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Migration of Additives from Poly(vinyl chloride) (PVC) Tubes into Aqueous Media

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Summary: The stability and migration product of medical PVC tubes plasticized with polyadipates were investigated by ageing in phosphate buffer at pH 1.679 and water at different temperatures. Changes in the PVC tubes were studied by water absorption, weight loss, Fourier infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The low molecular weight migration product that was released was extracted and silylanized before gas chromatography/mass spectroscopy (GC/MS) identification and quantification. After 70 days, the weight loss was less than 0.5% and only a small amount of adipic acid migrated when a tube was aged at 37°C in water and phosphate buffer (pH 1.679), and at 70°C in water after 56 days. However, when aged at 70 and 110°C, gradual deactivation of heat stabilizer after 21 days of ageing in buffer solution and separation of plasticizer from PVC matrix occurred. When the tube was aged at 110°C, significant degradation of both polyadipates and PVC were observed. Adipic acid and 1,4-butanediol monomers and oligomers of polyadipate were the major migration products from polyadipates in the water ageing solution, while only a relatively high amount of adipic acid was identified as the main product in the buffer ageing solution.

Keywords: ageing; migration products; polyadipates; poly(vinyl chloride) (PVC); thermal stability

Introduction

Plasticizers are incorporated into rigid PVC to make it soft and flexible. The most common plasticizers for PVC used to be phthalate esters. These have now been banned or are controlled by the European Union in making children toys and some medical devices due to their potential toxicity and low biodegradability.[1-4] High molecular weight, low migration plasticizers, such as trimellitate and aliphatic polyesters, are used nowadays as phthalates substitutes in soft PVC products.

Since the plasticizers are physically mixed with the PVC matrix, migration and release of plasticizers in the contact media will occur. The study of plasticizer migration from PVC can be classified into two approaches: one is to study the plasticizer remaining in PVC

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after migration,[5-9] the other is to investigate the migrated chemicals in the contact media, such as in the infusion liquid, blood, soil or sea water.[10-12] The analysis of the migration products in the contaminated medium can provide more information on the degraded and migrated chemicals. In order to determine the migrated products they are usually first extracted then identified and quantified. Liquid/liquid extraction, membrane solid-phase extraction or direct solid-phase micro extraction (SPME) can be utilized for extraction. High performance liquid chromatography (HPLC), gas chromatography (GC) and GC/MS are common techniques used for subsequent quantification and identification. Extensive studies on the migration of phthalate esters[3-5,10-14] have been reported but only a few investigations focused on the low migration plasticizers. For example, Hakkarainen[15] studied the degradation products of polycaprolactone-polycarbonate from PVC aged in aqueous media and Petersen et. al.[16] investigated the migration products of polyadipates from PVC packaging film into food.

Migration or degradation of plasticizers and other additives, such as heat stabilizer, can also lead to changes in the thermal stability of PVC. TGA showed that the thermal degradation behavior of plasticized PVC is different to that of the virgin PVC.[17-19] DSC results showed that the glass transition temperature (Tg) and the onset of PVC degradation changed in the presence of different quantities of plasticizer and heat stabilizer.[20,21] Other techniques, such as FTIR, and identification of the pyrolysis products with GC/MS or with MS directly, have also been used to study the degradation mechanism on both plasticized and virgin PVC.[22-24] However, the focus of most studies was on un-used PVC. Investigations into changes in the thermal stability of aged PVC can therefore provide more details, in conjunction with the results of the migration studies.

In this work, the commercial PVC tube plasticized with polyadipates, used for feeding infants in hospital, was aged in different aqueous media. The migration products of plasticizer in the ageing media were analyzed and the changes in the aged PVC tubes were investigated.

Experimental

Materials. The PVC tube (a type used for feeding infants) was supplied by Unomedical A/S Denmark. This type of tube is plasticized with polyadipate and phthalate free.

