Alloying of Poly(vinyl chloride) to Reduce Plasticizer Migration

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ABSTRACT: Concern over the migration of low molecular weight plasticizer from flexible poly(vinyl chloride) (PVC) used in toys and medical products has spearheaded the commercialization of a number of plasticizing polymers. In this study the plasticizing behavior of an ethylene/vinyl acetate/carbon monoxide terpolymer (Elvaloy® from DuPont) was investigated. Blends of PVC, Elvaloy 742, and dioctyl phthalate (DOP) were processed on a twin-roll mill and compression molded into plaques. These materials were characterized in terms of their hardness, glass-transition temperature (T_g), clarity, mechanical properties, and plasticizer migration behavior. The ratios of PVC/DOP/Elvaloy investigated were determined by experimental design. Using this approach it was possible to model the results and produce contour plots to map out the properties of a wide range of formulations. It was confirmed that Elvaloy 742 is compatible with PVC and has a plasticizing effect: this was demonstrated both in terms of a reduction in Shore A hardness and a reduction in T_g. Plasticizer migration was reduced in proportion to the amount of liquid plasticizer replaced. Plasticizing with Elvaloy gave an improvement in tear strength. However, at constant hardness there was no improvement in tensile strength from replacing DOP with Elvaloy. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2022–2031, 2004

Key words: poly(vinyl chloride) (PVC); blends; mechanical properties; dioctyl phthalate; Elvaloy®

INTRODUCTION

Despite assurances from independent experts that the plasticizers used in medical devices and soft toys pose no risk to human health, there are still calls for the phasing out of plasticized poly(vinyl chloride) (PVC). These concerns from environmental groups pose a question over the long-term use of low molecular weight plasticizers that can migrate into the environment and pose a dilemma for the compounders and end users of flexible PVC.[1] Environmental effects notwithstanding, plasticizer migration is undesirable because it can lead to staining, embrittlement, and stress cracking of adjacent materials.

In addition to the pressure from environmental groups, plasticized PVC products are potentially under threat from competitive materials currently being developed that are entirely free from low molecular weight species, such as metallocene-based polyolefin resins. The PVC applications that are under most pressure from substitution by metallocene-derived polyolefins are medical products, packaging, and clear, flexible sheeting.[2,3]

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The objective of this study was to investigate blending of PVC with a compatible polymer that has a lower glass-transition temperature (T_g) than that of PVC. This was expected to have a plasticizing effect on the polymer and thus reduce or even eliminate the need for low molecular weight plasticizer, such as dioctyl phthalate. The work was aimed at clear, flexible PVC formulations. The polymer chosen was Elvaloy 742, which is an ethylene/vinyl acetate/carbon monoxide terpolymer from DuPont (Wilmington, DE),[4] which has a high molecular weight (MW $>$ 250,000) and melting point of 45°C. The resulting blends were characterized in terms of their hardness, T_g, clarity, mechanical properties and plasticizer migration behavior.

The formulations examined in this study were determined by experimental design using the mixtures method. This approach has been used with other polymer blends and has been shown to facilitate modeling of the results and to enable the properties of a wide range of formulations to be predicted.[5]

EXPERIMENTAL

Formulations

The formulations used in this study are shown in Table I. The concentrations of PVC, plasticizer, and

TABLE I
Experimental Design

Sample	PVC %	Di-octyl phthalate %	Elvaloy 742 %
A	70	30	0
B	60	40	0
C	50	50	0
D	70	15	15
E	60	20	20
F	50	25	25
G	70	0	30
H	60	0	40
I	50	0	50

Elvaloy 742 are based on an experimental design derived from the ECHIP software package (ECHIP, Inc. Hockessin, DE).[6] Concentrations are expressed in terms of wt % and add up to 100%. The PVC was of *K*-value 70 and technical data for this polymer are given in Table II. The plasticizer used was dioctyl phthalate (DOP). The liquid Ba/Zn stabilizer was added at a level of 2 phr (parts per hundred parts of polymer) relative to the amount of PVC.

The PVC, DOP, and stabilizer were mixed on a high-speed Fielder mixer at a temperature of 120°C. The Elvaloy 742 (supplied in powder form) was subsequently added and the blend was mixed in a rotary mixer at a temperature not exceeding 60°C. Mixing was carried out in two stages to ensure that the liquid stabilizer and DOP were fully absorbed by the PVC. Elvaloy 742 has a high molecular weight (>250,000) and low melting point (45°C) and can cause nonuniform dispersion and agglomeration in the mixing process.[4]

Processing

The blends were processed into sheets on a twin-roll mill with the rolls set at a temperature of 140°C, roll speed of 10 m/min, and a friction ratio of 1.25. The sheets were compression molded to make plaques, which were required for some of the tests. The operating temperature was 180°C for 5 min with a hydraulic pressure of 20 tons.

