



Additional Studies on the Softening of Rigid PVC by Aqueous Solutions of Organic Solvents

Louise V. Parker and Thomas A. Ranney

March 1995

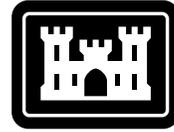
Abstract

This study examined whether an aqueous solution that contained 18 organic chemicals that are either solvents or good swelling agents of PVC are able to cause softening when combined in a solution, with each solute at an activity of 0.05. This activity was selected because there is no evidence that an individual organic solute with an activity of 0.05 can soften PVC. However, we found that this combined test solution rapidly softened PVC. We also examined whether organic chemicals that are either solvents or good softening agents of PVC and are also totally miscible in water are able to soften PVC when mixed with water. Four chemicals (tetrahydrofuran, acetone, dimethylformamide and pyridine) were tested in a study that ran for 20 weeks. Tetrahydrofuran, a PVC solvent, caused a significant change in the hardness readings of samples exposed to concentrations as low as 0.01% (w/v). Acetone, a good swelling agent of PVC, caused a significant change in the hardness readings of samples exposed to a 10% concentration but not a 5% concentration. Dimethylformamide, a poorer swelling agent of PVC, did not cause any measurable signs of softening at concentrations below 60%. The lowest concentration of pyridine tested (20%) was found to have a significant effect on the hardness readings. A preliminary short-term study (seven days) showed that n-butylamine was intermediate between pyridine and dimethylformamide in its ability to soften PVC.

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380-89a, *Standard Practice for Use of the International System of Units*, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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of Engineers**

Cold Regions Research &
Engineering Laboratory

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PREFACE

This report was prepared by Louise V. Parker, Research Physical Scientist, Applied Research Division, Directorate of Research and Engineering, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire, and Thomas A. Ranney, Staff Scientist, Science and Technology Corporation, Hanover, New Hampshire. Funding for this work was provided by the U.S. Army Environmental Center (USAEC), Aberdeen Proving Ground, Maryland, Martin H. Stutz, Project Monitor.

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LOUISE V. PARKER AND THOMAS A. RANNEY

INTRODUCTION

Materials used in groundwater monitoring wells must be able to withstand exposure to a variety of groundwater conditions. While it is commonly known that certain neat solvents (pure product) will degrade PVC pipe, the effects of high concentrations of these solvents in aqueous solution is not well understood.

This study examined whether an aqueous solution that contained 18 organic chemicals that are either solvents or good swelling agents of PVC are able to cause softening when combined in a solution, with each solute at an activity of 0.05. This study is one of a series designed to determine the ability of PVC to withstand long-term exposure to various organic contaminants in aqueous solutions.

BACKGROUND

Work by two researchers (Berens 1985, Vonk 1985, 1986) on the permeation of organic solutes through PVC pipe has shed some light on this topic. In these studies PVC was exposed to a range of concentrations, or activities, of organic solvents. Berens and Vonk noted that the solvent interaction parameter χ used in the Flory–Huggins equation* could be used as a measure of the solvent or swelling power of a particular organic solvent.

* The Flory–Huggins equation relates activity a to the volume fraction V_1 of the organic chemical in the polymer as follows:

$$\ln(a) = \ln V_1 + (1 - V_1) + \chi(1 - V_1)^2$$

where χ is the Flory–Huggins interaction parameter.

Table 1 gives the χ values Berens derived for a number of organic solvents (at 30°C). Table 2 gives values for χ that were determined (at 20°C) by Vonk (1985). PVC is only softened by solvents with a χ value less than 1 (Berens 1985) or 1.2 (Vonk 1985); the lower the number, the greater the solvent or swelling power. A neat solvent with a χ value less than 0.5 can completely dissolve PVC (Berens 1985). According to Vonk (1985), PVC is nearly inert to organic solvents if their χ value is greater than 3 (e.g., alcohols, aliphatic hydrocarbons and organic acids).

Berens observed that the rate of penetration of an organic solute in PVC changed by many orders of magnitude as the activity of the penetrant in the environment changed. He noted that at ambient temperatures, rigid PVC would only be softened by solvents or strong swelling agents of PVC at activities greater than 0.5. The less aggressive the solvent (i.e., the higher the χ value), the higher the activity required to cause softening. Figure 1 shows the isotherms Berens derived using the Flory–Huggins equation for various values of χ and the approximate softening range for PVC at 30°C. Berens predicted that for lower temperatures (such as those commonly encountered in groundwater), slightly higher activities would be needed to cause softening.

For aqueous solutions the activity of a solvent can be approximated by dividing the concentration of the compound in solution by its solubility in water. Thus, according to Berens, if aqueous solutions of solvents are going to soften rigid PVC, the pure (or neat) solvent must be able to soften or dissolve PVC and must exist in solution at a concentration that exceeds one-half its solubility in water (activity > 0.5).

One criticism of Berens's work is that the various test (activities) solutions he used in his ex-

Table 1. Equilibrium swelling and interaction parameters for PVC–organic liquid systems. (After Berens 1985.)

Compound	Weight gain (%)	Volume fraction (V_1)	Time* (hr)	Interaction parameter χ
Methylene chloride	>800**	>0.89	2	<0.53
Chloroform	227	0.68	6	0.64
Carbon tetrachloride	0	~0	(280)	—
1,1-dichloroethane	132	0.61	6	<0.68
1,2-dichloroethane	700**	>0.86	6	<0.55
1,1,1-trichloroethane	67	0.42	600	0.85
1,1,2-trichloroethane	>400**	>0.80	10	<0.56
Trichloroethylene	70	0.40	5	0.88
Tetrachloroethylene	35	0.23	800	1.17
1,2-dichloropropane	176	0.68	20	0.68
Benzene	50	0.44	12	0.83
Toluene	50–60	0.45–0.49	15	0.80
Xylene	42	0.40	100	0.88
Acetone	170	0.75	2	0.61
Methanol	~1.0	—	(300)	—
Ethanol	~0.1	—	(300)	—
i-propanol	~0.5	—	(300)	—
n-hexane	~0.6	—	(160)	—
Vinylchloride	~30	0.33	—	0.98

* Time to apparent equilibrium, 24-mil (0.6-mm) PVC sheet, or duration of experiment in parentheses.

** Soluble.

periments were prepared by dissolving the organic solvents in polyethylene glycol, so he never actually tested aqueous solutions of these organic solvents. Since it is possible that the partitioning of these organic solutes between the dissolved state and the polymer could differ between glycol and water, studies that use aqueous solutions

of (PVC) solvents are necessary to confirm Berens's predictions. While Vonk did use aqueous solutions of organics in his studies, we have been unable to find a thorough discussion of his methods that is available in English.

