Surface Treatment of Plasticized Poly(vinyl chloride) to Prevent Plasticizer Migration

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ABSTRACT: In this investigation, plasticized poly(vinyl chloride) (PVC) was treated with poly(azido acrylate)s to prevent plasticizer migration. This was achieved by modification of PVC sheets with poly(azido acrylate)s in a dichloromethane solution followed by irradiation under UV light. The surface-modified PVC sheets with poly (azido acrylate)s were characterized with Fourier transform infrared spectroscopy and scanning electron microscopy analyses. The migration of the plasticizer was prevented to a large extent from modified PVC in comparison with unmodified PVC. The amount of plasticizer migration with respect to the irradiation time, incubation time, and number of dipping times was evaluated. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1589–1597, 2010

Key words: functionalization of polymers; interpenetrating networks (IPN); poly(vinyl chloride) (PVC)

INTRODUCTION

Plasticized poly(vinyl chloride) (PVC) is one of the most widely used polymeric materials in the field of medicine and in pharmaceuticals. In medicine, flexible PVC is used for blood storage bags, endotracheal tubing, intravenous solution dispensing, and drug product storage.[1–4] Plasticizers are often added to PVC to improve its flexibility. Among phthalic acid esters, di-(2-ethylhexyl) phthalate (DEHP) is a preferred plasticizer for PVC. Because the plasticizer is not covalently bound to the polymer (PVC), there is a possibility of migration of the plasticizer from the polymer matrix. The migration of DEHP from PVC bags has been a major concern for many years.[1] Leakage of the plasticizer from plasticized PVC into an aqueous medium is influenced by the storage time, temperature, pH, concentration, shaking, thermal exposure, surfactants, and solution type.[1,2,5–13] The release of the plasticizer not only alters the long-term properties of the PVC material but also has toxic and biological effects.[14–18]

The migration of a plasticizer from medical devices can be prevented by either substitution of the harmful plasticizer or prevention of the mass transfer of the plasticizer from the polymer matrix by surface modification. Replacement of the plasticizer with low glass-transition temperature polymers such as ethylene/vinyl acetate/carbon monoxide terpolymer, polycaprolactone/polyurethane (PU), polyether/PU, polyolefin, and branched methyl ester end-group polyesters results in improved properties but often is expensive for the given application and performance.[19–21] For this particular reason, a number of surface coating, surface crosslinking, and multilayer coating methodologies have received much attention.[22,23] These processes alter the mesh sizes or pores between the polymer chains of PVC, and this results in a restriction of the release of plasticizers. The surface modification of PVC with any condensation polymers, polyacrylates, PUs, polyesters, or polyamides involves UV irradiation, γ-irradiation, and glow discharge.[24–26] Surface crosslinking can be achieved by irradiation of the polymer in the presence of multifunctional monomers. Instead of modifying PVC with various polymers, it is also possible to follow simple modifications of PVC by its reaction with sodium azide, thiosulfate, and sodium sulfide.[27–29] A recent study has described the properties of surface-modified PVC films in solvent and nonsolvent mixtures.[30] Surface-modified PVCs have shown less migration than unmodified polymers.[31]

An examination of plasticizer-migrated PVC objects that have deteriorated has shown that the plasticizer first migrates from the bulk to surfaces. This is manifested by increased tackiness evaporation of DEHP and later discoloration of the objects with the formation of conjugated polyenes of increasing length. Although discoloration is

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esthetically damaging, tackiness due to the presence of a plasticizer at PVC surfaces is of greater concern from a conservation perspective. Therefore, it is necessary to modify the surface of PVC to prevent the migration of DEHP to the surrounding media. This requires alternative and promising modification methods to obtain a safe plasticized PVC article that prevents plasticizer migration. In view of this, we have studied the surface modification of plasticized PVC sheets by irradiating PVC sheets with UV light in the presence of azido polymers, thereby forming cross-linked networks on the PVC surface through azido polymers. This entire process effectively prevents the migration of the DEHP plasticizer from PVC.

EXPERIMENTAL

Materials

Medical-grade PVC sheets containing the plasticizer DEHP were purchased from Hindusthan Latex, Ltd. (Trivandrum, India). Acryloyl chloride (ACl), methacryloyl chloride, triethyl amine, and methyl hydroquinone were purchased from Aldrich (Milwaukee, WI); chloroethanol (CE), chloropropanol (CP), sodium azide (NaN_3), tetrabutyl ammonium hydrogen sulfate, hexane, and dichloromethane (DCM) were obtained from SD Fine-Chem (Mumbai, India). CE was distilled *in vacuo* before being used.

Preparation of azido ethanol (AzE) and azido propanol (AzP)

AzE and AzP were prepared by the azidation of CE and CP according to a procedure available in our laboratory. In this preparation, 3-CE (50 mL, 36.24 g, 0.5 mol) was added to a mixture of water (60 mL) containing sodium azide (96.21 g) and tetrabutyl ammonium hydrogen sulfate (3 g). The mixture was stirred at 80°C for 24 h and then at room temperature for 13–14 h. The product was extracted with ether, the resulting solution was dried over sodium sulfate, and then the solvent was removed; after vacuum distillation, 3-AzE was obtained. The same procedure was adopted to obtain AzP from 3-CP.

