0032-3861(95)00501-3

Phase transfer catalysed surface modification of plasticized poly(vinyl chloride) in aqueous media to retard plasticizer migration

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(Received 12 July 1995)

Plasticized poly(vinyl chloride) (PVC) sheets were surface modified by nucleophilic substitution of chlorine by azide in aqueous media under phase transfer conditions. PVC was reacted with a 40% solution of sodium azide in water using tetrabutyl ammonium bromide as the phase transfer catalyst. The reaction was conducted at temperatures ranging from 50 to 80°C for various periods of time (1–4 h). The azidated PVC surface was then irradiated using u.v. light with a 125 W lamp for various time periods to crosslink the surface. Migration of the plasticizer di-(2-ethylhexyl phthalate) from surface modified and unmodified PVC was examined in a potential organic extractant such as hexane. It was found that considerable reduction in the migration of the plasticizer could be achieved by this technique depending on the extent of azidation of the PVC surface and the irradiation dose. Determination of the stress/strain properties of PVC sheets before and after modification showed that there was around 30% reduction in these properties after surface modification. However, the values were still much above the minimum prescribed for vinyl chloride polymers used in biomedical applications. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(vinyl chloride); di-(2-ethylhexyl phthalate); plasticizer migration)

INTRODUCTION

The migration of phthalate esters, which are commonly employed as plasticizers for imparting flexibility and low temperature properties to poly(vinyl chloride) (PVC), has been a subject of concern in PVC based medical devices[1–5]. Plasticized PVC used in sheet and tubular forms in medical devices contains up to 40% by weight of the plasticizer, usually di-(2-ethylhexyl phthalate) (DEHP)[6]. Various attempts have been made to reduce the migration of this plasticizer from PVC used in medical, pharmaceutical and food packaging applications. Techniques employed include coating the surface of PVC using various polymers such as acrylates, polyesters or polyurethanes, cross-linking the PVC during processing using peroxides or by radiation in the presence of multifunctional monomers, and grafting hydrophilic monomers onto the surface using gamma radiation[7–10].

PVC reacts with sodium azide in solvents such as dimethyl formamide, dimethyl sulfoxide or hexamethylphosphortriamide in the absence of a catalyst to yield the polymeric azide[11]. In a recent study, we have demonstrated that coating azidated PVC onto plasticized PVC sheets and photocrosslinking the coatings retard the plasticizer migration significantly[12]. A 50–80% reduction in migration could be achieved in potential organic solvents such as hexane depending on the concentration of the coating solution, coating thickness and irradiation dose. If the azidation reaction could be conducted

directly on the plasticized PVC surface and the photolytic instability of the azide groups thus generated on the surface could be exploited for surface crosslinking, such a method would be superior to the coating technique. Azidation of PVC is reported to proceed feasibly in water by the addition of quaternary salts as catalysts[13,14]. In the present work, this reaction was exploited to azidate plasticized PVC on its surface. The photolytic instability of the azide group was then made use of to crosslink the PVC surface using u.v. radiation. The surface modified PVC showed considerable reduction in migration of the plasticizer in comparison with controls depending on the reaction conditions employed.

MATERIALS AND METHODS

Materials

Medical grade PVC resin having a k value of 70 was from Sriram Vinyls and Chemicals, Kota, India. The sheets (thickness of 0.4 mm) were a generous gift from Technoport Co., Japan. Sodium azide was from Sigma Chemical Co., USA, and tetrabutyl ammonium bromide (TAB) was from Spectrochem Ltd, Bombay, India. All other reagents and solvents were of analytical or equivalent grade from E. Merck India, Ltd, Bombay, India.

Methods

The azidation of PVC resin was conducted according to the following procedure. PVC resin 0.5 g was taken in

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25 ml of a 40% aqueous solution of sodium azide containing various amounts of TAB at 50, 60, 70, 80 and 90°C for various periods of time under stirring. After the reaction, the contents were poured into a large volume of water and filtered. After several washings with water followed by methanol, the polymer was dissolved in tetrahydrofuran (THF) and reprecipitated in methanol three times. Finally, it was dried in an air oven at 60°C overnight. The extent of azidation was determined using i.r. spectrophotometry from the intensity of the azide peak in the spectrum at $2100\,cm^{-1}$ recorded using films cast from a THF solution of the polymer in a Perkin Elmer model 597 instrument.