Our laboratory has conducted several studies to test Berens's predictions for aqueous solutions (Parker et al. 1992, Parker and Ranney 1994). In our first study (Parker et al. 1992) we looked for softening of PVC exposed to aqueous solutions containing various activities of methylene chloride. According to Vonk (1985) the χ value for methylene chloride is 0.55. However, according to Berens (1985) the χ value is less than 0.53. Thus, depending on which χ value you use, methylene chloride is either a solvent or a good swelling agent of PVC. [We have observed pieces of PVC well casing dissolve when placed in neat methylene chloride (Ranney and Parker, 1995). Thus it appears that the true χ value for methylene chloride is less than 0.5.] In this study (Parker et al. 1992), small pieces of PVC well casing were exposed to solutions with a range of activities [1.0, 0.8, 0.6, 0.4, 0.2 and 0.0 (controls with only water)] for 33 days. Samples exposed to the 1.0- and 0.8-activity solutions became rubbery and could be bent easily by hand within 4 and 22 days, respectively. This agrees well with Berens's predic-

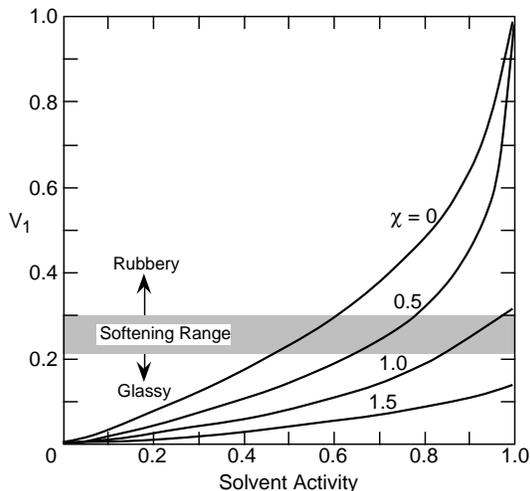


Figure 1. Flory–Huggins isotherms for various values of χ and approximate composition for softening of PVC at room temperature. (After Berens 1985.)

Table 2. Estimates of the Flory–Huggins interaction parameter χ .* (After Vonk 1985.)

<i>Organic compound</i>	χ
Benzene	0.83
Toluene	0.82
<i>o</i> -xylene	0.76
<i>m</i> -xylene	0.87
<i>p</i> -xylene	0.86
Ethylbenzene	0.89
1,3,5-trimethylbenzene	2.52
Propylbenzene	1.91
Methylethylketone	0.54
Di-isopropylketone	0.56
Methylene chloride	0.55
1,2-dichloroethane	0.56
1,1,1-trichloroethane	0.92
1,1,2-trichloroethane	0.58
1,1,2,2-tetrachloroethane	0.59
1,2-dichloropropane	0.65
Perchloroethylene	1.58
Trichloroethylene	0.90
Chlorobenzene	0.66
1,2-dichlorobenzene	0.63
1,3-dichlorobenzene	0.74
1,2,4-trichlorobenzene	1.52
<i>o</i> -chlorotoluene	0.74
<i>m</i> -chlorotoluene	0.69
<i>p</i> -chlorotoluene	0.75
Nitrobenzene	0.54
Aniline	0.87
2-chloroaniline	0.58
3-chloroaniline	0.61
<i>n</i> -methylaniline	0.59

* For segments of PVC pipe (O.D. = 32 mm and wall thickness = 1.6 mm) immersed in pure liquid compounds for 410 days at 20 ± 3°C.

tions. Also as Berens predicted, samples exposed to the lowest-activity solution (0.2) showed no signs of softening by the end of the study. However, samples exposed to the 0.4- and 0.6-activity solutions showed some slight changes (i.e., occasionally a sample could be bent and/or showed signs of curling), especially at the 0.6 activity. According to Berens, PVC should not be softened by any organic solvent at an activity of 0.4, even if χ were equal to 0.0. Using Vonk's value for χ (0.55) and Berens's isotherms (Fig. 1), we would also predict that softening should not occur at an activity of 0.6. However, if Berens is correct and χ is less than 0.53 and if the true value is 0.3 (or less), then softening would be expected (at 30°C). Thus, it appears that softening is occurring at slightly lower activities than would be expected. However, the problem with this study (Parker et

al. 1992) was that the method used to determine softening (i.e., manually bending the sample) was subjective and lacked quantification.

As reported in a subsequent paper (Parker and Ranney 1994), we conducted several studies (short term and long term) using a Barcol Impressor to quantitate hardness. In our short-term studies, small test pieces of PVC were exposed to various activity (0.8, 0.6, 0.4, 0.0) solutions of methylene chloride for a week. The pieces exposed to the 0.6- and 0.8-activity solutions had hardness readings that were significantly lower than the control samples, and these samples were rubbery in that they could easily be bent. This was not the case for the samples exposed to the 0.4-activity solution. Thus, we concluded that samples turned rubbery at a lower activity (0.6) than would be predicted using Berens' isotherms, unless the true χ value for methylene chloride is approximately 0.3 or less.

In a long-term study (Parker and Ranney 1994), PVC was exposed to lower activity solutions of methylene chloride (0.4, 0.2, 0.1, 0.05, 0.0) for 20 weeks. By the end of the study, there were significant changes in the hardness readings for samples exposed to 0.4-, 0.2- and 0.1-activity solutions but not to the 0.05-activity solutions. However, none of the samples with the lower hardness readings were actually rubbery or pliable. We concluded that softening had begun to occur at much lower activities than had been previously reported or predicted by either Berens or Vonk and that softening might occur at even lower activities (< 0.1) if given more time. However, we also thought that it might be possible that only partial softening occurs at these lower activities and that the samples never actually become rubbery or pliable. We concluded that a longer-term study is necessary to resolve this issue, and we are currently conducting such a study.

We also tested the ability of a second organic solvent, trichloroethylene (TCE), to soften PVC (Parker and Ranney 1994). TCE is one of the most common organic pollutants in the environment and is also a relatively good swelling agent of PVC [$\chi = 0.88$ (Berens 1985) or $\chi = 0.90$ (Vonk 1985)]. In our first study with TCE, pieces of PVC were exposed to various activity (1.0, 0.8, 0.6, 0.4, 0.2, 0.0) solutions for up to 68 days. By the end of the experiment, samples exposed to the 0.6-, 0.8- and 1.0-activity solutions had Barcol readings that were significantly lower than the controls, although none of these samples appeared to be plasticized or rubbery.

To confirm these findings, we (Parker and Ranney 1994) repeated the final set of samples from the previous experiment with a few modifications to improve the sensitivity of the test, including more replicates and a longer contact time (77 days). However, this time there was no significant difference in the hardness readings of the samples exposed to the 0.6-activity solutions and the controls. We did note that this time the samples exposed to the 1.0-activity solutions were pliable. Generally the TCE results agree well with what would be predicted using Berens's isotherms, i.e., PVC should be softened by TCE at activities of 0.8 and greater and should become rubbery at an activity of 0.95 (at 30°C). We are not certain why the results for the samples exposed to the 0.6-activity solutions from this study did not agree with those from the previous study. We thought that if these samples had been given more time, then softening might have occurred, or it may be that since PVC is known to be very heterogeneous, then these different results were due to differences between the test pieces. These studies were relatively short term, and equilibrium was not reached at the lower activities. We concluded that a longer-term study would help resolve whether TCE can soften PVC at an activity of 0.6, and we are currently conducting such a study.