Physical and mechanical property measurements

Shore A hardness

Shore A hardness measurements were carried out according to ASTM D2240-97. This method is based on an indenter penetration test and requires a sample thickness of at least 6 mm. For this test specimens of 7 mm thickness were produced by compression molding. Ten measurements were made on each sample type. The mean values and standard deviations of these measurements are given in Table III.

Glass-transition temperature

Glass-transition temperature was measured by thermomechanical analysis (TMA) using a DuPont 941 TMA instrument (Boston, MA), which measures the change in volume of the specimens as a function of temperature. The test was conducted in the temperature range of −100 to +100°C, with a heating rate of 10°C/min. The glass-transition temperature was taken from the extrapolation of the change in gradient of the slope. Results of the glass-transition temperatures of the various formulations obtained in this way are shown in Table III.

Clarity

Clarity was measured by the haze test, conforming to ASTM D1003-61. This test measures the percentage of incident light transmitted with more than a certain angular deviation by forward scattering. The higher the haze value, the worse the clarity. Five haze measurements were made for each sample type. Table III shows the results from this test.

Plasticizer migration

Plasticizer migration tests were carried out according to the ISO 177 test method, which is equivalent to DIN 53 405. Compression-molded samples were cut into squares with sides measuring 50 mm. Each specimen was weighed to four decimal places and sandwiched between two pieces of rigid PVC. These "sandwiches" were stacked in an oven at 80 ± 2°C and a 5 kg weight was placed on each stack. The extent of plasticizer migration was assessed by measuring the weight gain of the rigid PVC plaques after 1, 3, 7, and 14 days. The results in Table III are expressed in terms of % weight loss from each specimen after 14 days.

Tear strength

Tear strength was measured on the Lloyd tensile testing machine (Type L2000R; JJ Lloyd Instruments,

TABLE II
Technical Data for PVC Polymer

K-value	70
Viscosity number, mL/g	125
Weight-average molecular weight, M_w	200,000
Number-average molecular weight, M_n	64,000
Apparent density, kg/m^3	500
Particle size > 250 μm, %	<0.5

TABLE III
Results of Physical Property Measurements

Sample	Formulation	Shore A hardness	T_g (°C)	Haze value	Plasticiser migration, % wt loss after 14 days
A	70/30/0	84 ± 2.0	−25	7.2 ± 0.7	5.74
B	60/40/0	71 ± 1.8	−46	6.6 ± 0.5	11.65
C	50/50/0	54 ± 1.4	−52	4.6 ± 1.6	17.70
D	70/15/15	91 ± 1.8	−17	31.1 ± 1.8	1.16
E	60/20/20	77 ± 3.0	−24	18.6 ± 0.7	2.08
F	50/25/25	58 ± 2.2	−46	16.0 ± 0.3	5.33
G	70/0/30	95 ± 1.5	−6	69.3 ± 4.1	0.29
H	60/0/40	91 ± 0.7	−20	54.4 ± 2.0	0.41
I	50/0/50	78 ± 2.0	−29	13.8 ± 0.8	2.52

Hampshire, UK). In accordance with ASTM D1938-94, test specimens were prepared with a longitudinal slit of 50 mm. A testing speed of 250 mm/min was used and the average force required to propagate the tear was then determined. Ten samples were tested for each formulation type. The thickness of each specimen was measured and tear strength (S) determined from the equation: $S = F/t$, where F is the tearing force (N) and t is the thickness (mm). The results of tear strength measurements are given in Table IV.

Tensile properties

Tensile properties were measured on the Lloyd Type L2000R tensile testing machine. Molded sheets were cut into dumbbell-shaped specimens conforming to ASTM 882-95a. Tests were carried out at 23 ± 2°C, with a crosshead speed of 50 mm/min. Ten specimens from each formulation were tested. Table IV shows the results of tensile strength measurements.

RESULTS AND DISCUSSION

Multiple regression analysis was carried out on the data using ECHIP software to model the results. For each response parameter a 2D contour plot is shown.