Azidation of plasticized PVC sheets was conducted in the following manner. Sheets ($40\,mm \times 10\,mm$) were treated in 25 ml of a 40% solution of sodium azide containing different amounts of TAB for various time periods at different temperatures. After the reaction, they were washed with plenty of distilled water and dried in the air oven at 60°C overnight. Irradiation of the samples was carried out using a Philips HPL-N 125 W u.v. lamp at room temperature. The samples were hung in air at a distance of 15 cm from the lamp and irradiated.

Migration of DEHP from surface modified and unmodified specimens was examined in n-hexane at 30°C. Specimens were kept in 50 ml of hexane in stoppered Erlenmeyer flasks and were shaken occasionally. Aliquots of 1 ml were withdrawn at various time intervals and the amount of DEHP migrated was assayed spectrophometrically using a u.v.-vis spectrophotometer (Hitachi, Model 220) at 275 nm where DEHP has a characteristic absorption maximum. An equal volume of the dissolution medium was immediately added to the flask after withdrawal of each aliquot.

Differential thermal analysis (d.t.a.) of the modified and unmodified PVC was carried out using a Dupont 990 Thermal Analyser with standard d.t.a. cell accessory in a dynamic atmosphere of nitrogen at a heating rate of 10°C per min. Resin having a particle size of $63–150\,\mu m$ was used in the experiments.

Surface morphology of the PVC sheets was examined before and after azidation and photocrosslinking using scanning electron microscopy. Sheets were vacuum coated with gold and examined using a Hitachi model S-2400 microscope.

Tensile strength and percentage elongation of PVC sheets before and after surface modification were measured according to ASTM D 882 using an Instron automated material testing system 1.09 at a cross-head speed of $10\,cm\,min^{-1}$. Five to six specimens were tested and the data averaged[15].

Interaction between the plasticizer DEHP and sodium azide in the presence of PTC, if any, was checked under reaction conditions employed for surface modification of PVC using u.v. and i.r. spectroscopy and thin layer chromatography (t.l.c.). DEHP was treated with sodium azide in the presence of TAB in water at 80°C for 4 h. After the reaction, the oily layer of the plasticizer in the reaction mixture was separated from the aqueous phase, washed several times and the spectra of the plasticizer thus extracted were compared with the original spectra of DEHP before the reaction. For t.l.c., the organic layer in the reaction mixture was extracted using hexane. A chromatogram of this fraction was run side-by-side with DEHP on TLC plates (type T-6895, Sigma, USA) using 1 : 1 methanol/hexane as the eluent.

RESULTS AND DISCUSSION

According to the scheme of PTC, the soluble organic cation $N^+(Bu)_4^-$ transports N_3^- from the aqueous phase to the organic solid phase of PVC and substitution takes place. The reaction product Cl^- is transported to the aqueous phase by the catalyst and repetition of this process accelerates the reaction. Colour changes occur due to this reaction and these are believed to be due to dehydrochlorination that accompanies nucleophilic substitution. The process is schematically shown in *Scheme 1*.