Another issue that we addressed in our most recent study (Parker and Ranney 1994) is what effect an aqueous solution that contains a mixture of several different organic solvents would have on PVC. Since groundwater is much more likely to contain a mixture of organic contaminants, this is an important question for the groundwater monitoring industry. Neither Berens nor Vonk has addressed this issue. For 21 days, pieces of PVC were exposed to an aqueous solution that contained three organic solvents that were either good swelling agents or solvents of PVC [methylene chloride, 1,1,2-trichloroethane and 1,2-dichloroethane ($\chi < 0.6$ for all three compounds)], each at an activity of 0.3. At this activity level, none of these organic solutes should be able to soften PVC by themselves, at least in the time frame of this study. [In fact, previously in this study we found that it took eight weeks before there was a significant change in the hardness readings of samples exposed to a solution containing one of these solvents (methylene chloride) at a nearly equivalent activity (0.4).] Statistical analyses of these data revealed that after two days, the Barcol readings of the samples exposed to the mixed-organic solution were significantly lower than

those of the controls. These samples were also rubbery and could be bent easily. We concluded that there was evidence of a cumulative or interactive effect for solutions containing multiple organic solutes that are PVC solvents or good swelling agents when the activity of each organic solute is 0.3 or more. We recommended that future studies should look at mixtures containing more solutes, each at lower activities.

One other issue that had not been addressed previously in the literature was whether an organic solvent that is a good solvent or swelling agent of PVC and that is also totally miscible in water can soften PVC when mixed with water. For solvents that are totally miscible in water, it is impossible to estimate the activity of these solutions using the method described above since this would involve dividing the analyte's concentration by an infinite number. To answer this question, we conducted a study using acetone (Parker and Ranney 1994). Acetone is a good swelling agent of PVC [$\chi = 0.61$ (Berens 1985)] and is totally miscible in water. In this study, pieces of PVC were subjected to a range of concentrations (75, 50, 25, 5.0, 0.5, 0.05, 0.0% w/v) for seven days. Because there were no replicates in this study, statistical analyses could not be conducted on these data. However, after three days we found a very large change in the Barcol readings for the samples exposed to the 50 and 75% solutions. These samples were rubbery and could be bent easily by hand. In contrast, by the end of the study (seven days) the Barcol readings for the samples exposed to the 5, 0.5 and 0.05% solutions did not appear to be different from those of the control samples. There may have been some change in the samples exposed to the 25% solution, as the Barcol readings were slightly lower. We concluded that a 50% solution of acetone rapidly softens PVC and that a longer-term study would better define the effects of lower concentrations.

The purpose of the current study was to answer the following questions:

- What concentrations of acetone are able to soften PVC when exposure is longer than one week?
- Are there other organic solvents (besides acetone) that are totally miscible in water and are either good swelling agents or solvents of PVC that can soften PVC when dissolved in water?
- Is a mixture of several PVC solvents in aqueous solution, each at an activity of 0.05, able to soften PVC?

An activity of 0.05 was selected because, according to Vonk (1985, 1986), diffusion of an organic solute (that is a solvent or good swelling agent of PVC) with an activity that is less than 0.1 should be Fickian and thus concentration independent and slowest. At these activities the rate of diffusion is considered so slow that diffusion of an organic solute through PVC pipe would take thousands of years (Berens 1985, Vonk 1985, 1986, Olson et al. 1987). Therefore, we would not anticipate any softening to occur at an activity of 0.05 for any (single) organic solute. (So far in our own tests we also have not observed any softening at an activity of 0.05.) A combination of 18 solvents and swelling agents of PVC was used in this study.

MATERIALS AND METHODS

Small pieces of PVC were cut from 2-in- (5.1-cm-) diameter schedule-40 well casing. The overall dimensions of the pieces were approximately $9 \times 9 \times 0.8$ mm (L \times W \times H), giving a total surface area of approximately 1.9 cm^2 and an approximate weight of 0.09 g. Special care was taken to eliminate contamination from grease or oil during the cutting procedure. The pieces of PVC were washed by placing them in a glass beaker containing a 2% solution of Liquinox detergent and deionized (Millipore) water and stirring them with a glass rod for approximately five minutes. The pieces were then rinsed with copious amounts of deionized water until there were no signs of sudsing, then rinsed with several additional volumes of deionized water to assure complete removal of the detergent. The pieces were then spread on paper towels, blotted and left to air dry.

Short-term miscible solvent study

In this study, pieces of PVC were exposed to four concentrations (20, 40, 60 and 80% w/v) of five organic solvents that are totally miscible in water. The five solvents used were: acetone, n-butylamine, dimethylformamide, pyridine and tetrahydrofuran. The contact times were three and seven days. For each time, solvent and concentration, there were five replicate samples. The test solutions were made up in 22-mL borosilicate glass vials with Teflon-lined plastic caps. The vials were filled almost to the top with Milli-Q water, solvent was added using a microliter syringe, and the vials were then filled to capacity with water to eliminate any headspace, capped and placed

horizontally on an orbital shaking table for approximately 48 hours. After mixing, the vials were opened and previously weighed pieces of PVC were added to the test solutions. When necessary, a few drops of water were added to ensure that there was no headspace, and the vials were re-capped.

Long-term miscible solvent study

In this study, pieces of PVC were exposed to a range of concentrations of the same solvents as the previous study, with the exception of n-butylamine. The concentrations of acetone were 40, 20, 10 and 5% (w/v). The concentrations of dimethylformamide and pyridine were 80, 60, 40 and 20%. The concentrations of tetrahydrofuran (the most aggressive solvent in the previous study) were 10, 1.0, 0.1 and 0.01%. The contact times were 2, 4, 8, 12, 16 and 20 weeks. For each sample, time and concentration, there were four replicate samples, except for acetone, where there were five replicates. The test solutions were made up as described for the short-term miscible solvent study, except for the acetone solutions.

The acetone solutions were made up by adding acetone to deionized water in 1-L volumetric flasks, each containing a glass-covered magnetic stirring bar. The flasks were then filled with deionized water, leaving approximately 1 mL of headspace so that the test solution would not be lost when the glass stopper was inserted. The stoppers were then wrapped tightly with parafilm to reduce vapor loss, and the solutions were mixed for approximately two days on magnetic stirring plates. When the solutions were mixed, preweighed PVC pieces were added to vials, and the vials were filled to capacity with solution to eliminate any headspace and capped.

Mixed-solvent study

In this study, pieces of PVC were exposed to an aqueous solution of 18 organic chemicals shown to be solvents or good swelling agents of PVC (Table 3). The activity of each analyte was 0.05, giving a total activity of 0.9. Samples were taken after 1, 3, 7, 14, 21 and 42 days. Five replicate samples were taken on each sampling day. The mixed-solvent solution was made by adding a volume of each analyte using a microliter syringe to deionized water in a 1-L volumetric flask containing a glass-covered magnetic stirring bar. The flask was then filled with deionized water, leaving approximately 1 mL of headspace. The stop-

Table 3. Properties of the organic solvents used in the mixed-solvent study.