TABLE IV
Results of Mechanical Property Measurements

Sample	Formulation	Tear strength (N/mm)	Tensile strength (MPa)
A	70/30/0	47 ± 4.0	24.4 ± 0.8
B	60/40/0	25 ± 3.0	17.7 ± 0.7
C	50/50/0	13 ± 1.3	11.9 ± 0.8
D	70/15/15	62 ± 4.2	24.6 ± 0.9
E	60/20/20	36 ± 3.6	18.6 ± 0.5
F	50/25/25	20 ± 2.9	12.6 ± 0.5
G	70/0/30	80 ± 6.9	34.1 ± 1.9
H	60/0/40	54 ± 4.5	29.4 ± 1.3
I	50/0/50	40 ± 4.6	20.4 ± 1.0

This maps out the relationship between the response parameter and the three formulation variables: PVC, DOP, and Elvaloy. The equation describing the relationship is also given. There is a complication in writing equations for a mixtures design, however, because the variables are not independent and thus the coefficients are not unique. In this case the model is of the Scheffé form, and so there is no constant in the equation.

Shore a hardness

Shore A hardness results are plotted in Figure 1. As expected, it can be seen that increasing the level of DOP (Samples A–C) produced a reduction in hardness. Also the addition of increasing amounts of Elvaloy 742 (Samples G–I) produced a reduction in hardness, but less than that achieved with DOP. Mixtures of DOP and Elvaloy were effective in softening the PVC. The mixture containing a ratio of PVC : DOP : Elvaloy of 50 : 25 : 25 gave a hardness value of 58 compared with a value of 54 for the formulation made up of 50 : 50 PVC and DOP.

When the hardness data were analyzed with the ECHIP software, an additional reference data point was added in terms of the hardness of unplasticized PVC (i.e., 100 wt % PVC), which has a Shore A value of 100. The 2D contour plot obtained after analysis of the data is shown in Figure 2. This plot shows how Shore A hardness varies as a function of the concentration of PVC, DOP, and Elvaloy. The numbered lines on the plot are contour lines of constant hardness. The diagram is annotated to show the lines of constant DOP and Elvaloy concentration.

Furthermore, Figure 2 clearly shows that Elvaloy does have a plasticizing effect on PVC. For example, replacing 50 wt % of the PVC with Elvaloy in the absence of DOP gives a reduction in hardness from 100 to 78 units. On the other hand, Elvaloy is less effective than DOP as a plasticizer: to obtain the same

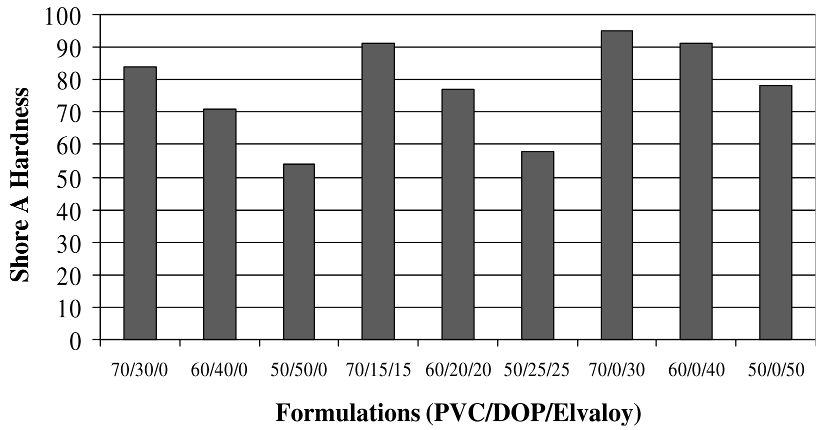

Figure 1 Shore A hardness.

reduction in hardness it is necessary to replace only 35.5 wt % of the PVC with DOP.

The best-fit model describing the effects of the formulation variables on Shore A hardness is given below. In this equation the concentration of each variable is expressed on a scale from 0 to 1.00, rather than 0 to 100% (i.e., weight fraction rather than weight percentage). The residual standard deviation of the model is 2.00 and the model gives a statistically significant fit.

$$\begin{aligned}\text{Shore A hardness} &= 199.78(\text{PVC-0.5}) + 106.62(\text{DOP}) \\ &+ 156.34(\text{Elvaloy}) + 224.56(\text{PVC-0.5})(\text{DOP}) \\ &+ 173.48(\text{PVC-0.5})(\text{Elvaloy}) - 105.36(\text{DOP})(\text{Elvaloy})\end{aligned}$$

This equation can be used to predict the Shore A hardness of any combination of PVC, DOP, and Elvaloy in the range of 50 to 100 wt % PVC, 0 to 50 wt % DOP, and 0 to 50 wt % Elvaloy, with the constraint that the sum of the concentrations must add up to 100 wt %.