IR: 3368 (broader —OH), 2103 cm^{-1} (υ_{-N3}). ^{1}H-NMR for 3-AzP ($CDCl_3$, δ): 3.76 (t, 2H, CH_2—O), 3.46 (t, 2H, CH_2—N_3), 1.84 ppm (tt, 2H, C—CH_2—C).

No unreacted 3-CP was detected by NMR.

Synthesis of azidoethyl acrylate (AzEA), azidopropyl acrylate (AzPA), and azidopropyl methacrylate (AzPMA)

A solution of AzE (7 mL, 0.25 mol), triethyl amine (14 mL, 0.323 mol), and hydroquinone (0.1 g) was cooled in an ice–water bath. ACl (9 mL, 0.32 mol) was added dropwise over a period of 20 min, and the reaction solution was stirred in the cooling bath for 1 h; this was followed by stirring at room temperature for 14 h. DCM (70 mL) was added to the reaction solution, and the azido acrylates extracted into the organic layer were washed with aqueous HCl (1/10 v/v, 200 mL), water (200 mL), 10% aqueous NaOH, and water (200 mL) sequentially to purify the azido acrylates. Finally, DCM was removed by vacuum distillation, and the resulting product was stored with the addition of 10 mg of methyl hydroquinone. Similarly, AzPA and AzPMA were prepared from 3-azidopropanol, ACl, and methacryloyl chloride.

IR (neat liquid, NaCl plates): 2100 (υ_{-N3}), 1721 cm^{-1} ($\upsilon_{C=O}$). ^{1}H-NMR of AzPMA ($CDCl_3$, δ): 6.11 (t, 1H, =CH), 5.58 (t, 1H, =CH), 4.24 (t, 2H, CH_2—O), 3.52 (t, 2H, CH_2—N_3), 1.91–2.02 ppm (m, 5H overlapping CH_3C= and C—CH_2—C).

Synthesis of poly(azidoethyl acrylate) (PAzEA), poly(azidopropyl acrylate) (PAzPA), and poly(azidopropyl methacrylate) (PAzPMA)

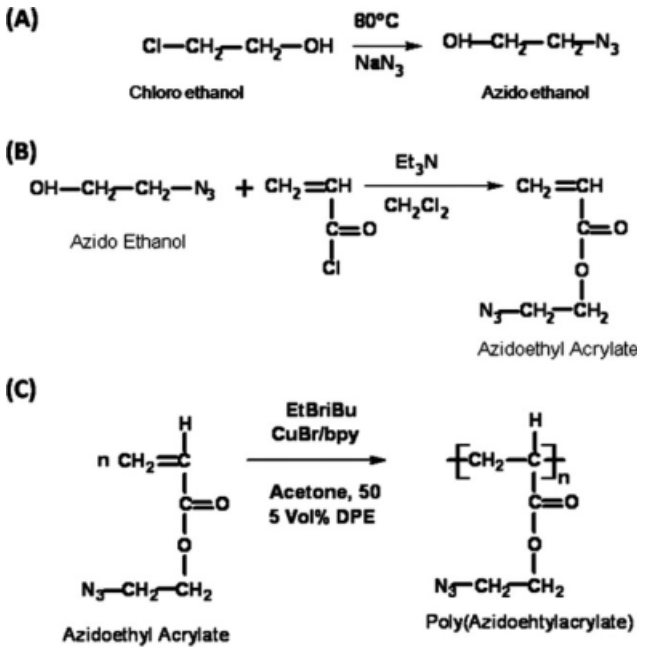
The synthesis of PAzEA, PAzPA, and PAzPMA was performed with the following procedure. A mixture of AzEA (2.0 mL, 13 mmol), acetone (2 mL), and diphenyl ether (0.15 mL) was placed in a 100-mL, round-bottom flask. To this solution, CuBr (9.3 mg, 0.065 mmol) and 2,2′-bipyridine (20.2 mg, 0.129 mmol) were added, and the reaction solution was heated to 50°C under a nitrogen atmosphere. After 8 h of reaction, the flask was brought to room temperature and opened to expose the catalyst to air. The resulting solution was diluted with chloroform and precipitated with methanol. The precipitate yielded PAzEA. In a similar fashion, PAzPA and PAzPMA were synthesized.

Coating of polymeric azides onto plasticized PVC

For coating experiments, the prepared azido polymers PAzEA, PAzPA, and PAzPMA were dissolved in 10 mL of DCM. PVC sheets (100 mg) were weighed and coated with the azido polymers via dipping in solutions for 1, 2, 3, and 4 min. These samples were irradiated with UV light with a Genei (Bangaluru, India) UV apparatus (15 W) for 5 h. Samples were placed at a distance of 15 cm from the light source. After irradiation, the samples were stored in a desiccator for plasticizer migration studies.