PVC softening agent or solvent*	Density [†] (g/mL)	Solubility (mg/L)	χ value	
			Berens (1985)	Vonk (1985)
Cyclohexanone ^c	0.9478 ²	23,000 ²		
Methylene chloride ^{a,b,c}	1.3266 ¹	19,000 ¹	< 0.53	0.55
Methyl isobutyl ketone ^c	0.7978 ¹	17,000 ¹		
Bromochloromethane ^c	1.9344 ¹	16,691 ¹		
1,2-dichloroethane ^{a,b,c}	1.2351 ¹	8,690 ¹	< 0.55	0.56
Chloroform ^{b,c}	1.4832 ¹	8,000 ¹	0.64	
<i>cis</i> -1,2-dichloroethylene ^d	1.2818 ³	7,700 ³		
<i>trans</i> -1,2-dichloroethylene ^d	1.2565 ¹	6,300 ¹		
Bromodichloromethane ^d	1.9800 ¹	4,500 ¹		
1,1,2-trichloroethane ^{a,b,c}	1.4397 ¹	4,500 ¹	< 0.56	0.58
1,2-dibromoethane ^d	2.1802 ¹	4,300 ¹		
Dibromochloromethane ^d	2.4510 ¹	4,000 ¹		
Bromoform ^d	2.8899 ¹	3,010 ¹		
Benzonitrile ^d	1.0006 ³	2,000 ³	0.54	
2-nitrotoluene ^d	1.1629 ²	600 ²		
3-nitrotoluene ^d	1.1571 ²	500 ²		
Chlorobenzene ^{a,c}	1.1058 ¹	500 ¹	0.66	

* These compounds were determined to be either solvents or good softening agents of PVC based on information from the following sources:

^a Vonk (1985)

^b Berens (1985)

^c Cole-Parmer (1992) and verified by tests in our laboratory

^d Determined in our laboratory

[†] Densities and solubility sources:

¹ Montgomery *Ground Water Chemical Desk Reference*

² Montgomery *Ground Water Chemical Desk Reference*, vol. 2

³ Dean *Lange's Handbook of Chemistry*, 13th Edition

per was then inserted (leaving almost no headspace) and the top of the flask was wrapped tightly with parafilm to reduce vapor loss. The solution was mixed for approximately three days on a magnetic stirring plate. When the solution was mixed, preweighed PVC pieces were added to empty vials, the vials were filled with the mixed-solvent solution to capacity so there was no headspace and then capped.

General

In all the studies the pieces of PVC were handled using stainless steel forceps. The ratio of surface area of PVC to solution volume was 0.074 cm²/mL, and the ratio of solution volume to volume of PVC was approximately 386:1. PVC pieces added to deionized water served as controls. All the prepared solutions were checked with a magnifying glass to ensure that there were no undissolved droplets of solvent visible. The test samples were stored in the dark at room temperature.

On the sampling day the pieces of PVC were removed from the solution, placed on paper towels, blotted and allowed to air dry for 1 minute before weighing. Immediately after weighing, a

Model 935 Barcol Impressor was used to measure the hardness of the PVC. A description of the use of the Barcol Impressor on rigid plastics can be found in ASTM Standard Test Method D2583-87 (ASTM 1988). However, the impressor employed in this study is made for indenting softer plastics and is not the model described in the ASTM test method. This model was selected so that measurements could be taken during the softening process. Observations were also made of any curvature in the PVC pieces, and the flexibility was tested by holding the pieces with forceps and noting the amount of force necessary to bend the sample.

In all these studies, analysis of variance and Duncan's New Multiple Range tests were performed on the Barcol readings for each time and for each analyte in the miscible solvent studies.

RESULTS AND DISCUSSION

Short-term miscible solvent study

In this study we exposed pieces of PVC to aqueous solutions of five PVC solvents or good swelling

Table 4. Mean weight gain and relative hardness (Barcol) values of PVC exposed to miscible solvent solutions after three and seven days of exposure.

Solution (%)	3 days		7 days	
	% Wt. gain	Barcol	% Wt. gain	Barcol
<i>Control</i>				
0.0	0.07	79.0	0.07	79.0
<i>Acetone</i>				
20	0.07	79.7	0.22	78.3
40	4.29	64.7*	7.76	50.0*
60	20.39	39.0*	20.14	37.0*
<i>n-butylamine</i>				
20	0.14	78.3	0.07	79.0
40	0.22	79.3	0.03	78.7
60	0.21	78.0	0.22	78.7
<i>Dimethylformamide</i>				
20	0.08	79.3	0.00	79.0
40	0.10	79.3	0.04	78.0
60	0.08	79.0	0.04	79.0
<i>Pyridine</i>				
20	0.13	79.0	0.16	78.0
40	0.20	79.0	0.11	78.7
60	0.24	78.0	0.30	78.3
<i>Tetrahydrofuran</i>				
20	29.68	35.7*	29.66	S [†]
40	86.53	S	86.66	S
60	D		D	

* Value significantly (95% level) different from controls

[†] **D** PVC dissolved and couldn't be tested

S Softened PVC couldn't be tested

agents (tetrahydrofuran, acetone, dimethylformamide, pyridine and n-butylamine) for up to seven days. Acetone and pyridine are EPA priority pollutants and/or target analytes (Montgomery and Welkom 1989), and the rest are common in the work environment according to the National Institute of Occupational Safety and Health (Montgomery 1991) and thus potential groundwater contaminants. The change in weight data and hardness readings are summarized in Table 4, and the complete data set can be found in Appendix A. Tetrahydrofuran is a solvent of PVC and is commonly used as a component in PVC glues. The aqueous solution of this chemical was also the most aggressive. After seven days the 20% solution (2.8 M) softened PVC, and the 60% solution (8.4 M) dissolved it! Acetone has a χ value of 0.61 and thus is a good swelling agent of PVC. The aqueous acetone solution was the next most aggressive aqueous solution. The lowest concentration tested (20% or 3.4 M) did not cause a signifi-

cant change in the Barcol readings, but the 40% (6.8 M) and 60% (10.2 M) solutions did. The PVC pieces exposed to the 40% solutions were noticeably softened when tested manually, and those exposed to the 60% solutions were pliable (i.e., could be bent in half easily). In contrast, the highest concentrations tested (60%) of n-butylamine (8.2 M), pyridine (7.5 M) and dimethylformamide (8.2 M) had no effect on the hardness readings. We do not have any χ values for these organic solvents.

As a result of this study we know that aqueous solutions of at least two organic solvents that are either solvents or good swelling agents of PVC and are totally miscible in water can soften PVC. Because this study only ran for seven days, it is possible that exposure to solutions of n-butylamine, pyridine or dimethylformamide may cause softening if given more time.

Long-term miscible solvent study

Since the performance of n-butylamine was between that of dimethylformamide and pyridine in the previous study and since n-butylamine is a dangerous and highly toxic chemical to work with, we decided that further study with this chemical was neither warranted nor desirable. Therefore, in this study we exposed pieces of PVC to aqueous solutions of tetrahydrofuran, acetone, pyridine and dimethylformamide for a much longer time than in the previous study, up to 20 weeks. The range in concentrations for these test solutions was determined based on the results from the previous study (Table 4). The mean changes in hardness readings for this study are given in Table 5, and the complete set of hardness readings and change in weight values can be found in Appendix B. Again tetrahydrofuran was the most aggressive solvent. By the end of this study (20 weeks), even the hardness readings for the samples exposed to the lowest concentration tested (0.01%, or 0.0014 M) were significantly lower than the controls. None of these samples were noticeably softened when tested manually, even the samples exposed to the highest concentration tested, a 10% solution (1.4 M). Although there is a lot of variability in the weight change data, it appears that the samples exposed to the 1.0, 0.1 and 0.01% solutions may have reached equilibrium. If this is the case, then no further changes would be expected.

For acetone there was a significant change in the Barcol readings of samples exposed to the 10% (1.7 M), 20% (3.4 M) and 40% (6.9 M) solutions

Table 5. Means of relative hardness (Barcol) values of PVC exposed to miscible solvent solutions for various contact times.