Figure 1 shows the extent of azidation of PVC resin with TAB as the catalyst under various conditions determined using i.r. spectrophotometry. It is seen that as the concentration of the catalyst is increased, increased azidation results, as expected. However, increasing the catalyst concentration beyond a certain limit ($0.04\,mol\,dm^{-3}$) was not found to increase the extent of azidation significantly. At TAB concentrations of $0.04\,mol\,dm^{-3}$ and above, the polymer formed was not found to be completely soluble in THF due to gel formation. It is assumed that the reason for this kinetic behaviour is the aggregation of the quarternary salt azide around or through the polymer chains and the adsorbed azide salt reacts with PVC in a bimolecular process[16]. As
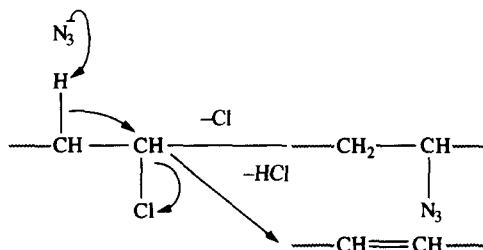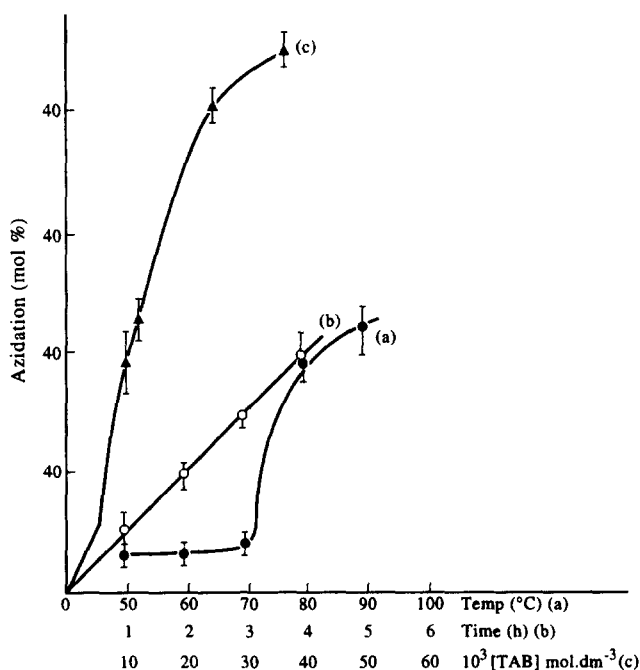
Scheme 1

Figure 1 Extent of azidation of PVC as a function of temperature (a), time (b) and TAB concentration (c). (a) [TAB] = $0.01\,mol\,dm^{-3}$, time = 4 h; (b) [TAB] = $0.01\,mol\,dm^{-3}$, temperature = 80°C; (c) temperature = 80°C, time = 4 h

the temperature of the reaction is increased, increased azidation was seen, though there was no significant reaction below 80°C. The nucleophilic substitution of Cl^- by the azide anion in aqueous media, normally not facilitated in the absence of a catalyst, has been reported to take place in the presence of TAB only at high temperatures[13]. Increased reaction time also results in increased conversion. There is steady increase in the extent of azidation with increase in the reaction time.

The d.t.a. of the unmodified and the azidated resin, having azide contents of 4, 17 and 45 mol%, is shown in *Figure 2*. The endotherm at 285°C for the unmodified resin is due to the decomposition of the resin. For the azidated polymer, this endotherm shifts to progressively lower temperatures as the azide content in the polymer is increased, again due to the decomposition of the polymer. The shift in decomposition to a lower temperature is due to the lower thermal stability of the azide.

The effect of u.v. irradiation on the azidated PVC was studied by irradiating films cast from the modified resin for various periods of time. Since the extent of azidation was a maximum at 80°C, the resin azidated for 4 h at 80°C was employed for this study. Films were cast from the azidated resin from a 10% solution of the polymer in THF and were irradiated with u.v. light for various periods of time. *Figure 3* gives the i.r. spectra of the irradiated polymer films showing progressive decrease in the intensity of the azide peak at $2100 \, cm^{-1}$ due to the crosslinking reaction.

The amount of the plasticizer migrated in 24 h from sheets modified at various temperatures under PTC conditions and irradiated for 1 h is depicted in *Figure 4* (line *a*). As can be seen, the extent of migration is the least from specimens modified at 80°C, in accordance with the data obtained in the case of the resin. The extent
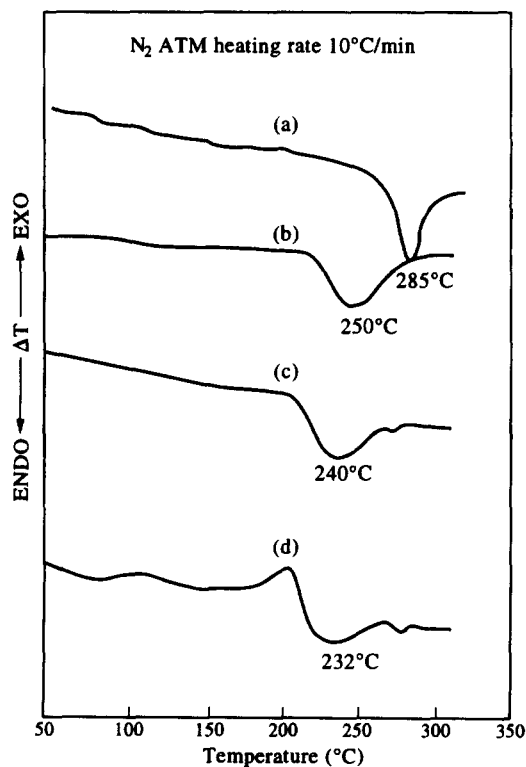