Migration studies

Migration studies of the coated and uncoated sheets were carried out in the solvent hexane at 30 ± 1°C. Approximately 30-mg samples were weighed and



Scheme 1 Schematic representation of the preparation of PAzEA: (A) the azidation reaction of CE to AzE, (B) the acryloylation of AzE to AzEA, and (C) the polymerization of AzEA to PAzEA.

kept in 30 mL of the solvent hexane in stoppered Erlenmeyer flasks, and the flasks were manually shaken occasionally. Some of this solution (1 mL) was withdrawn at different intervals over a period of 72 h. An equal volume of the solvent was immediately added to the flask after the withdrawal. After dilution, the absorbance of the DEHP solution was measured with an Elico (Sanat Nagar, Hyderabad, A.P., India) SL-164 double-beam UV–vis spectrophotometer at 275 nm, at which DEHP had its maximum characteristic absorbance. The amount of the plasticizer that migrated into the medium was then calculated from a calibration curve of the DEHP plasticizer in hexane.

Instrumentation

^{1}H-NMR spectra of azido polymers were measured with a JEOL (Tokyo, Japan) Delta2-NMR 500-MHz spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. Fourier transform infrared (FTIR) spectra of azido-polymer-modified plasticized PVC samples were recorded on a Thermo Nicolet (Washington, D.C., USA) Nexus 670 spectrophotometer. Thin sheets of PVC samples ($\sim$ 0.2 mm) were inserted into a standard magnetic plate sample holder and operated at a resolution of 2 cm^{-1}. The averages of 64 scans results were plotted as FTIR spectra from 4000 to 600 cm^{-1}. Scanning electron microscopy (SEM) was employed to observe the morphological changes between plasticized PVC sheets and azido-polymer-coated plasticized PVC. For this experiment, these plasticized sheets were coated with a thin layer of a palladium–gold alloy, and the surfaces were imaged at 15–20 kV on a JEOL (Tokyo, Japan) JSM-5300 scanning electron microscope.

RESULTS AND DISCUSSION

In this study, we have designed a novel route to prevent the migration of a plasticizer from plasticized PVC by coating the surface of the plasticized PVC with PAzEA, PAzPA, and PAzPMA polymers. A complete schematic representation of the synthesis of PAzEA is depicted in Scheme 1. The formation of azido polymers or poly(azido acrylate)s was confirmed with their ^{1}H-NMR spectra (Fig. 1). All three polymers (PAzEA, PAzPA, and PAzPMA) were shown to have a characteristic peak in the range of 3.25–3.36 ppm, which confirmed the presence of an azide moiety. The peaks at 3.61 and 4.09 ppm demonstrate the incorporation of ester groups into the polymer backbones. The details of the assigned ^{1}H-NMR peaks of the azido polymers are presented here.

^{1}H-NMR of PAzEA (500 MHz, $CDCl_3$): 0.993 (1H, CH), 1.32 (2H, CH_2), 3.24 (2H, CH_2—N_3), 3.61 ppm (2H, CH_2O).

^{1}H-NMR of PAzPA (500 MHz, $CDCl_3$): 1.993 (1H, CH), 2.20 (2H, CH_2), 3.36 (4H, CH_2—CH_2—N_3), 4.09 ppm (2H, CH_2O).

^{1}H-NMR of PAzPMA (500 MHz, $CDCl_3$): 1.82 (3H, CH_3), 2.02 (2H, CH_2), 3.25 (4H, CH_2—CH_2—N_3), 4.06 ppm (2H, CH_2O).

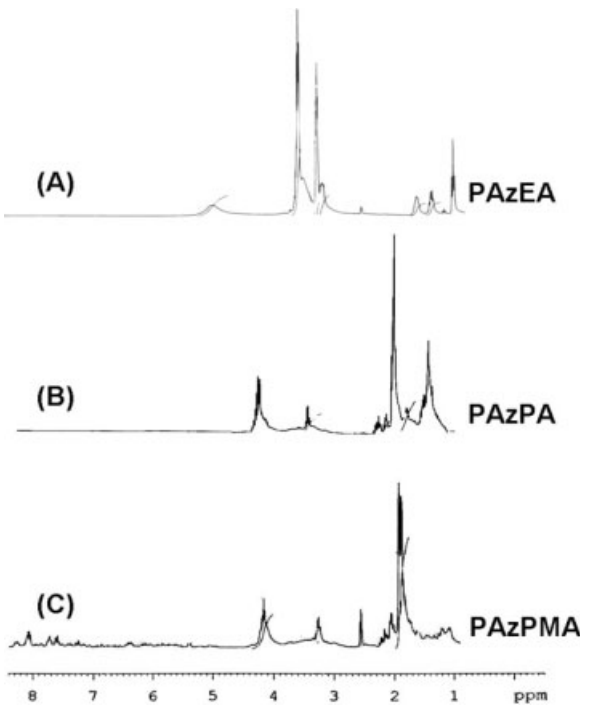
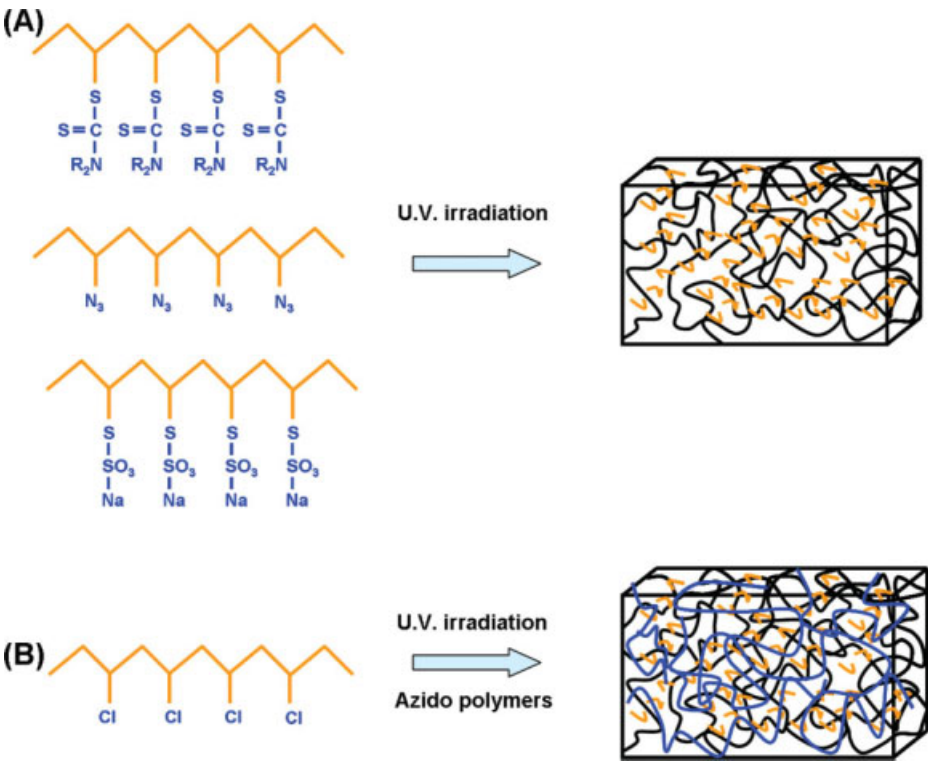