Ageing procedure. About 0.3 g of small PVC tube pieces were put into a 4 ml glass vial together with 3 ml of distilled water or phosphate buffer pH 1.679 (IUPAC standard, Radiometer analytical, France). The ageing in low pH buffer at 1.679 was investigated because the PVC tube is used for feeding milk, via insertion into an infant's stomach. The ageing was done by placing the closed vials in an oven and aging at 37, 70 or 110°C in water or at 37°C in buffer. The ageing time varied from 1 to 70 days for the samples aged at 37 and 70°C and from 1 to 14 days for the samples aged at 110°C. After each ageing time and temperature the contents of three vials were analysed.

Water absorption and weight loss. After ageing under specific conditions, the PVC tubes were separated from the water or buffer solution and weighed (wet weight), after which they were dried until constant weight in a desiccator containing P_2O_5 (dry weight). Water absorption and weight loss were calculated from the following formulae according to [25]:

Water abs (%) = [(wet weight – dry weight)/dry weight] × 100%

Weight loss (%) = [(original weight – dry weight)/original weight] × 100%

Extraction and quantification of low molecular weight compounds. The low molecular weight products that had migrated from the PVC tube during ageing were extracted twice with ethyl acetate (10 ml for each extraction). Before extraction, 70 μl of 10% HCl, 0.33 g of NaCl and 60 μl of internal standard maleic acid (3.3 mg/ml in distilled water, Fluka, Switzerland) were added into 2 ml of water ageing solution. Each extraction took 30 minutes. For the buffer ageing solutions, only the internal standard was spiked into the solution before extraction. The ethyl acetate layer was collected and dried in anhydrous $MgSO_4$ overnight, after which it was removed by vacuum evaporation at 45°C. The residual solvent was removed by flushing with nitrogen flow. A quantity of 100 μl of bis(trimethylsilyl)trifluoroacetamide (BSTFA, 99+%, from Sigma) containing 1% of trimethylsilylchloride (TMS, from Fluka) was added into the sample and the derivatization was done at 70°C for 30 minutes. After derivatization, the sample solution was diluted with 1 ml of n-heptane (analytical grade, from J.T. Baker, Holland) and analysed by GC/MS. Identification of unknown compounds was considered positive when both the elution time and mass spectra were identical with those of the standards. Calibration curves were prepared by dissolving different quantities of standard adipic acid (Fluka, Switzerland) and internal standard in water and phosphate buffer. These standard solutions were then extracted by the same method and analysed by GC/MS.

Gas chromatography - mass spectrometry (GC-MS). GC/MS analysis was performed on a Varian 3800 GC connected with a Saturn 2000 MS detector. Samples were injected by an 8200 CX autosampler (all from Varian Chromatography Systems, Walnut Creek, CA, USA). The 30 m capillary column was a Restek XTI-5 (Restek, Bellefonte, PA, USA) with an i.d. of 0.25 mm and film thickness of 0.25 μm. The column temperature was initially held at 70°C for 4 min, then increased to 250°C at a heating rate of 7°C/min and held at 250 °C for 10 min. Helium was used as carrier gas, at a constant velocity of 1.7 ml/min. 1 μl of sample was injected for each analysis and the injector was operated in split mode at a ratio of 10:1. The EI mode at an electron energy of 70 eV was used and the total ion counts (TIC) was used for quantification.

Fourier transform infrared spectroscopy (FTIR). Changes in the surface composition during ageing were followed by a Perkin-Elmer Spectrum 1000 FTIR (Llantrisant, UK) equipped with a single reflection ATR accessory (Performer Swap-Top module) from Thermo Nicolet Corp. (USA). The scan range was 650-4000 cm^{-1} and an average of 20 scans was measured.

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal stability of the PVC tube during the ageing was monitored either by TGA or DSC (Mettler Toledo 822^e module from Schwerzenbach, Switzerland) analysis. Dynamic DSC analysis was carried out by heating the samples from 25 to 300°C at a heating rate of 10°/min. The TGA measurement was carried out by heating the samples from 25 to 550 °C at a heating rate of 10°C/min. A N_2 flow of 50 ml/min was used for all measurements.