<i>Solution (%)</i>	2	4	8	12	16	20 days
<i>Acetone</i>						
0.0 control	77.0	79.4	80.0	79.2	78.6	79.6
2.5	76.6	78.8	79.8	79.0	75.0*	77.6
5.0	76.6	78.4	79.2	79.0	77.0	76.4
10.0	76.4	78.2	79.4	79.2	72.4*	73.8*
20.0	76.2	76.4	77.6	75.4	72.8*	70.2*
40.0	37.2*	26.0*	30.6*	21.6*	29.4*	23.2*
<i>Dimethylformamide</i>						
0.0 control	79.8	79.5	79.3	79.5	79.5	79.3
20.0	79.3	78.3	79.3	76.5	76.3	76.8
40.0	79.0	78.5	78.3	76.5	75.8	76.8
60.0	78.3	75.8	78.3	76.0*	73.5*	71.3*
80.0	33.0*	29.3*	10.0*	14.8*	12.5*	16.5*
<i>Pyridene</i>						
0.0 control	79.8	79.5	79.3	79.5	79.5	79.3
20.0	77.8	77.5	78.0	78.8	76.8*	73.3*
40.0	77.0	76.8	76.5*	74.0*	74.5*	71.5*
60.0	76.3*	75.8	75.3*	72.8*	72.5*	66.0*
80.0	28.0*	17.8*	22.0*	10.8*	10.8*	7.0*
<i>Tetrahydrofuran</i>						
0.0 control	79.8	79.5	79.3	79.5	79.5	79.3
0.01	79.0	77.8	79.5	79.5	78.0	74.8*
0.10	78.5	77.8	77.0*	78.8	78.5	73.5*
1.00	78.5	78.0	76.8*	76.8*	78.3	73.0*
10.00	76.8*	77.0	75.5*	70.8*	74.8*	67.8*

* Value significantly different from controls (95% level).

but not for the samples exposed to the 2.5% (0.43 M) and 5% (0.86 M) solutions. Again, only the samples exposed to the 40% solution were noticeably softened when tested manually. It may be that given more time the other solutions (10 and 20%) would also have caused pronounced softening. Although the weight gain data were highly variable, it did appear that the samples exposed to the 40, 10 and 5% solutions had reached equilibrium (Table B2). A longer-term study would show whether equilibrium had been reached or whether further change occurs.

There was a significant change in the hardness readings for the samples exposed to the lowest concentration (20%, or 2.5 M) of pyridine. Samples exposed to the highest concentration tested, the 80% (10 M) solutions, were actually pliable (i.e., easily bent in half).

Dimethylformamide again was the least aggressive solvent, and only the test pieces exposed

to the 60% (8.2 M) and 80% (10.9 M) solutions had Barcol readings that were significantly lower than the controls. The samples that were exposed to the 80% solution were also pliable (i.e., easily bent in half). The weight change data indicate that all these samples may have reached equilibrium, as there was no additional weight gain during the last four weeks of the study.

It is clear from this study that several organic solvents that are totally miscible in water can soften PVC when dissolved in aqueous solutions and that the ability of an organic solvent to soften PVC when dissolved in aqueous solution is correlated with the neat organic solvent's ability to dissolve or soften PVC.

Mixed-solvent study

This study was conducted to determine if a combined solution of 18 PVC solvents and swelling agents, each at an activity of 0.05, can soften

Table 6. Mean relative hardness (Barcol) values and percent relative standard deviations for the mixed-solvent study for various contact times.

<i>Treatment</i>	<i>1</i>	<i>3</i>	<i>7</i>	<i>14</i>	<i>21</i>	<i>42 days</i>
control						
\bar{X}	80.0	78.6	77.8	78.8	80.0	79.0
%RSD	1.3	1.9	1.4	2.4	1.5	2.4
test soln						
\bar{X}	74.8*	74.2*	72.0*	68.2*	67.0*	65.4*
%RSD	1.7	2.4	1.4	5.2	5.3	4.1

* Values significantly different from controls at 95% confidence level

PVC. In this study we saw a statistically significant change in the Barcol readings of samples exposed to the solution of mixed organic solutes after only one day (Table 6, App. C). After 14 days, several of the test pieces were noticeably softened when tested manually, although none became pliable. Thus, even solutes at activities as low as 0.05 can soften PVC if enough organic compounds that are good solvents or swelling agents of PVC are present.

Based on the results from this study, we now wonder whether a mixture of organic solutes at even lower activities could also soften PVC and whether chemicals that are solvents and good swelling agents of PVC have any synergistic effect on other poorer swelling agents. We also wonder what happens in solutions that contain several different activities and what happens if you have a solution that contains low activities of several different PVC solvents or swelling agents plus some dissolved PVC solvent or swelling agent that is totally miscible in water. We have started several studies to address these issues.

CONCLUSIONS

Knowing whether the initial softening we have measured in this study and in previous studies will progress and understanding what happens in a solution that contains several organic solutes is essential if we are to develop any guidance for predicting the ability of PVC to withstand exposure to various organic contaminants over the long term. While we still cannot give definitive guidance, these studies have increased our knowledge and moved us closer to being able to do that.

In a previous study (Parker and Ranney 1994), we found no softening of PVC that was exposed

to a solution of methylene chloride (either a solvent or a good swelling agent of PVC) at an activity of 0.05 for 20 weeks. Previous work by other researchers (Berens 1985, Vonk 1985, 1986) also predicts that an aqueous solution of a PVC solvent or swelling agent should not be able to soften PVC at this low an activity. However, we found that a solution containing a mixture of 18 good swelling agents of PVC, each at an activity of 0.05, was able to rapidly soften PVC. Clearly there is an additive effect of organic solutes, and a solution containing several organic solutes has a much greater ability to soften PVC than does a solution containing any one of the solutes by itself.

In this study we also found that several organic solvents that are either solvents or good swelling agents of PVC and are totally miscible in water can soften PVC. Tetrahydrofuran is a solvent commonly used in PVC glues. After 20 weeks the lowest concentration we tested (0.01%, or 0.0014 M) was able to cause a significant change in the hardness readings. Lower concentrations were not tested but may also have an effect. Acetone is a good swelling agent of PVC and was able to cause a significant change in the hardness readings of test pieces exposed to concentrations of 10% (1.7 M) but not 5% (0.86 M). Dimethylformamide was the least aggressive solvent tested and was able to cause a significant change in the hardness readings in 60% (8.2 M) and 80% (10.9 M) solutions but not at 40% (5.5 M).

Currently we are conducting several additional longer-term studies (1 year or more) that may allow us to determine:

- Whether softening progresses further in those solutions already showing a significant change in hardness readings;
- Whether a mixture of good swelling agents of PVC, at lower activities than we tested (0.05), will soften PVC;
- Whether PVC solvents and good swelling agents have some type of synergistic effect on poorer swelling agents;
- What occurs in an aqueous solution that contains a number of PVC solvents and good swelling agents at varying activities; and
- Whether lower concentrations of PVC solvents and swelling agents that are totally miscible in water can soften PVC and what occurs when these chemicals are also present in a mixture of organic solutes.