Figure 1 ^{1}H-NMR spectra of (A) PAzEA, (B) PAzPA, and (C) PAzPMA.



Scheme 2 Hypothesis of irradiated, crosslinked, and plasticized PVCs that can reduce plasticizer migration by network formation. (A) The conventional and simple modification of plasticized PVC with thiosulfate, sodium azide, and sodium sulfides indicates modification only on the surface of plasticized PVC in orange. (B) The modification of plasticized PVC with azido polymers such as PAzEA, PAzPA, and PAzPMA is shown. Azido polymers facilitate crosslinks throughout the plasticized PVC [i.e., surface (orange) and cross-sectional (blue) areas]. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The absence of peaks at δ values of 6.11 and 5.58 ppm related to the vinyl group (CH_2=CH—) and the presence of peaks at δ values of 0.993 and 2.2 ppm related to CH and CH_2 indicated the formation of azido polymers.

Simple modification of pendent groups of plasticized PVC with various chemical groups, as reported earlier, may provide changes only on the surface of PVC films, but there still is a chance to release the plasticizer from the surface of the films with time [Scheme 2(A)]. Our experimental design involves coating azido acrylate polymers onto plasticized PVC to overcome the conventional plasticizer migration phenomenon by forming a surface network barrier on the PVC polymer film and thereby arresting the migration of the plasticizer [Scheme 2(B)]. To confirm this, the plasticized PVC was modified with azido acrylate polymers and then subsequently irradiated with UV light to induce crosslinks throughout the PVC films, and migration studies were performed.

Coating of plasticized PVC

Polyacrylates are known to induce crosslinks in plasticized PVC upon UV irradiation, but they can produce protective coating layers only on the PVC surfaces. To overcome this problem, we chose azido acrylate polymers [poly(azido acrylate)s] because they can form fast crosslink networks by photochemical reactions of the pendent azide groups not only on the surface of PVC sheets but also throughout PVC sheets (cross sections of PVC sheets) and thereby arrest plasticizer migration within the PVC polymer chain networks also. This might be possible because of their greater reactivity with PVC sheets.

The crosslinking of azido acrylate polymers both on the surfaces and in the cross-sectional areas of plasticized PVC films was confirmed by FTIR spectral analysis. Figure 2(A) illustrates the surface-modified PVC sheets with azido acrylate polymers (PAzEA, PAzPA, and PAzPMA). The disappearance of the characteristic absorption peak at 2100 cm^{-1} indicates the involvement of azido groups in photocrosslinking on the PVC surface.[32] The peak at 1720 cm^{-1} of the carbonyl group of the acrylate moiety indicates the presence of acrylate polymers on the modified PVC surface. The band at 1635 cm^{-1} is due to the presence of —C=C— groups formed in the PVC sheet by the elimination of HCl molecules during crosslinking reactions. All these peaks were also found in cross-sectional areas of plasticized PVC films [Fig. 2(B)]. It is very important to mention