Results and Discussion

Low molecular weight compounds migrated from PVC tubes

As shown in Figure 1, the chemicals found in the water were the low molecular weight migration products from polyadipate: adipic acid, oligomeric polyadipate, 1,4-butanediol, and various carboxylic acids, probably from degraded epoxidized soybean oil, which included: hexadecanoic acid, octadecanoic acid, and occasionally small quantities of tetradecanoic and dodecanoic acid. For the samples aged at 110°C, an oxidation product of butanediol was detected. The structure is proposed to be $Me_3SiO(CH_2)_4OOSiMe_3$ (from the NIST library search). Figure 2 shows the mass spectra of adipic acid and the two oligomeric polyadipates products (compounds 2 and 3). The formula of compound 3 is proposed to be $Me_3SiOOC(CH_2)_4COO(CH_2)_4OSiMe_3$; it is the condensation product of adipic acid and 1,4-butanediol, with a molecular weight of 362, whose ion fragment at 201 could be $OC(CH_2)_4COO(CH_2)_4O^{+\cdot}$. The ion fragments of compound 2 contain 111, 201, 275 and 291, which implies that this compound is an oligomeric polyadipate that contains adipic acid and diol segments. Different from the products from ageing in water, the migration products in buffer solution contained a more adipic acid, and only traces of 1,4-butanediol and oligomeric polyadipate were identified in all the aged solutions. This result implies that more oligomeric polyadipate was further broken down to adipic acid. Both the ageing solution in buffer at 37°C and in water at 110°C after 7 days ageing had a strong smell, similar to that of butyric acid, which suggests that further oxidation of 1,4-butanediol occurred during the ageing. However, further identification of the oxidized products was difficult due to the overlap of peaks in the early retention time period.

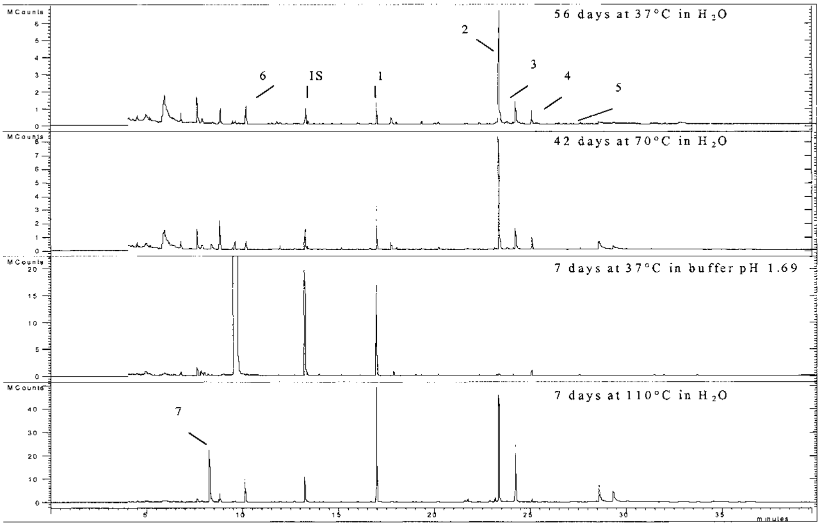

Figure 1. GC/MS chromatograms of the extracted migration products in the aged solutions. IS: maleic acid, 1: adipic acid, 2 and 3: adipic acid oligomer, 4: hexadecanoic acid, 5: octadecanoic acid, 6: 1,4-butanediol, and 7: $Me_3SiO(CH_2)_4OOSiMe_3$. The ageing solutions were extracted directly.

Figure 3 shows the quantity of adipic acid extracted from water and phosphate buffer as a function of ageing time at different temperatures. Trace amount of adipic acid were found in the samples aged at 37°C in water, even after one day's ageing. They could be residual monomers and oligomers in the original tube. The migrated adipic acid increased slowly and remained practically constant after 42 days of ageing in water at 37°C. For samples aged at 70°C, the amount of migrated adipic acid was close to that detected in samples aged at 37°C for the first week, but increased slightly later, followed by significant increase in adipic acid after 70 days of ageing. The quantity of adipic acid found in the buffer ageing solutions was much higher than in water, aged at 37 and 70°C, since nearly no polyadipate oligomers remained in the buffer solution. When the tubes were aged at 110°C in water, large quantities of adipic acid were found in the ageing solution after 14 days ageing. This indicates the fast hydrolysis of polyadipates under drastic condition.