LITERATURE CITED

- ASTM** (1988) *ASTM Standard Test Method D 2583-7 for Indentation Hardness of Rigid Plastics by Means of a Barcol Impressor*. Philadelphia, Pennsylvania: American Society for Testing and Materials, p. 337-339.
- Berens, A.R.** (1985) Prediction of organic chemical permeation through PVC pipe. *Journal of the American Water Works Association*, p. 57-65.
- Cole-Parmer Instrument Company** (1992) Cole-Parmer Instrument Company 1993-1994 Catalogue. Niles, Illinois: Cole-Parmer Instrument Company.
- Dean, J.I., Ed.** (1985) *Lange's Handbook of Chemistry, Thirteenth Edition*. New York: McGraw-Hill Publishers.
- Montgomery, J.H.** (1991) *Groundwater Chemicals Desk Reference*. Volume 2. Chelsea, Michigan: Lewis Publishers, Inc.
- Montgomery, J.H. and L.M. Welkom** (1989) *Groundwater Chemicals Desk Reference*. Chelsea, Michigan: Lewis Publishers, Inc.
- Olson, A.J., D. Goodman and J.P. Pfau** (1987) Evaluation of permeation of organic solvents through PVC, asbestos/cement, and ductile iron pipes. *Journal of Vinyl Technology*, 9(3): 114-118.
- Parker, L.V. and T.A. Ranney** (1994) Softening of rigid PVC by aqueous solutions of organic solvents. USA Cold Regions Research and Engineering Laboratory, Special Report 94-27.
- Parker, L.V., T.A. Ranney and S. Taylor** (1992) Softening of rigid polyvinyl chloride by high concentrations of aqueous solutions of methylene chloride. USA Cold Regions Research and Engineering Laboratory, Special Report 92-12.
- Ranney, T.A. and L.V. Parker** (1995) Susceptibility of ABS, FEP, FRE, FRP, PTFE and PVC well casings to degradation by chemicals. USA Cold Regions Research and Engineering Laboratory, Special Report 95-1.
- Vonk, M.W.** (1985) Permeatie van organische verbindingen door leiding-materialen. In *Permeatie en drinkwaterleidingen*, KIWA, N.V, Nieuwegein, The Netherlands, KIWA Report 85 (in Dutch with English summary).
- Vonk, M.W.** (1986) Permeation of organic soil contaminants through polyethylene, polyvinyl chloride, asbestos-cement and concrete water pipes. In *Proceedings of the American Water Works Association Water Quality Technical Conference, 1985*, vol. 13, p. 701-714.

APPENDIX A: RESULTS OF THE SHORT-TERM MISCIBLE SOLVENT STUDY

Table A1. Weight gains and relative hardness (Barcol) values of PVC exposed to miscible solvent solutions for the short-term study.

Solution (%)	Weight gain (%)		Barcol values		Solution (%)	Weight gain (%)		Barcol values	
	3 days	7 days	3 days	7 days		3 days	7 days	3 days	7 days
<i>Control</i>									
0.0	0.09	0.00	80	79	40	0.00	0.00	79	77
0.0	0.00	0.12	79	78	40	0.09	0.00	80	79
0.0	0.11	0.09	78	80	40	0.20	0.11	79	78
\bar{X}	0.07	0.07	79.0	79.0	\bar{X}	0.10	0.04	79.3	78.0
<i>Acetone</i>									
20	0.00	0.22	80	80	60	0.00	0.00	79	79
20	0.11	0.21	79	78	60	0.00	0.12	78	78
20	0.11	0.23	80	77	60	0.23	0.00	80	80
\bar{X}	0.07	0.22	79.7	78.3	\bar{X}	0.08	0.04	79.0	79.0
<i>Pyridine</i>									
40	3.86	8.58	64	47	20	0.11	0.18	80	78
40	4.61	6.57	66	52	20	0.10	0.12	79	77
40	4.38	8.11	64	51	20	0.18	0.18	78	79
\bar{X}	4.29	7.76	64.7	50.0	\bar{X}	0.13	0.16	79.0	78.0
60	19.29	19.90	38	37	40	0.17	0.24	80	77
60	20.04	20.51	37	39	40	0.21	0.00	77	80
60	21.83	20.02	42	35	40	0.23	0.09	80	79
\bar{X}	20.39	20.14	39.0	37.0	\bar{X}	0.20	0.11	79.0	78.7
<i>n-butylamine</i>									
20	0.11	0.10	77	78	60	0.21	0.38	79	77
20	0.09	0.10	79	80	60	0.20	0.21	79	79
20	0.21	0.00	79	79	60	0.31	0.31	76	79
\bar{X}	0.14	0.07	78.3	79.0	\bar{X}	0.24	0.30	78.0	78.3
<i>Tetrahydrofuran</i>									
40	0.12	0.00	78	77	20	30.69	28.06	38	S*
40	0.23	0.00	80	80	20	29.67	31.77	35	S
40	0.31	0.09	80	79	20	28.69	29.15	34	S
\bar{X}	0.22	0.03	79.3	78.7	\bar{X}	29.68	29.66	35.7	
60	0.22	0.21	78	79	40	88.07	88.95	S	S
60	0.21	0.20	77	79	40	83.19	86.14	S	S
60	0.20	0.26	79	78	40	86.53	84.89	S	S
\bar{X}	0.21	0.22	78.0	78.7	\bar{X}	85.93	86.66		
<i>Dimethylformamide</i>									
20	0.00	0.00	79	78	60	D	D	D	D
20	0.11	0.00	80	79	60	D	D	D	D
20	0.12	0.00	79	80	60	D	D	D	D
\bar{X}	0.08	0.00	79.3	79.0	\bar{X}				

*S Softened PVC couldn't be tested
D PVC dissolved

APPENDIX B: RESULTS OF THE LONG-TERM MISCIBLE SOLVENT STUDY

Table B1. Relative hardness (Barcol) values of PVC exposed to miscible solvent solutions for the long-term study.