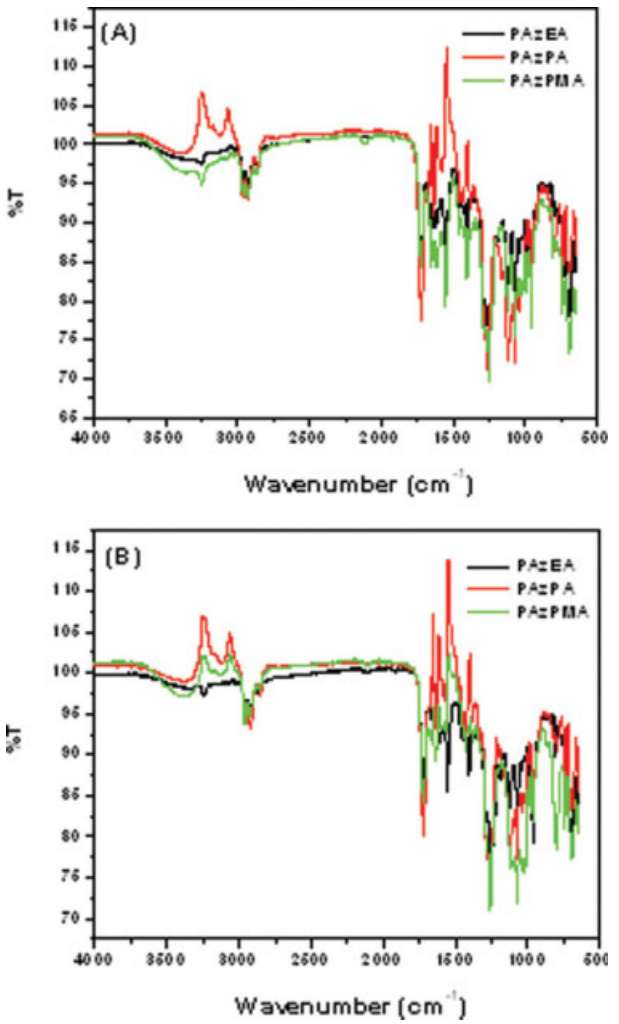


Figure 2 FTIR spectra of PAzEA-, PAzPA-, and PAzPMA-modified plasticized PVC sheets dipped for 5 min and irradiated under UV for 5 h: (A) surfaces of the PVC sheets and (B) cross-sectional areas of the PVC sheets. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

here that the characteristic peaks corresponding to azide groups were clearly not observed in the FTIR spectra of modified and crosslinked plasticized PVC samples, and this indicated their involvement in the crosslinking reactions with PVC on UV irradiation, which changed their functional moiety.[32] The FTIR spectra of surface and cross-sectional plasticized PVC films also showed the presence of peaks characteristic of plasticized PVC. Therefore, the azido polymers have the ability to diffuse throughout PVC films.

SEM analysis

The crosslinking formation of azido acrylate polymers on plasticized PVC sheets was further supported by SEM analysis. The plasticized PVC surface morphology was nonuniform in appearance [Fig. 3(A)] and was very similar to the findings of previous reports.[27–29] When the plasticized PVC was modified with PAzEA, PAzPA, and PAzPMA, the morphology of the PVC surface showed more crosslinked networks over the surface of the plasticized PVC [Fig. 3(B–D)]. In contrast, the azide- and thiosulfate-modified plasticized PVC surfaces did not show any crosslinked morphologies, as reported earlier.[27,28] Cross sections of azido acrylate polymer modified plasticized PVC sheets suggested the formation of crosslinked layers throughout the PVC sheets, as shown in the SEM images [Fig. 4(A–C)]. This is the major advance and novelty of our current coating technology, in which tightly crosslinked surface-networked barrier layers of azido acrylate polymers are formed on the surface/cross sections of PVC sheets and are responsible for the greater reduction in the plasticizer migration.

Migration studies

As mentioned earlier, this investigation involved the crosslinking of azido acrylate polymers onto the surface and into the cross sections of PVC sheets by UV irradiation. However, it is also known that photochemical degradation occurs simultaneously along with crosslinking when PVC is irradiated with UV light.[27,28] At the same time, it is known that UV radiation is not very harmful to PVC when it is exposed for a short time.[29] In most cases, polymers with azide pendent groups are taken into consideration for photocrosslinking because they are highly photoresponsive on account of their fast photodecomposition. These irradiated azide systems are highly reactive and can react immediately with PVC sheets via different selective chemical reactions, thereby converting azide-functional groups into anionic nitrogen species by eliminating nitrogen molecules and reacting with PVC and thus forming strong covalent bonds.

Effect of the incubation time on the plasticizer migration

To test the migration of the plasticizer from PVC sheets, the modified PVC sheets (PVC films dipped in PAzEA/PAzPA/PAzPMA solutions for 1, 2, 3, and 4 min) and unmodified PVC films were placed in hexane, and the release of the plasticizer was estimated for prolonged periods with a UV spectrophotometer at 275 nm, at which the plasticizer had maximum UV absorption. The migration of the plasticizer was faster during the initial periods for all the unmodified and modified PVC films and plateaued at about 70 h [Fig. 5(A)]. Lower release of the plasticizer was noticed for the PVC film treated with PAzEA for 4 min versus the 3-, 2-, and 1-min treated