Glass-transition temperature

An interesting observation from the glass-transition temperature measurements was that the mixtures of the two polymers, PVC and Elvaloy 742, showed a single glass transition temperature over the range of formulations investigated, indicating that there is complete miscibility between these polymers over this range.

Figure 3 is a plot of the glass-transition temperatures of the various formulations. These results confirm that addition of both DOP and Elvaloy causes a reduction in T_g of the PVC compound, but that DOP has a more efficient plasticizing action than that of Elvaloy. Mixtures of DOP and Elvaloy (Samples D–F) have a plasticizing action intermediate between the two.

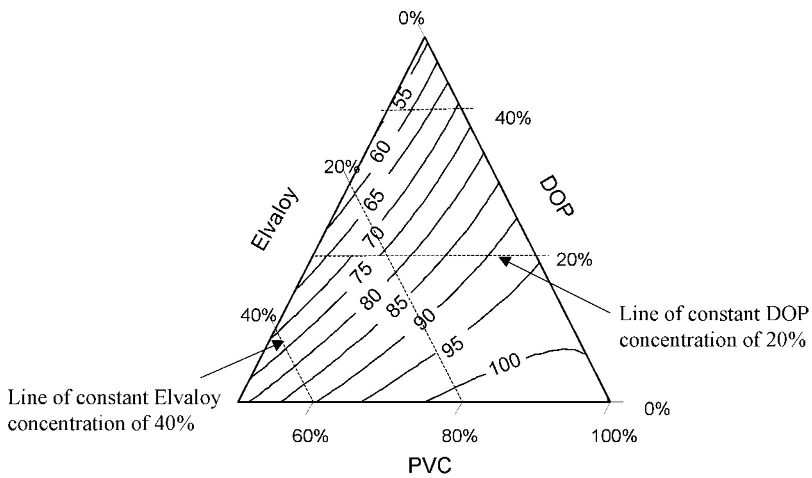

Figure 2 Two-dimensional contour plot of Shore A hardness as a function of formulation ingredients. (Contour lines are lines of constant Shore A hardness.)

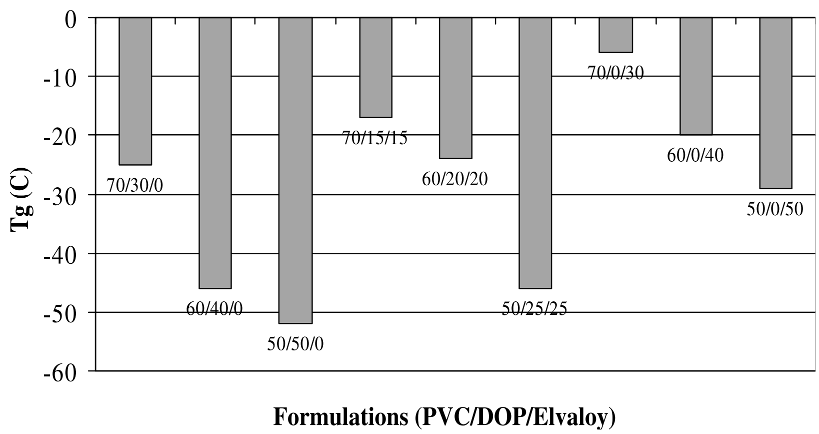

Figure 3 Glass-transition temperature.

Analysis of the results using the ECHIP software produced a model relating T_g to the three formulation variables, which is represented by the 2D contour plot in Figure 4. Included in the data for this analysis was the reference data point for the T_g of unplasticized PVC, which is 78°C. It is seen from the contour plot that replacement of PVC with up to 30 wt % of DOP or Elvaloy is predicted to give a relatively linear reduction in T_g. However, beyond this it becomes increasingly difficult to achieve further reductions in T_g, particularly below −30°C for Elvaloy. However, this is not surprising, given that the T_g of Elvaloy 742 is −32°C.

The equation relating T_g to the formulation parameters is shown below. This model has a residual standard deviation of 4.37 and gives a statistically significant fit to the data.

$$T_g = 155.3(\text{PVC-0.5}) - 107.32(\text{DOP}) - 59.26(\text{Elvaloy}) - 401.2(\text{PVC-0.5})(\text{DOP}) - 296.24(\text{PVC-05})(\text{Elvaloy})$$

Clarity

Results from the haze test are plotted in Figure 5. The three samples plasticized with DOP all showed excellent clarity. Plasticizing with Elvaloy 742 produced a significant reduction in clarity (increased haze), although the blend containing 50/50 PVC/Elvaloy (i.e., Sample I) had a haze value of only 13.8, which was much lower than expected. Samples plasticized with a mixture of Elvaloy 742 and DOP generally had haze values between the two extremes.