<i>Solution (%)</i>	2	4	8	12	16	20 weeks	<i>Solution (%)</i>	2	4	8	12	16	20 weeks
<i>Controls for acetone</i>							<i>Controls for dimethylformamide, pyridine and tetrahydrofuran</i>						
0.0	77	80	81	80	80	78	0.0	81	81	78	79	78	81
0.0	77	79	77	81	79	81	0.0	81	78	79	81	79	79
0.0	78	79	82	78	78	79	0.0	78	80	81	78	81	80
0.0	77	81	79	79	77	80	0.0	79	79	79	80	80	77
0.0	76	78	81	78	79	80	\bar{X}	79.8	79.5	79.3	79.5	79.5	79.3
\bar{X}	77.0	79.4	80.0	79.2	78.6	79.6	<i>Dimethylformamide</i>						
<i>Acetone</i>							20	80	78	78	78	74	77
2.5	76	77	77	80	73	79	20	78	77	79	76	78	75
2.5	77	79	82	79	75	77	20	80	80	80	76	77	77
2.5	77	80	81	81	76	79	20	79	78	80	76	76	78
2.5	78	78	81	77	76	75	\bar{X}	79.3	78.3	79.3	76.5	76.3	76.8
2.5	75	80	78	78	75	78	40	79	78	79	75	77	77
\bar{X}	76.6	78.8	79.8	79.0	75.0	77.6	40	81	81	79	77	76	76
5	76	78	78	80	79	77	40	78	76	77	76	74	78
5	78	77	81	79	76	75	40	78	79	78	78	76	76
5	77	79	77	77	79	77	\bar{X}	79	78.5	78.3	76.5	75.8	76.8
5	77	79	81	80	76	76	60	79	74	79	74	74	71
5	75	79	79	79	75	77	60	78	77	78	75	71	72
\bar{X}	76.6	78.4	79.2	79.0	77.0	76.4	60	79	74	79	77	75	70
10	75	79	80	78	73	74	60	77	78	77	78	74	72
10	77	78	79	79	75	76	\bar{X}	78.3	75.8	78.3	76.0	73.5	71.3
10	77	77	80	81	73	75	80	30	37	8	17	16	16
10	75	79	79	80	72	72	80	36	20	17	18	4	22
10	78	78	79	78	69	72	80	28	26	5	14	13	10
\bar{X}	76.4	78.2	79.4	79.2	72.4	73.8	80	38	34	10	10	17	18
20	76	76	78	76	72	66	\bar{X}	33.0	29.3	10.0	14.8	12.5	16.5
20	77	75	77	73	73	72	<i>Pyridine</i>						
20	77	77	76	75	72	71	20	76	79	79	77	78	74
20	76	78	79	76	73	73	20	77	76	78	79	75	73
20	75	76	78	77	74	69	20	79	78	77	80	77	76
\bar{X}	76.2	76.4	77.6	75.4	72.8	70.2	20	79	77	78	79	77	70
40	31	26	36	29	29	23	\bar{X}	77.8	77.5	78.0	78.8	76.8	73.3
40	36	28	28	27	22	30	40	78	78	77	73	77	70
40	35	32	27	18	31	16	40	75	78	78	76	75	69
40	45	20	32	24	33	25	40	77	75	76	73	74	75
40	39	24	30	10	32	22	40	78	76	75	74	72	72
\bar{X}	37.2	26.0	30.6	21.6	29.4	23.2	\bar{X}	77.0	76.8	76.5	74.0	74.5	71.5

Table B1 (cont'd). Relative hardness (Barcol) values of PVC exposed to miscible solvent solutions for the long-term study.

<i>Solution (%)</i>	2	4	8	12	16	20 weeks
<i>Pyridine (cont'd)</i>						
60	79	77	77	73	70	67
60	74	76	75	71	72	62
60	78	75	74	74	73	65
60	74	75	75	73	75	70
\bar{X}	76.3	75.8	75.3	72.8	72.5	66.0
80	28	10	21	11	9	5
80	30	22	22	17	10	11
80	25	15	24	10	13	10
80	29	24	21	5	11	2
\bar{X}	28	17.8	22.0	10.8	10.8	7.0
<i>Tetrahydrofuran</i>						
0.01	78	75	79	81	79	76
0.01	80	80	80	79	78	73
0.01	79	78	79	80	78	75
0.01	79	78	80	78	77	75
\bar{X}	79.0	77.8	79.5	79.5	78.0	74.8
0.1	79	78	77	78	77	73
0.1	79	78	76	80	79	75
0.1	78	77	77	77	78	73
0.1	78	78	78	80	80	73
\bar{X}	78.5	77.8	77.0	78.8	78.5	73.5
1	79	78	77	76	81	74
1	77	81	78	74	76	73
1	78	77	76	79	79	75
1	80	76	76	78	77	70
\bar{X}	78.5	78.0	76.8	76.8	78.3	73.0
10	76	76	75	69	77	68
10	76	75	74	73	72	70
10	77	77	77	69	75	64
10	78	80	76	72	75	69
\bar{X}	76.8	77.0	75.5	70.8	74.8	67.8

Table B2. Percent weight gain of PVC exposed to miscible solvent solutions for the long-term study.

<i>Solution (%)</i>	2	4	8	12	16	20 weeks
<i>Controls for acetone</i>						
0.0	0.00	0.11	0.11	0.22	0.09	0.11
0.0	0.11	0.23	0.25	0.10	0.11	0.00
0.0	0.11	0.18	0.19	0.10	0.24	0.22
0.0	0.09	0.09	0.22	0.00	0.09	0.21
0.0	0.23	0.24	0.29	0.11	0.12	0.11
\bar{X}	0.11	0.17	0.21	0.11	0.13	0.13
<i>Acetone</i>						
2.5	0.24	0.17	0.11	0.28	0.23	0.36
2.5	0.18	0.21	0.21	0.37	0.00	0.34
2.5	0.00	0.38	0.24	0.32	0.09	0.31
2.5	0.00	0.12	0.27	0.21	0.24	0.58
2.5	0.00	0.22	0.45	0.23	0.28	0.36
\bar{X}	0.08	0.22	0.26	0.28	0.17	0.39
5.0	0.11	0.24	0.22	0.28	0.23	0.38
5.0	0.29	0.11	0.20	0.17	0.21	0.47
5.0	0.10	0.09	0.23	0.44	0.10	0.20
5.0	0.18	0.22	0.10	0.46	0.11	0.21
5.0	0.20	0.21	0.22	0.30	0.35	0.23
\bar{X}	0.18	0.17	0.20	0.33	0.20	0.30
10	0.24	0.32	0.32	0.33	0.35	0.24
10	0.12	0.35	0.22	0.37	0.67	0.33
10	0.10	0.23	0.32	0.21	0.43	0.20
10	0.09	0.18	0.21	0.12	0.48	0.35
10	0.11	0.23	0.23	0.32	0.41	0.43
\bar{X}	0.13	0.26	0.26	0.27	0.47	0.31
20	0.42	0.65	0.72	0.81	0.84	1.19
20	0.53	0.64	0.88	1.12	0.84	1.48
20	0.77	0.93	0.87	1.12	1.00	1.11
20	0.54	0.53	0.71	1.02	0.96	1.03
20	0.54	0.63	0.64	0.97	0.90	1.35
\bar{X}	0.56	0.67	0.76	1.01	0.91	1.23
40	12.94	13.36	12.85	13.50	13.05	13.37
40	13.52	13.43	13.25	13.08	12.98	13.37
40	13.54	13.37	13.43	13.15	13.19	13.42
40	13.09	13.33	13.33	13.04	13.08	13.35
40	12.92	13.43	13.36	13.07	12.91	13.40
\bar{X}	13.20	13.39	13.24	13.17	13.04	13.38

Table B2 (cont'd).