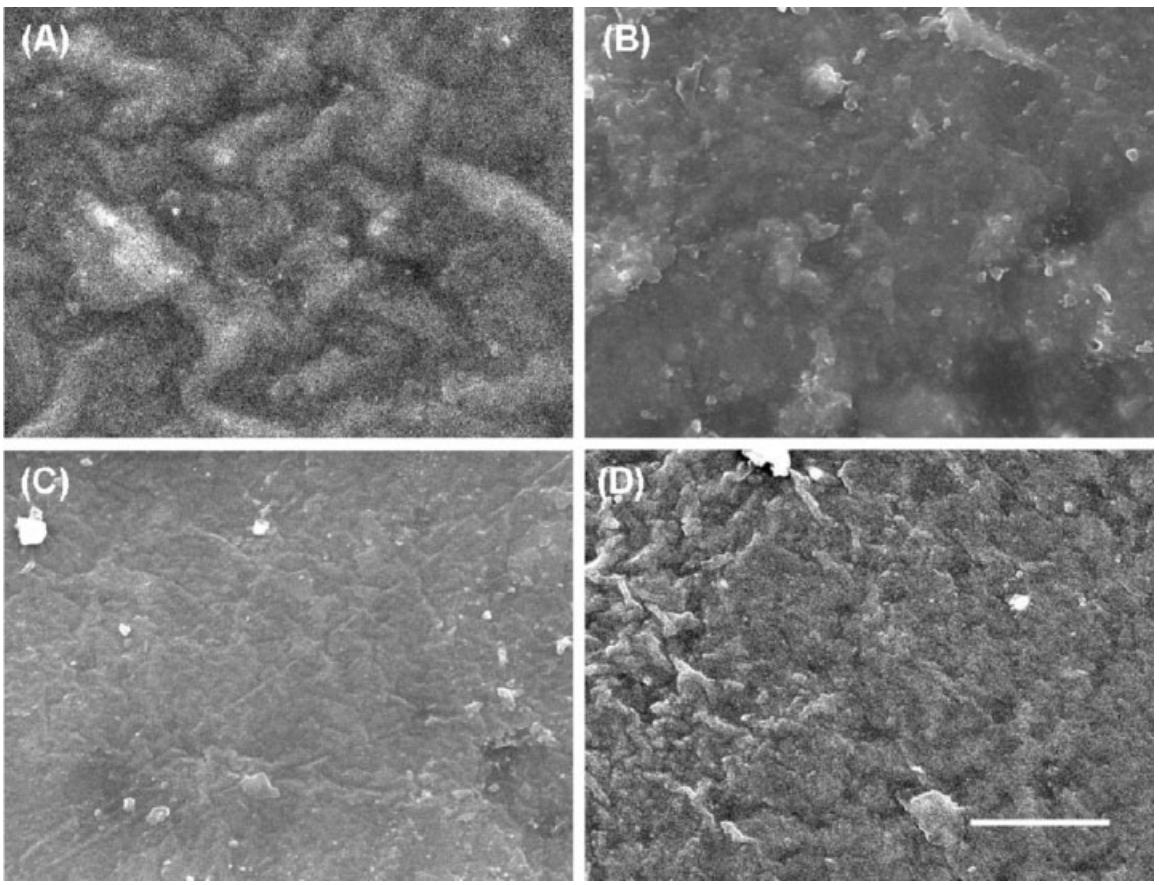


Figure 3 SEM images of (A) plasticized PVC and (B–D) plasticized PVC sheets modified with PAzEA, PAzPA, and PAzPMA (dipped for 5 min) and irradiated under UV for 5 h. All the images were taken of the sheet surfaces (scale bar = 5 μm).

PVC [Fig. 5(A)]. A similar pattern was also observed for PAzPA- and PAzPMA-treated PVC sheets. In all the cases, the DEHP release was faster from unmodified PVC in comparison with azido acrylate polymer modified PVCs [Fig. 5(B,C)]. The order of the migration of the plasticizer from unmodified PVC and modified PVC films was found to be as follows: PVC > PVC–PAzEA > PVC–PAzPA ≥ PVC–PAzPMA.

The experimental observations indicated that there was a considerable reduction in the plasticizer migration with coated PVC sheets versus uncoated PVC sheets [Fig. 5(A–C)]. Furthermore, as the dipping time increased (from 1 to 4 min); there was a gradual decrease in the plasticizer migration. The reason is the greater amount of deposition of azido acrylate polymers onto the plasticized PVC surface as the dipping time increased. In other words, the density of the polymeric azides was greater on the PVC sheets, and so the number of crosslinked polymeric azide chains increased throughout the PVC sheets. Therefore, there was a probability of creating a greater barrier for the plasticizer to prevent migration from the PVC sheets. As a result of this, the amount of the plasticizer that leached out from the PVC sheets gradually decreased. At the same time, the experimental results indicated some minor variations in the migration of the plasticizer from the sheets coated with different poly(azido acrylate)s such as PAzEA, PAzPA, and PAzPMA. We observed that the sheets coated with PAzPMA showed good reduction in comparison with PAzEA- and PAzPMA-coated PVC sheets. This variation may be due to the presence of flexible pendent azido groups, which allowed extensive crosslinking behavior in comparison with the other two polymers. Therefore, the lower amount of plasticizer migration from PAzPMA-modified PVC was due to the presence of a high number of crosslinks throughout the PVC films in comparison with the other two azido acrylate polymer modified PVC sheets [Fig. 5(A–C)].

