transition temperature (T_g) shifts to the lower temperatures. In fact, plasticizers decrease interactions between the polymer chains and increase the motion and flexibility of the macromolecules. In the contrary, the migration of the plasticizers causes an increase in the T_g value of the polymers. The T_g values of PVC in the samples were determined with DSC measurements. For each sample, the measurements were carried out under two different conditions: $t = 0$ (where t is time) (before the samples were placed in the activated carbon) and $t =$ after a week (in the activated carbon at 70°C). By comparing the differences between T_g at $t = 0$ (before migration of the plasticizer) and $t =$ after a week (after migration of the plasticizer to the activated carbon) for different samples, we assessed the relative degree of migration. Figure 9 illustrates the DSC curves of the neat PVC films and relative composites at $t = 0$ and $t =$ after a week. Also, the T_g values under two conditions and ΔT_g were calculated from the following equation and are presented in Table III:

$$\Delta T_g = |T_g(t=0)| + |T_g(t=\text{after a week})|$$
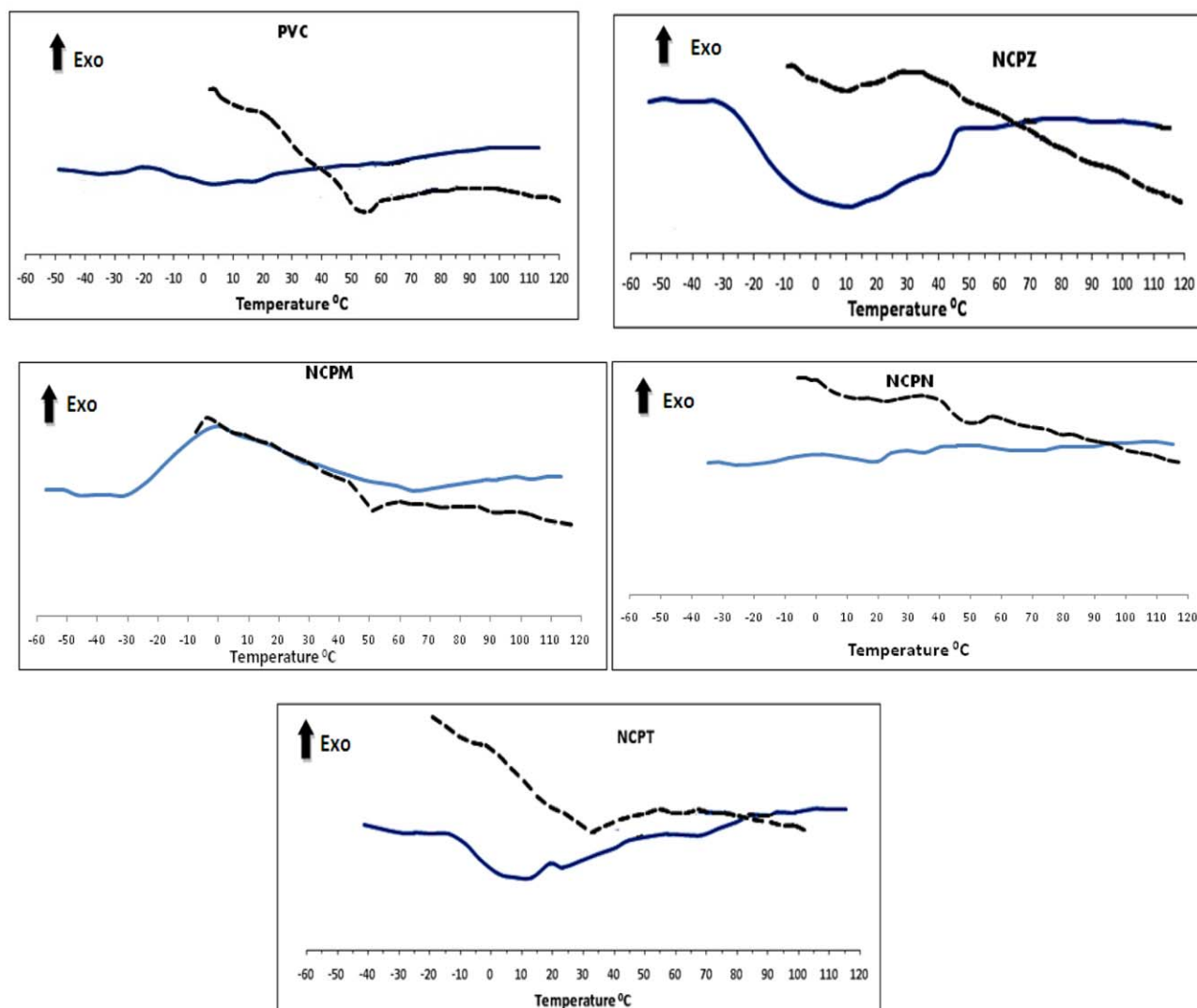
Figure 9. DSC curves for the PVC and composites containing different nanofillers at $t = 0$ (blue line) and after a week (black line) at a heating rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown, the data were in good agreement with the previous tests. So, the capability of the nanofillers in acting as an antimigration agent are as follows:

$$SWCNT > TiO_2 \text{ nanoparticles} > ZnO \text{ nanoparticles} > Organoclay$$

Table III. T_g Values for Different Samples at $t = 0$ and $t =$ After a Week and Changes in T_g as Measured by DSC