<i>Solution (%)</i>	2	4	8	12	16	20 weeks	<i>Solution (%)</i>	2	4	8	12	16	20 weeks
<i>Controls for dimethylformamide, pyridine and tetrahydrofuran</i>													
0.0	0.10	0.20	0.19	0.20	0.30	0.30	40	0.48	0.60	0.78	0.75	1.01	1.12
0.0	0.08	0.10	0.20	0.11	0.20	0.20	40	0.40	0.88	0.74	1.02	1.10	1.30
0.0	0.20	0.19	0.09	0.11	0.30	0.30	40	0.32	0.83	0.75	1.06	1.18	1.29
0.0	0.10	0.16	0.10	0.22	0.27	0.20	40	0.43	0.81	0.65	0.80	0.98	1.58
\bar{X}	0.12	0.16	0.15	0.16	0.27	0.25	\bar{X}	0.41	0.78	0.73	0.91	1.07	1.32
<i>Dimethylformamide</i>							<i>Pyridine (cont'd)</i>						
20	0.00	0.00	0.10	0.21	0.10	0.20	60	1.22	1.26	1.73	2.25	3.05	3.06
20	0.11	0.10	0.10	0.23	0.20	0.11	60	1.53	1.92	1.57	2.40	2.90	2.83
20	0.09	0.20	0.10	0.10	0.30	0.30	60	1.29	1.52	1.56	2.31	1.92	3.04
20	0.11	0.10	0.00	0.11	0.29	0.28	60	1.57	1.68	1.65	2.36	2.38	3.16
\bar{X}	0.08	0.10	0.08	0.16	0.22	0.22	\bar{X}	1.40	1.59	1.63	2.33	2.56	3.02
40	0.00	0.00	0.08	0.19	0.20	0.09	80	20.36	23.20	24.75	24.33	24.26	24.75
40	0.21	0.00	0.08	0.22	0.31	0.29	80	22.74	24.01	32.83	25.98	24.88	24.22
40	0.00	0.10	0.08	0.11	0.39	0.32	80	24.95	25.69	17.71	25.61	24.84	25.25
40	0.00	0.09	0.10	0.21	0.31	0.23	80	26.49	26.12	24.73	25.72	22.30	25.49
\bar{X}	0.05	0.05	0.08	0.18	0.30	0.23	\bar{X}	23.63	24.76	25.00	25.41	24.07	24.93
60	0.10	0.19	0.20	0.36	0.48	0.40	<i>Tetrahydrofuran</i>						
60	0.00	0.40	0.10	0.10	0.43	0.45	0.01	0.00	0.20	0.10	0.28	0.30	0.34
60	0.10	0.10	0.09	0.28	0.58	0.59	0.01	0.19	0.10	0.19	0.39	0.43	0.39
60	0.22	0.12	0.10	0.41	0.40	0.74	0.01	0.10	0.00	0.10	0.56	0.70	0.40
\bar{X}	0.11	0.20	0.12	0.28	0.47	0.55	0.01	0.00	0.11	0.28	0.42	0.81	0.54
80	21.59	16.43	20.82	20.14	19.60	20.33	\bar{X}	0.07	0.10	0.17	0.41	0.56	0.42
80	14.67	21.09	18.61	18.79	19.61	20.24	0.10	0.10	0.21	0.08	0.24	0.47	0.21
80	14.74	19.70	18.25	19.17	20.42	19.09	0.10	0.10	0.59	0.19	0.28	0.40	0.20
80	9.41	14.88	19.10	18.60	19.52	19.92	0.10	0.10	0.40	0.11	0.29	0.49	0.30
\bar{X}	15.10	18.02	19.20	19.18	19.79	19.89	0.10	0.10	0.64	0.20	0.41	0.49	0.40
<i>Pyridine</i>							\bar{X}	0.10	0.46	0.14	0.30	0.46	0.28
20	0.10	0.31	0.52	0.59	0.76	0.70	1.0	0.00	0.20	0.35	0.32	0.53	0.30
20	0.00	0.40	0.65	0.43	0.67	0.71	1.0	0.08	0.30	0.30	0.22	0.42	0.30
20	0.10	0.28	0.46	0.50	0.74	0.74	1.0	0.09	0.12	0.43	0.21	0.58	0.50
20	0.10	0.45	0.44	0.60	0.75	0.59	1.0	0.00	0.10	0.23	0.38	0.64	0.40
\bar{X}	0.08	0.36	0.52	0.53	0.73	0.68	\bar{X}	0.04	0.18	0.33	0.28	0.54	0.38
							10	0.75	0.95	2.04	2.11	2.45	3.36
							10	0.87	1.16	2.17	2.06	3.02	3.19
							10	0.77	1.40	2.29	2.91	3.29	4.36
							10	0.96	1.32	2.03	2.01	2.93	3.94
							\bar{X}	0.84	1.21	2.13	2.27	2.92	3.71

APPENDIX C: RESULTS OF THE MIXED-SOLVENT STUDY

Table C1 Weight gain and relative hardness (Barcol) values of PVC exposed to mixed solvents for various contact times.

<i>Treatment</i>	<i>1 day</i>		<i>3 days</i>		<i>7 days</i>	
	<i>Wt. gain (%)</i>	<i>Barcol</i>	<i>Wt. gain (%)</i>	<i>Barcol</i>	<i>Wt. gain (%)</i>	<i>Barcol</i>
control	0.115	80	0.107	79	0.107	79
control	0.102	81	0.103	78	0.091	76
control	0.122	79	0.091	81	0.000	78
control	0.116	79	0.123	77	0.120	78
control	0.000	81	0.000	78	0.219	78
\bar{X}	0.091	80	0.085	78.6	0.107	77.8
test soln.	2.747	76	5.316	72	5.374	73
test soln.	3.580	74	3.823	74	6.288	71
test soln.	2.580	73	1.687	76	6.215	73
test soln.	3.302	76	2.090	73	5.508	71
test soln.	3.215	75	1.838	76	7.564	72
\bar{X}	3.085	74.8	2.951	74.2	6.190	72

<i>Treatment</i>	<i>14 days</i>		<i>21 days</i>		<i>42 days</i>	
	<i>Wt. gain (%)</i>	<i>Barcol</i>	<i>Wt. gain (%)</i>	<i>Barcol</i>	<i>Wt. gain (%)</i>	<i>Barcol</i>
control	0.103	81	0.107	81	0.000	79
control	0.000	79	0.000	81	0.000	80
control	0.207	78	0.102	80	0.109	81
control	0.171	76	0.110	78	0.000	76
control	0.093	80	0.115	80	0.000	79
\bar{X}	0.115	78.8	0.087	80	0.022	79
test soln.	7.675	63	9.091	71	10.821	66
test soln.	4.220	71	7.898	70	10.955	65
test soln.	6.674	67	9.069	67	10.627	61
test soln.	5.903	68	6.480	64	4.551	68
test soln.	4.178	72	7.956	63	5.587	67
\bar{X}	5.730	68.2	8.099	67	8.508	65.4

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13. ABSTRACT (<i>Maximum 200 words</i>) This study examined whether an aqueous solution that contained 18 organic chemicals that are either solvents or good swelling agents of PVC are able to cause softening when combined in a solution, with each solute at an activity of 0.05. This activity was selected because there is no evidence that an individual organic solute with an activity of 0.05 can soften PVC. However, we found that this combined test solution rapidly softened PVC. We also examined whether organic chemicals that are either solvents or good softening agents of PVC and are also totally miscible in water are able to soften PVC when mixed with water. Four chemicals (tetrahydrofuran, acetone, dimethylformamide and pyridine) were tested in a study that ran for 20 weeks. Tetrahydrofuran, a PVC solvent, caused a significant change in the hardness readings of samples exposed to concentrations as low as 0.01% (w/v). Acetone, a good swelling agent of PVC, caused a significant change in the hardness readings of samples exposed to a 10% concentration but not a 5% concentration. Dimethylformamide, a poorer swelling agent of PVC, did not cause any measurable signs of softening at concentrations below 60%. The lowest concentration of pyridine tested (20%) was found to have a significant effect on the hardness readings. A preliminary short-term study (seven days) showed that n-butylamine was intermediate between pyridine and dimethylformamide in its ability to soften PVC.			
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