Effect of the UV irradiation time on the plasticizer migration

The effect of the UV irradiation time on the DEHP migration of PVC sheets modified with azido acrylate polymers is shown in Figure 6. This study was done for PVC sheets dipped for a fixed time and kept in a UV chamber for different times to obtain

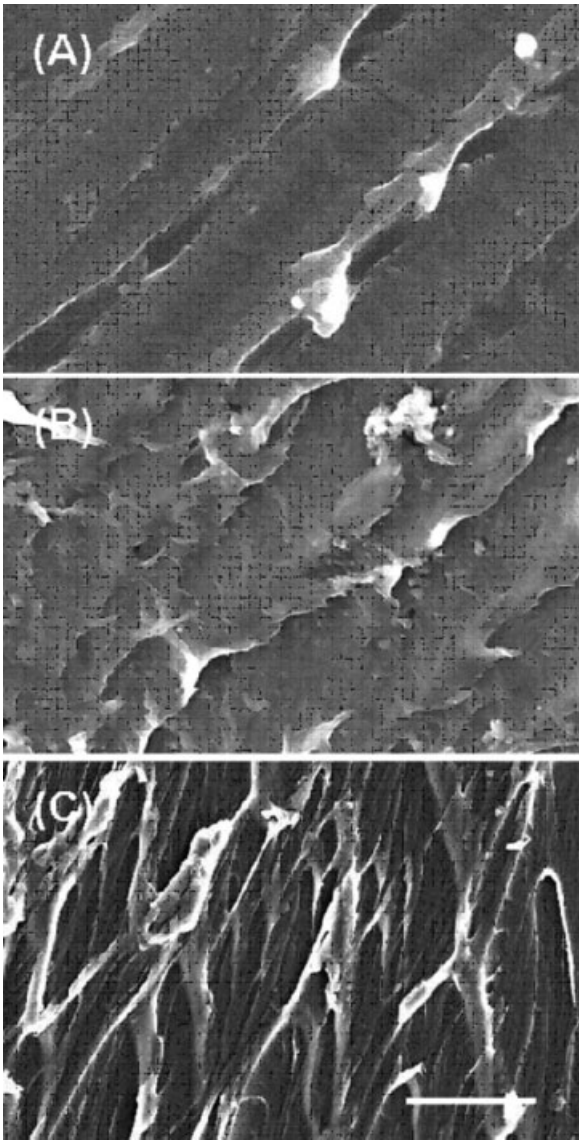


Figure 4 SEM images of (A–C) plasticized PVC sheets modified with PAzEA, PAzPA, and PAzPMA (dipped for 5 min) and irradiated under UV for 5 h. All the images were taken at the interface of the cross-sectional area (scale bar = 5 μm).

effective curing as well as crosslinking. The azide polymers, which are highly photoresponsive, might have photocrosslinked with PVC sheets during UV irradiation and developed denser surface barriers. This barrier property of crosslinked polymers prevented plasticizer migration. As the time of UV irradiation increased, the migration of the plasticizer decreased slightly. This was due to the increase in the extent of crosslinking with the irradiation time. However, prolonged UV irradiation induced color changes in the specimen because of the formation of more C=N and N=N bonds to a great extent on account of more photodecomposition reactions.