Multiple regression analysis reveals a complex relationship between haze and the formulation variables,

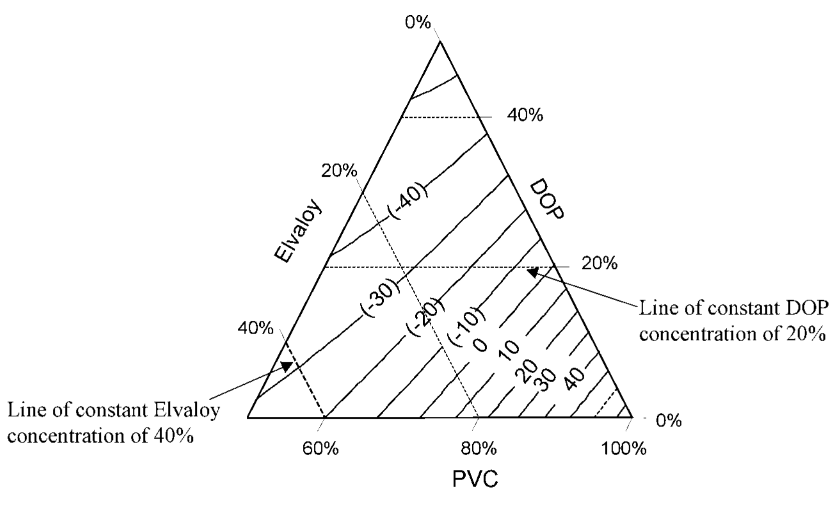

Figure 4 Two-dimensional contour plot of glass-transition temperature (°C) as a function of formulation ingredients. (Contour lines are lines of constant T_g.)

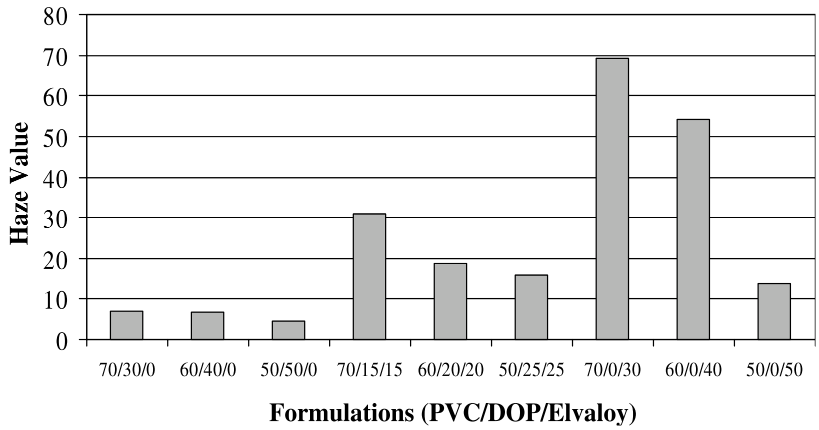

Figure 5 Haze test results.

as shown in the contour plot of Figure 6. Note that the model is valid only within the trapezium (defined by the bold black lines), which represents the experimental window investigated. Extra data for the formulation representing 100% PVC were not available in this case. The best clarity is obtained for formulations plasticized solely with DOP or for formulations with around 50% PVC plasticized with a mixture of DOP and Elvaloy.

The equation relating haze to the formulation parameters is shown below. This model has a residual standard deviation of 5.81 and gives a statistically significant fit to the data.

$$\text{Haze} = 2.36(\text{PVC-0.5}) + 11.39(\text{DOP}) + 32.02(\text{Elvaloy}) + 942.28(\text{PVC-0.5})(\text{Elvaloy})$$

Plasticizer migration

Plasticizer migration results are expressed in terms of the percentage weight loss after 14 days and these data are plotted in Figure 7. Not surprisingly, it is found that the percentage weight loss correlates strongly with the amount of liquid plasticizer (i.e., DOP) in the formulation. Formulations containing a mixture of DOP and Elvaloy show greatly reduced weight loss because of the much lower amount of liquid plasticizer present. The presence of Elvaloy does not reduce the migration of plasticizer over and above the necessity to have less plasticizer present.

Other points to note are that there is a surprisingly high weight loss from Sample I, which contained 50% PVC and 50% Elvaloy but no DOP. Also, the samples containing Elvaloy, particularly Samples G–I, were found to have discolored after the plasticizer migration test, implying that thermal degradation had occurred during the course of the test.