Sample	T_g at $t = 0$	T_g after a week	$\Delta T_g{}^a$
PVC	−45	30	75
NCPZ	−50	2	52
NCPM	−49	18	67
NCPT	−34	11	45
NCPN	−29	1	30

$^a \Delta T_g = |T_g(t = 0)| + |T_g(t = 7 \text{ days})|$.
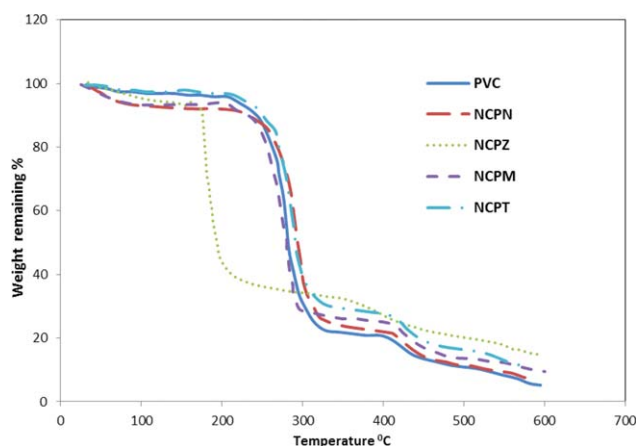
Figure 10. TGA curves of the P-PVC and related composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Thermal Stability Parameters for the PVC and PVC Composites

Sample	Weight loss in first step (%)	Residual yield (%)
PVC	77.5	5.1
NCPZ	62.4	14.8
NCPM	68.6	9.5
NPCT	66.6	12.6
NCPN	71.3	6.7

Furthermore, in all of the composite samples, the polymer chains were above T_g even after they placed 7 days in the activated carbon. This means that the composites were in the rubbery state at ambient temperature, whereas the pure PVC film was in the glassy state ($T_g = 30°C$). This was a very important factor for the performance of P-PVC in different applications.

As observed in Table III, at $t = 0$ (normal conditions), NCPM had a slightly lower T_g value than the pure PVC. There are different reports in the literature about the effect of the clay or organoclay on T_g of the polymeric matrix. In some cases, the T_g values shifted slightly to higher temperatures in the presence of MMT;[41,42] this resulted from the fact that layered silicates prevented the mobility of the polymer chains. On the other hand, a decrease or no change in T_g was observed in some composite systems, including in reports by Xu et al.[40] and Awad et al.[43] This could have been related to the fact that the interlayer of the montmorillonite increased the distance between the polymer chains and acted as a plasticizer. So, in the NCPM sample, DOP and organoclay plasticized PVC simultaneously.

Also, T_g of the polymer increased through the addition of SWCNTs and TiO_2 nanoparticles. This stemmed from the high surface area of these nanofillers, which provided good interfacial interactions between them and the PVC chains. As a result, the free volume of the polymer decreased, and higher temperatures were needed for the transition from the glassy to the rubbery state.[44,45] The higher T_g for NCPT as compared to NCPZ was due to the lower size and better dispersion of the TiO_2; this restricted motion of the PVC chains more effectively.

TGA

In this section, the effect of the nanofillers on the thermal stability of the PVC is presented. PVC degraded in two steps. In the first step (200–350°C), the dehydrochlorination of PVC was observed, whereas the second step of the degradation was attributed to chain scission, and aromatic compounds were produced (400–500°C).[46] The TGA curves of the prepared samples are presented in Figure 10. The data for the thermal properties of the samples are collected in Table IV. As shown, the addition of the nanofillers improved the thermal stability of PVC. The nanofillers decreased the weight loss in the steps and increased the residual mass. The presence of the highly active unsaturated bonds on the surface of the TiO_2 and ZnO nanoparticles allowed them to absorb chlorine and slow down the rate of the degradation process.[28] SWCNTs have a high thermal conductivity, which dissipates heat in polymers. Also, the absorption of chlorine on carbon nanotubes has been reported.[38,47]

CONCLUSIONS

To hinder plasticizer migration, different nanofillers were added to P-PVC.

The migration and exudation tests showed that all of the nanofillers (at low contents) decreased the degree and rate of migration. The SWCNTs presented the best performance as antimigration agents and significantly prevented DOP from migration. Also, the TiO_2 nanoparticles hindered plasticizer migration more effectively compared to the ZnO ones. On the basis of SEM micrographs, XRD data, and FTIR spectra, the TiO_2 nanoparticles had a lower size, higher surface area, and better dispersion in the PVC matrix than the ZnO ones. So, they had better interaction with the plasticizer molecules and prevented migration more effectively. The DSC curves revealed that for composites containing SWCNTs, ΔT_g was lowest. This indicated that the amount of DOP migration in this sample was lower than that for other composites. So, the DSC data were in a good agreement with the migration tests. Also, TGA showed that the addition of nanofillers improved the thermal stability of PVC.

The results of this work could be important for performance of the artificial leather in applications. The behavior of the PVC composites containing aforementioned nanofillers in extraction of the plasticizer by different solvents will be presented in other work.

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