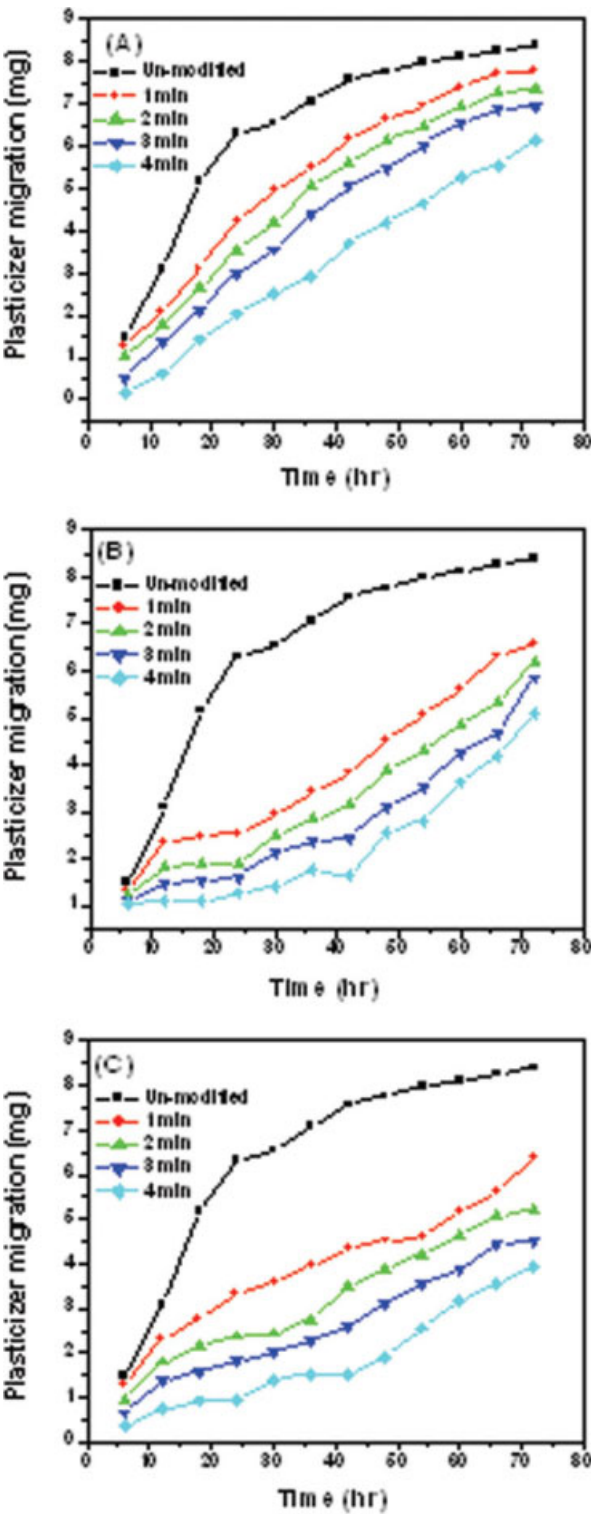


Figure 5 Migration of the plasticizer from unmodified plasticized PVC and azido-polymer-modified plasticized PVC: (A) PAzEA-, (B) PAzPA-, and (C) PAzPMA-modified plasticized PVC dipped for 1, 2, 3, or 4 min and irradiated for 5 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

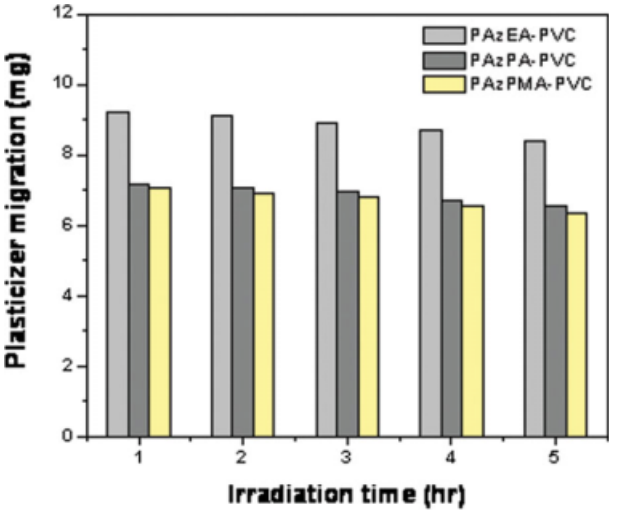


Figure 6 Migration of the plasticizer from azido-polymer-modified plasticized PVC: PAzEA-, PAzPA-, and PAzPMA-modified plasticized PVC dipped for 4 min and irradiated for different times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Influence of the number of dipping times on the plasticizer migration

Figure 7 shows the effect of the number of dipping times on the plasticizer migration. PVC sheets that were coated once or twice were used for the plasticizer migration studies. From Figure 7, it is very clear that there was a slight reduction in the migration of the plasticizer from the sheets coated twice versus that from the sheets coated only once. However, the migration was considerably less in comparison with that of the unmodified PVC. The reason could be, as explained earlier, that as the dipping time increased, the amount of polymeric azides on the PVC surface also increased, and they formed more polymer networks on the surface of PVC. At the same time, when these dipped sheets were subjected to UV irradiation, the crosslinking density on the surface of the PVC sheets also increased. Thus, migration of the plasticizer automatically decreased.

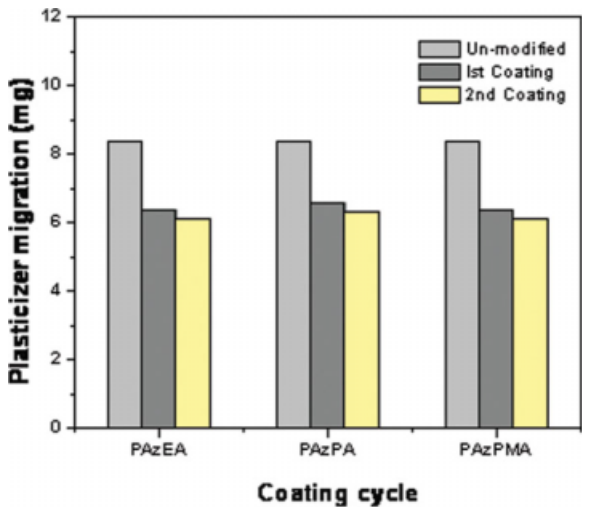


Figure 7 Influence of the migration of the plasticizer from azido-polymer-modified plasticized PVC with the number of cycles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

Poly(azido acrylate)s were synthesized, and their effect on the migration of the plasticizer DEHP was studied through the coating of these polymers onto plasticized PVC sheets. The migrated DEHP plasticizer, which is commonly used in PVC sheets, is under control after coating. This method of preparation of azide polymers is simple and straightforward. Therefore, this modified PVC is suitable for food and blood packaging and also is safe for use in other medical applications.

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