Figure 8 shows the contour plot from the regression analysis. Included in the analysis of these data is the reference data point for unplasticized PVC (i.e., 100 wt % PVC), which is zero plasticizer weight loss. As expected, the contour lines of plasticizer weight loss

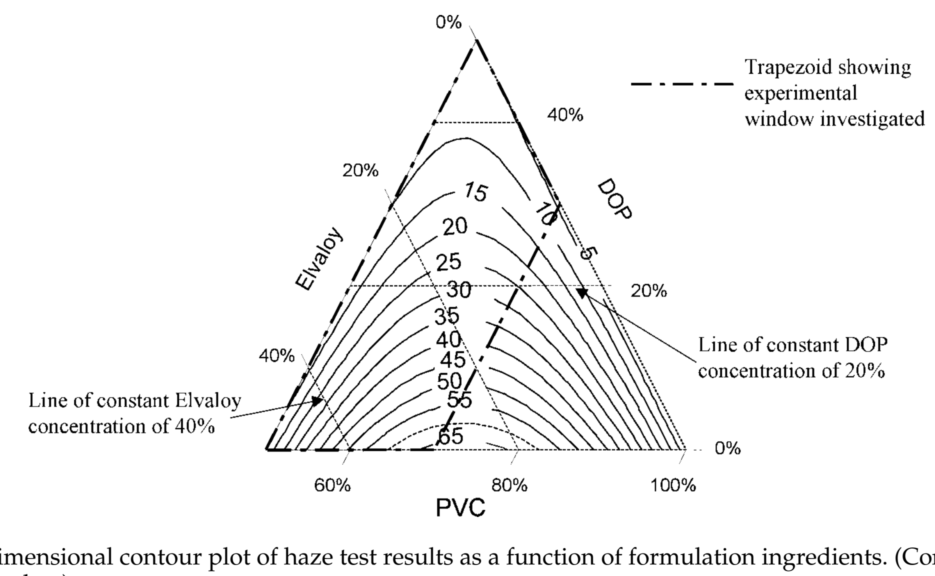

Figure 6 Two-dimensional contour plot of haze test results as a function of formulation ingredients. (Contour lines are lines of constant haze value.)

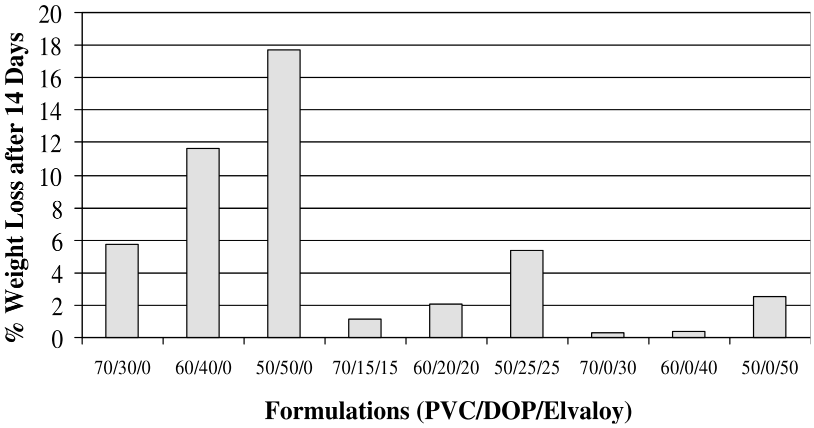

Figure 7 Plasticizer migration % weight loss after 14 days.

lie more or less parallel to the lines of constant DOP concentration, illustrating the overriding dependency of weight loss on the level of DOP in the formulation.

The equation relating % weight loss to the formulation parameters is shown below:

$$\text{Weight loss (\%)} = 0.072(\text{PVC-0.5}) + 35.90(\text{DOP}) + 4.78(\text{Elvaloy}) - 80.73(\text{PVC-0.5})(\text{DOP}) - 26.57(\text{PVC-0.5})(\text{Elvaloy}) - 82.91(\text{DOP})(\text{Elvaloy})$$

For this model the standard deviation of the residuals is 0.56, which gives an acceptable fit to the data.

Tear strength

The results of tear strength measurements are plotted in Figure 9. It is seen that replacing PVC with either DOP or Elvaloy 742 causes a reduction in tear strength, but that the effect of DOP is greater than that of Elvaloy.