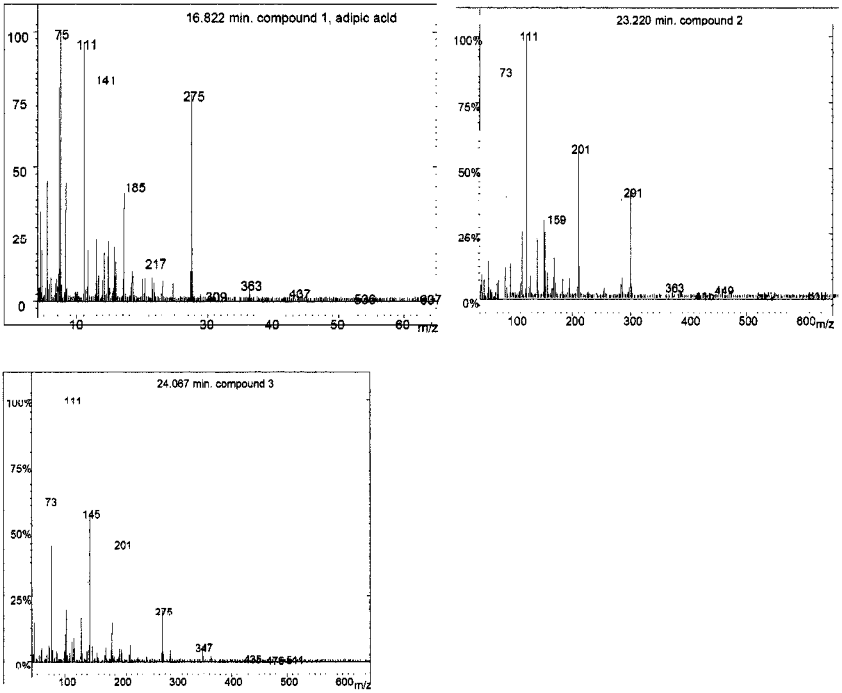

Figure 2. The mass spectra of adipic acid, compounds 2 and 3 in Figure 1.

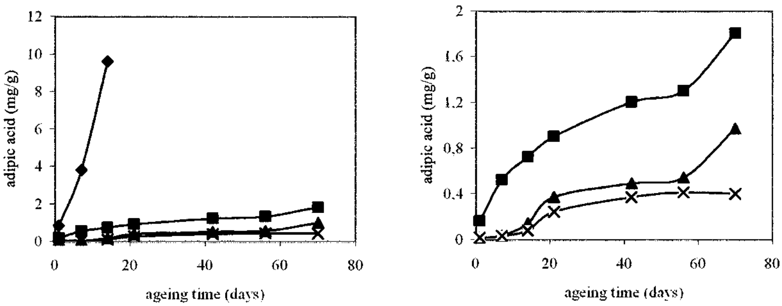

Figure 3. The amount of adipic acid extracted from water at (♦) 110 °C, (▲) 70 °C , (x) 37 °C and from (■) phosphate buffer pH 1.679 at 37 °C after different ageing times.

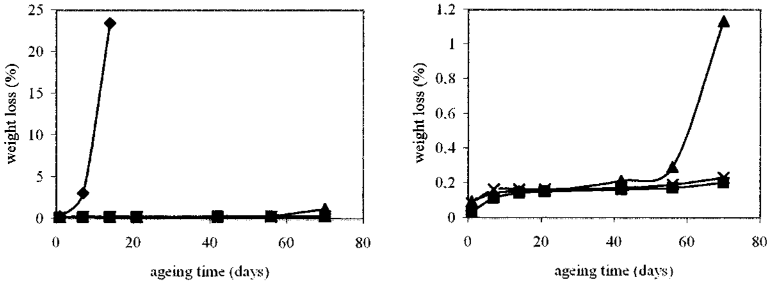

Figure 4. Weight loss of PVC tube as a function of time afer ageing in water at (♦) 110 °C, (▲) 70 °C , (x) 37 °C and in (■) phosphate buffer pH 1.679 at 37 °C.