Figure 3 I.r. spectra of azidated PVC films cast from a THF solution and u.v. irradiated for various periods of time showing progressive decrease in azide absorption due to crosslinking. Unirradiated (a), irradiated for 30 min (b), 60 min (c), 120 min (d) and 180 min (e)

Figure 2 D.t.a. of PVC resin showing an endotherm at 285°C due to the decomposition of the polymer (a) and azidated PVC resin showing reduced thermal stability with increase in the degree of azidation: 5% (b), 17% (c) and 45% (d)
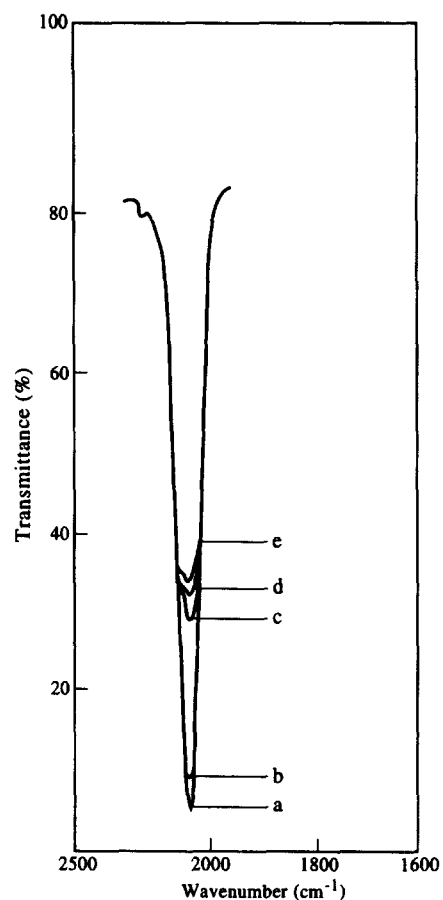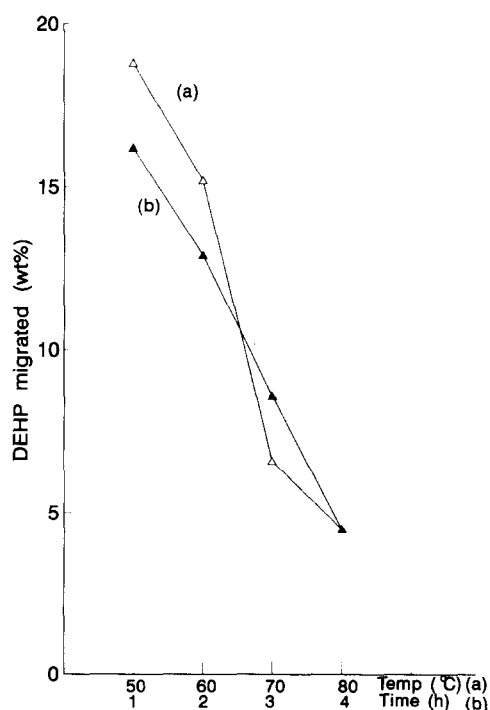

Figure 4 Amount of DEHP migrated into hexane at 30°C in 24 h from PVC sheets modified at different temperatures at [TAB] $0.037 \, mol \, dm^{-3}$ for 4 h and irradiated for 1 h (a), and DEHP migrated from sheets azidated for various time periods at [TAB] $0.037 \, mol \, dm^{-3}$ and irradiated for 1 h (b)