The model obtained from the regression analysis of the tear strength data is shown graphically in Figure 10, which shows contour lines of constant tear strength as a function of the formulation. The model is valid only within the trapezium defined by the bold black lines. The residual standard deviation of this model is 1.30, which gives an acceptable fit to the data. The equation is given below:

$$\text{Tear strength} = 402(\text{PVC-0.5}) + 26.64(\text{DOP}) + 78.74(\text{Elvaloy}) - 672.96(\text{PVC-0.5})(\text{DOP}) - 409.8(\text{PVC-0.5})(\text{Elvaloy}) - 96.48(\text{DOP})(\text{Elvaloy})$$

For formulations of a given hardness, it is possible to obtain a higher tear strength by using a larger quantity of Elvaloy 742. For example, a hardness of 70 is ob-

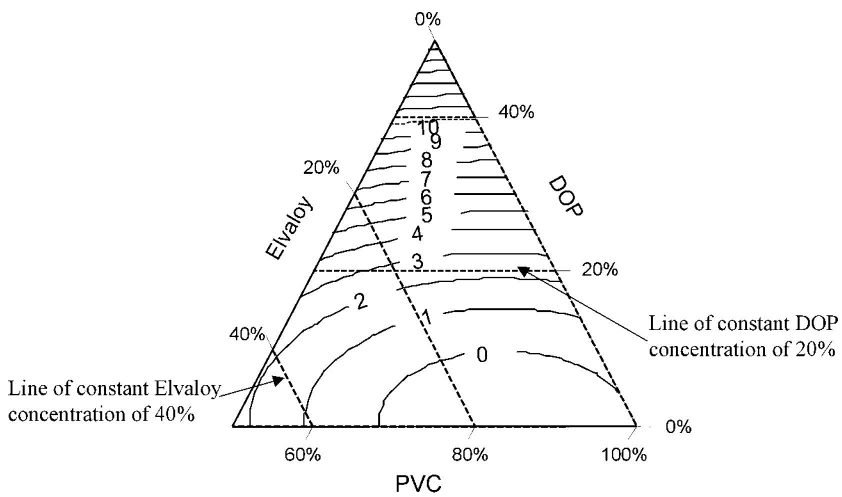

Figure 8 Two-dimensional contour plot of plasticizer migration results (% weight loss after 14 days) as a function of formulation ingredients. (Contour lines are lines of constant % weight loss.)

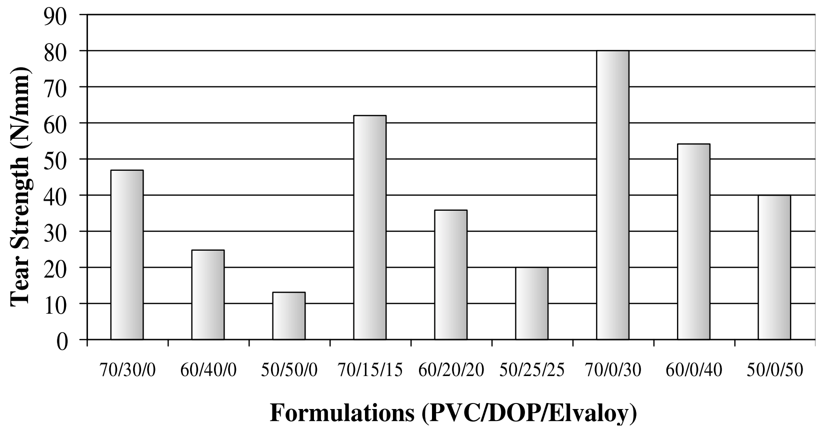

Figure 9 Tear strength.

tained with formulations containing ratios of PVC/DOP/Elvaloy of both 59/41/0 and 50/8.5/41.5. The predicted tear strength of the former is 22 N/mm, whereas that of the latter is 32 N/mm.

Tensile strength

Figure 11 shows the tensile strength data for each sample measured. It is seen that as the percentage of both DOP and Elvaloy 742 in the formulation increases, there is a reduction in tensile strength. However, samples plasticized with Elvaloy alone show a smaller reduction in tensile strength than that of samples plasticized with DOP or a mixture of DOP and Elvaloy.

The best-fit equation, derived from the multiple regression analysis to describe the relationship between tensile strength and the formulation variables, is given below. The residual standard deviation of this model is 1.57, which gives a statistically significant fit to the data.

$$\text{Tensile strength} = 98.74(\text{PVC-0.5}) + 24.76(\text{DOP}) + 44.39(\text{Elvaloy}) - 59.44(\text{PVC-0.5})(\text{DOP}) - 88.76(\text{DOP})(\text{Elvaloy})$$

Figure 12 is the 2D contour plot showing a graphical representation of the above equation. It is seen that tensile strength is reduced when PVC is replaced by either Elvaloy or DOP, but the reduction is considerably greater with DOP.