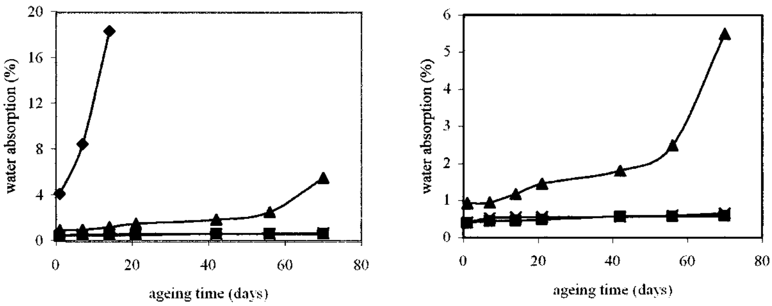

Figure 5. Water absorption of PVC tube as a function of time afer ageing in water at (♦) 110 °C, (▲) 70 °C , (x) 37 °C and in (■) phosphate buffer pH 1.679 at 37 °C.

Changes in the aged tubes

Figures 4 and 5 show the weight loss and water absorption for PVC tubes as a function of ageing time. Only minor weight loss, 0.19% after 70 days, occurred after ageing at 37°C. The water absorption was 0.4% after one day and increased slowly to 0.66% after 70 days of ageing. The weight loss and water absorption at 70 °C was 1.1% and 2.5% after 70 days of ageing. Due to the absorption of water, whitening of the tube was observed. This was reversible, i.e. it changed back to transparent after drying. A large increase in weight loss and water absorption occurred when the tubes were aged at 110°C. After only 14 days the weight loss was 23.4% and the water absorption was 18.3%. Hardening and yellowing of the PVC tubes occurred and the tubes were no longer transparent. Upon ageing at 37°C, the water absorption and weight loss in buffer solution were all slightly lower than in water. The results shows that no significant degradation of the PVC tubes occurred upon ageing at 37°C for 70 days or at 70°C for 56 days. These results correlate well with the GC/MS results.

Figure 6 shows that the FTIR spectra remained mostly unchanged after 70 days ageing in water and buffer solution at 37°C, or in water at 70°C after 56 days. A change that was observed however was the disappearance of the band at 1538 cm^{-1}, which could be absorbance from zinc carboxylate.[26] This band was observed only in the original tube and in the tube after one day ageing at 37°C in water. Results of elemental analysis showed only a trace amount of Zn, with a concentration of 120 ppm, present in the tube. In addition, it was found that the bands for this metal stabilizer remained in the PVC/polycaprolactone-polycarbonate film during the entire period of ageing in water.[25] Therefore, the origin of this band is proposed to be mainly a result of the residual processing aids. There was a small increase in the two $-CH_2$ vibration bands at 2913 and 2845 cm^{-1}, and a broad band at 3369 cm^{-1} appeared after 42 days of ageing. This indicates that a notable amount of monomers and oligomers migrated from the tube and resulted in a higher PVC content on the surface, with the simultaneous absorption of water on the tube surface. This agrees well with the GC/MS results; more adipic acid was found in the solution after 42 days ageing and increased only slowly afterwards, especially for samples aged at 37°C.