of migration in 24 h from sheets azidated for various time periods and irradiated for 1 h is shown in *Figure 4* (line *b*). In the case of unmodified sheets, the migration was found to be 21% in 24 h. As observed in the case of the resin, increased reaction time results in increased concentration of the azide on the surface of the PVC sheet, which is believed to produce a higher crosslinking density on the surface under u.v. irradiation, resulting in decreased migration of DEHP. The kinetics of plasticizer migration from sheets modified at 70 and 80°C and irradiated for 1 h is shown in *Figure 5*. Values obtained in the case of control sheets both unirradiated and irradiated for 1 h are also shown for comparison. There is a reduction in migration from samples modified at both temperatures in comparison with control samples. U.v. irradiation alone does not have any effect on the migration of the plasticizer. It has been reported that short time irradiation does not have any effect on the plasticizer migration and irradiation times of several days were required to see any reduction in migration even into high viscosity oils[7]. Increased radiation time (radiation dose) had a pronounced effect on migration. *Figure 6* shows the kinetics of migration of DEHP from sheets azidated for 4 h at 80°C and u.v. irradiated for various periods of time. It can be seen that as the time of irradiation increased, the amount of plasticizer migrated is also reduced correspondingly. Considering the fact that hexane is a potential extractant for DEHP, for the specimen irradiated for 3 h there is less than 5% migration in 7 days. For comparison, migration observed from control sheets irradiated for 3 h is included in this figure. There was hardly any decrease in migration from sheets irradiated for 3 h compared to unirradiated sheets (see *Figure 5*). It is thus evident that increased radiation dose produces increased crosslinking density on the surface of PVC which acts as a barrier for diffusion of the plasticizer.
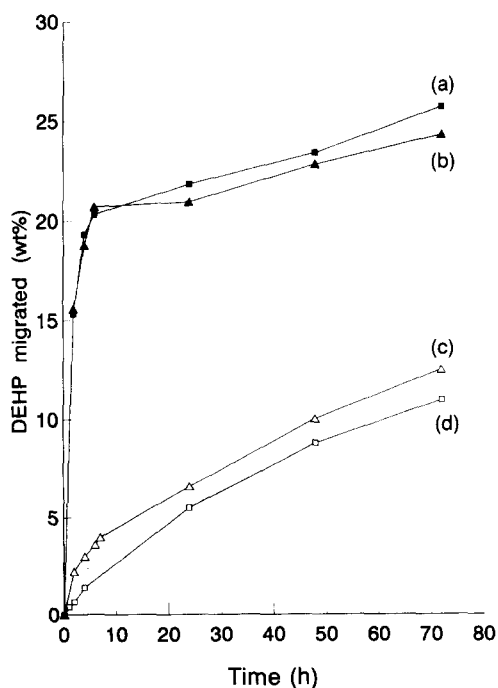

Figure 6 Effect of radiation dose on the extent of migration of DEHP from PVC sheets azidated at [TAB] 0.037 mol dm^{-3} at 80°C. Control sheet irradiated for 3 h (a), sheets azidated and irradiated for 30 min (b), 1 h (c), 2 h (d) and 3 h (e)

Figure 7 shows the kinetics of migration of DEHP into hexane from sheets azidated for 4 h at 80°C at different concentrations of TAB and irradiated for 1 h. While at very low concentrations of TAB there seems to be little effect on the plasticizer migration, as the concentration is gradually increased, reduced migration is seen. At very low concentrations of the catalyst, it appears that there is no significant azidation. *Figure 8* shows the kinetics of

Figure 5 Kinetics of DEHP migration from sheets azidated at 70 and 80°C for 4 h at [TAB] 0.037 mol dm^{-3} and irradiated for 1 h. Control sheet unirradiated (a), control sheet irradiated for 1 h (b), sheet reacted at 70°C (c) and sheet reacted at 80°C (d)
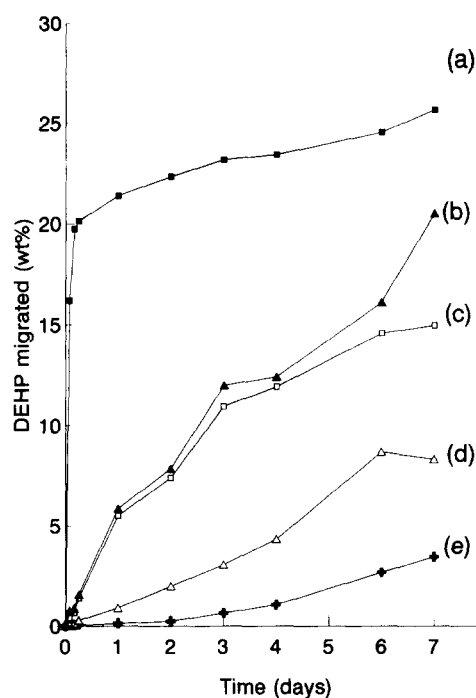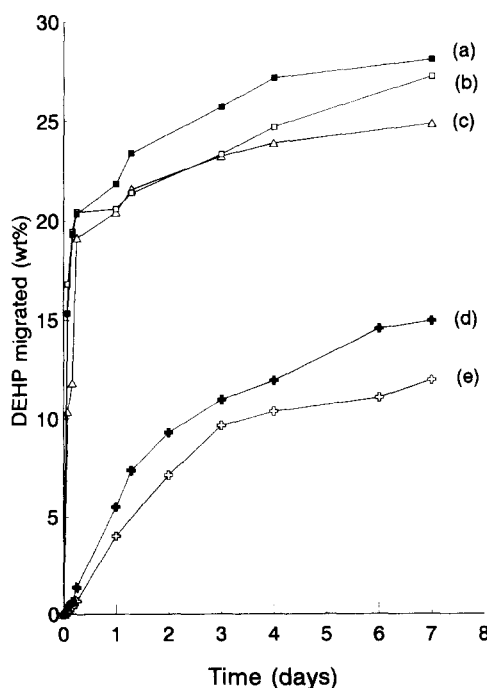