Figure 7 shows the surface composition changes in the samples cured at 110°C. No obvious changes were observed after 1 day of ageing. However, after 7 days of ageing, there was a broadening of the carboxyl group peak and a broad peak at around 3417 cm^{-1} appeared. These changes became more distinguish after 14 days of ageing. The intensity

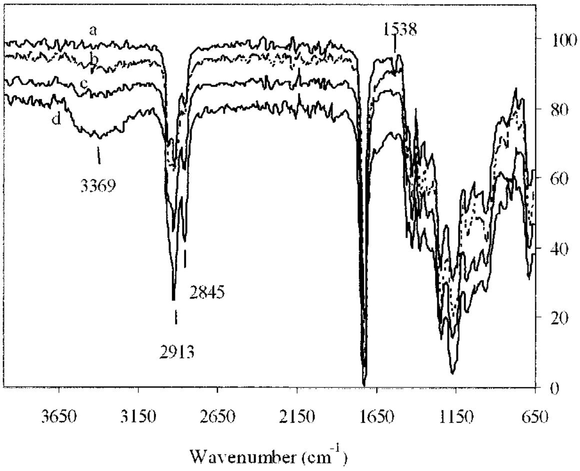

Figure 6. The FTIR spectra of a) original and aged PVC tube at b) 37°C in water for 70 days, c) 37°C in buffer pH 1.679 for 70 days, d) 70°C in water for 56 days.

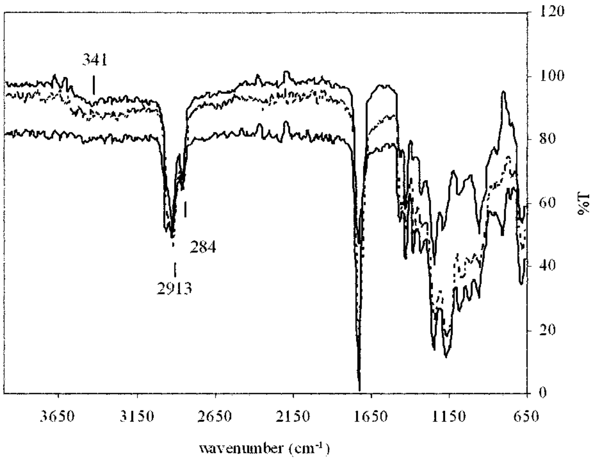

Figure 7. The FTIR spectra of an aged PVC tube at 110°C in water for 1, 7 and 14 days (from bottom to top).

of the carbonyl band at 1732 cm^{-1} decreased significantly. This is in agreement with the GC/MS result, namely that a large quantity of adipic acid was found in water after 7 days ageing and increased even further after 14 days due to the degradation of polyadipates. The appearance of carbonyl absorption around 1705 cm^{-1} indicates the oxidation of the PVC backbone. This was accompanied by yellowing of the tube.[23]

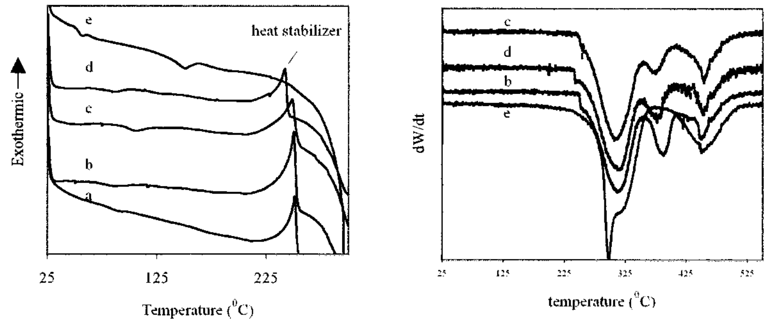

Figure 8. The DSC (to the left) and the DTG (to the right) curves of a) original tube, and tubes aged at b) 37°C in water for 70 days, c) 70°C in water for 56 days, d) 37°C in buffer pH 1.679 for 70 days, e) 110°C in water for 14 days.

Table 1. Thermal properties of aged PVC tube.