Figure 7 Kinetics of migration of DEHP into hexane from PVC sheets azidated for 4 h at 80°C at different [TAB] and irradiated for 1 h. Control sheet (a), [TAB] = 0.006 (b), 0.012 (c), 0.037 (d) and 0.05 mol dm^{-3} (e)

migration from sheets azidated for 4 h at 80°C at various concentrations of sodium azide at a TAB concentration of $0.037 \, mol \, dm^{-3}$ and irradiated for 1 h. Until the azide concentration is around 40% (nearly saturated solution), no significant reduction in migration could be seen. Unlike in non-aqueous media such as DMF, where the nucleophilic substitution of chlorine by the azide anion proceeds feasibly even in the absence of a catalyst[11], in aqueous solutions a very high concentration of the nucleophile is essential for the replacement to take place even in the presence of PTC.

Figure 9 shows the SEM of the unmodified PVC sheet and sheet azidated at 80°C for 4 h and u.v. irradiated for the maximum dose employed in this study. There appeared to be no significant change in the surface morphology of the sample before and after the reactions.

The results of mechanical testing of the PVC sheets before and after surface modification are shown in *Table 1*. There is around 35% reduction in percentage strain for the sample treated for the maximum duration of reaction (4 h) followed by the maximum duration of irradiation (3 h). The decrease in stress at peak for the sample under these conditions is around 30%. Treatment of PVC at 80°C in water for 4 h or irradiation for 3 h did not alter the properties of the sheets. However, even after the decrease in the stress/strain properties of the sheets following surface modification, the values are well above the standards prescribed for vinyl chloride plastics used in biomedical applications[17]. The reduction in the stress/strain properties is believed to be due to the crosslinking induced on the surface of PVC.

Spectroscopic and t.l.c. analysis showed that there was no interaction between DEHP and sodium azide in the presence of PTC. The i.r. spectra of DEHP before and after treatment with sodium azide in the presence of TAB were identical. The u.v. spectra of DEHP were also identical before and after the reaction. T.l.c. analysis
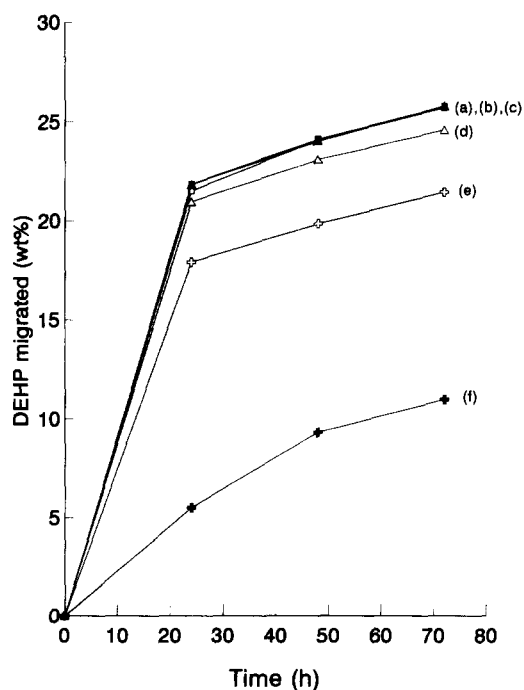
(a)   x1.5k 0415   15kV   20μm