Sample[a]	DSC[b]		DTG[c]			
	Tg (°C)	T_{dec}(°C)	T_{onset}(°C)	Tp_1(°C)	Tp_2(°C)	Tp_3(°C)
A0	82.0	250	251	316	382	455
A1	81.7	250	251	316	380	455
A70	79.8	250	251	316	391	455
B1	82.0	250	Nd.	Nd.	Nd.	Nd.
B21	82.0	248	249	318	382	455
B42	79.8	245	247	318	382	455
B70	79.8	242	243	318	382	455
C56	100	249	251	312	378	455
C70	109	228	Nd.[d]	Nd.	Nd.	Nd.
D1	53.6 (127)	251	251	316	382	455
D7	52.8 (139)	224	Nd.	Nd.	Nd.	Nd.
D14	53.8 (143)	none	176	299	none	455

[a] A-D stand for different ageing conditions: A (37°C in water), B (37°C in buffer), C (70°C in water), D (110°C in water); the numbers after the letters denote the ageing days. A0 is the original tube.
[b] T_{dec} is the exothermic peak temperature; values in parenthesis for D sample are the second Tg observed.
[c] T_{onset} is the temperature at which the sample started to lose weight; Tp_1 to Tp_3 are the peak temperatures.
[d] Nd.: not measured.

The thermal stability of the tubes during ageing was studied by TGA and DSC analysis. Figure 8 shows the DSC curves (to the left) for samples aged in different media and at different temperatures. The glass transition temperature (Tg) and the exothermic peak, which could originate from the heat stabilizer,[21] are compared in Table 1. An increase in Tg was observed for the samples aged at 70 and 110°C, which indicates separation of plasticizer from the PVC matrix. The longer the ageing time, the higher the increase in Tg. In addition, two Tg were observed when the tube was aged at 110 °C, where the lower Tg could be caused by the low molecular weight degradation product from polyadipate. The heat exothermic peak for samples aged at 37°C for 70 days and at 70°C for 56 days in water was at 250°C, but disappeared after 14 days of ageing at 110°C, when the stabilizer was totally degraded. For samples cured in buffer solution at 37°C, as gradual decrease in the exothermic temperature after only 21 days of ageing was observed. Since HCl catalyses the dehydrochlorization of PVC, the absorption of HCl in the buffer solution on the tube surface could deactivated some heat stabilizers and lower the heat exothermic peak temperature.

The DSC curves shown in Figure 8 (to the right) were obtained by plotting dW/dt against temperature, where the dW/dt was the first differential of the TGA curve (weight percentage against time). Three degradation peaks were observed. The first two peaks, belonging to the first stage of PVC degradation, had higher peak temperatures than those of the virgin PVC resin.[17] According to literature,[18,19] the first peak relates to the PVC fraction that is more interactive with plasticizer and the second peak may be from the unplasticized PVC part. In Table 1, the onset temperature of degradation and the peak temperature of the three stages are listed. The onset degradation temperature observed from TGA analysis is the same as the heat stabilizer exothermic peak temperature observed in a DSC study, which shows that the results from DSC and TGA analysis agree well with each other. Except for the samples aged at 110 °C, the onset of degradation of other aged tubes was characterized by a sudden increase in the weight loss rate, which implies the total consumption of heat stabilizer at that temperature and the start of degradation of PVC. For the tube aged at 110 °C for 14 days, it started to degrade at low temperature and lost weight gradually until the first peak was reached. This is consistent with the DSC result, namely that no protection of heat stabilzer was present. Furthermore, the first degradation peak was split into two and the second peak disappeared due to the significant degradation of both polyadipates and PVC.

Conclusions

The results from GC/MS, FTIR, weight loss, DSC and TGA analysis all showed that the polyadipate was stable during the 70 days ageing at 37°C in water and low pH buffer solution and 56 days ageing at 70°C in water. The weight loss was under 0.5% and only small amounts of adipic acid migrated to the liquid. Low molecular weight polyadipate oligomers, adipic acid and 1,4-butanediol were the main migration chemicals found in water ageing solution. The polyadipate oligomers degraded further to adipic acid in buffer solution (pH 1.679) and heat stabilizer was deactivated gradually after 21 days ageing. Phase separation of plasticizer from the PVC matrix, rapid loss of heat stabilizer and polyadipates, large amount of water absorption and weight loss, as well as the high amount of migrated adipic acid and oxidation product of 1,4-butanediol found in water indicated significant degradation of both polyadipates and PVC when the PVC tube was aged at 110°C.

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