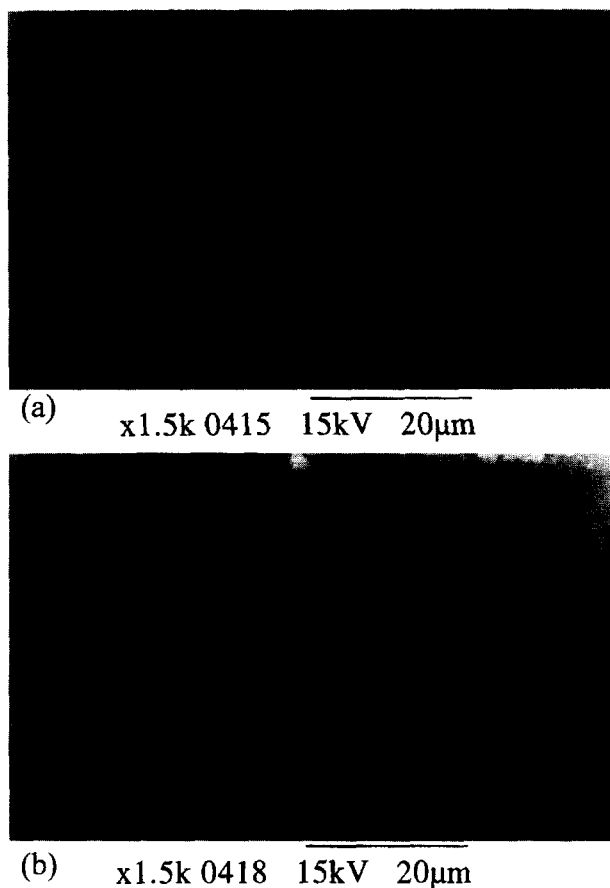(b)   x1.5k 0418   15kV   20μm

Figure 9 SEM of unmodified PVC sheet (a) and sheet azidated for 4 h at 80°C at [TAB] $0.037 \, mol \, dm^{-3}$ and irradiated for 3 h (b)

showed that no reaction product is formed when DEHP was treated with sodium azide in the presence of TAB in water. Only a single spot could be detected in the fraction extracted using hexane, the R_f value of which was the same as that of DEHP (0.65). Thus, the only reaction between the plasticized PVC and sodium azide in the presence of TAB is the nucleophilic substitution of chlorine on the surface of PVC by the azide anion.

CONCLUSION

It can be said that phase transfer catalysed azidation of plasticized PVC offers an opportunity to contain plasticizer migration to some extent. The azidation of PVC under PTC conditions produces pronounced colour changes in the PVC, due to dehydrochlorination that accompanies nucleophilic substitution. However, it may be possible to suppress the dehydrochlorination by conducting the reaction in the presence of dithiocarbamates which are known to suppress

Figure 8 Kinetics of migration of DEHP from PVC sheets azidated for 4 h at 80°C at various azide concentrations using [TAB] $0.037 \, mol \, dm^{-3}$. Control sheet (a), 5% azide (b), 10% (c), 20% (d), 30% (e) and 40% (f)

Table 1 Stress–strain properties of PVC sheets before and after surface modification

Sample	Strain ± SD (%)	Stress ± SD (MPa)
Unmodified PVC sheet	606 ± 69	33 ± 3.3
Sheet at 80°C in water, 4 h	595 ± 45	32 ± 4.2
Sheet 3 h irradiated	528 ± 72	30 ± 5.0
Sheet autoclaved	620 ± 35	33 ± 2.8
Sheet 4 h reacted, unirradiated	504 ± 55	30 ± 4.5
Sheet 4 h reacted, 3 h irradiated	393 ± 12	23 ± 0.5

dehydrochlorination of PVC extremely well[18]. Furthermore, as the azidated PVC can undergo a number of chemical reactions[19], it would be possible to induce surface crosslinking by chemical means without resorting to photolysis of the azide. It thus seems probable that PTC modification of plasticized PVC surface would be a promising method to tackle the problem of plasticizer migration.

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