It is interesting to compare Figure 12 with Figure 2 to see whether formulations of a given hardness show differences in tensile strength depending on composition. Unlike the case of tear strength discussed above,

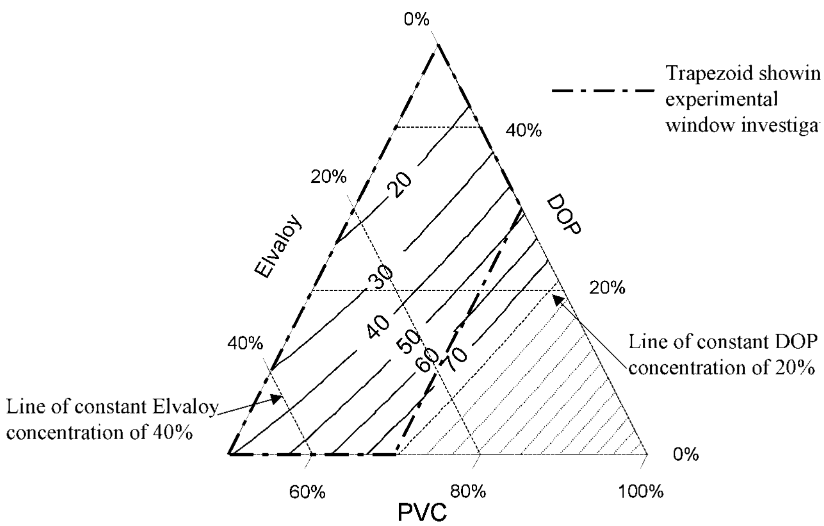

Figure 10 Two-dimensional contour plot of tear strength (N/mm) as a function of formulation ingredients. (Contour lines are lines of constant tear strength.)

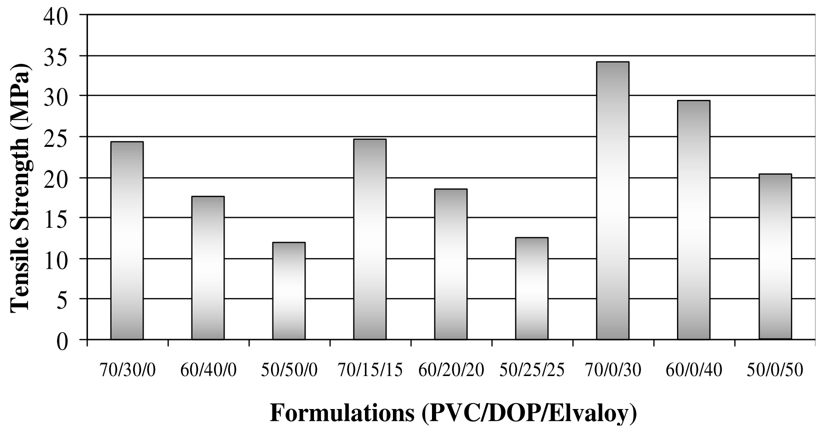

Figure 11 Tensile strength.

there does not seem to be any advantage in plasticizing with Elvaloy to obtain a higher tensile strength for a given hardness. For example, formulations containing ratios of PVC/DOP/Elvaloy of 59/41/0 and 50/8.5/41.5 both give a hardness value of 70. The predicted tensile strengths of these two formulations are 16.8 and 17.4 MPa, respectively, which, given the reproducibility of the test, are not significantly different.

CONCLUSION

It is concluded from this study that Elvaloy 742 is compatible with PVC and has a plasticizing effect. This is demonstrated both in terms of a reduction in Shore A hardness and a reduction in T_g. However, Elvaloy is much less efficient than DOP as a plasticizer: it was necessary to add DOP to obtain materials of Shore A hardness values of 75 and below. Plasticizing with Elvaloy produces a reduction in plasticizer migration according to the amount of DOP replaced.

Apart from the increased formulation costs, a disadvantage of plasticizing with Elvaloy is a reduction in clarity, although formulations containing around 50% PVC, plasticized with a mixture of DOP and Elvaloy, did show good clarity.

With respect to mechanical properties, it is found that replacing PVC with either DOP or Elvaloy causes a reduction in tear strength, but that this effect is less with Elvaloy than with DOP. For a given hardness it is possible to obtain a higher tear strength by using a larger proportion of Elvaloy. Samples plasticized with Elvaloy also show a smaller reduction in tensile strength than that of samples plasticized with DOP. However, it is found that at constant hardness there

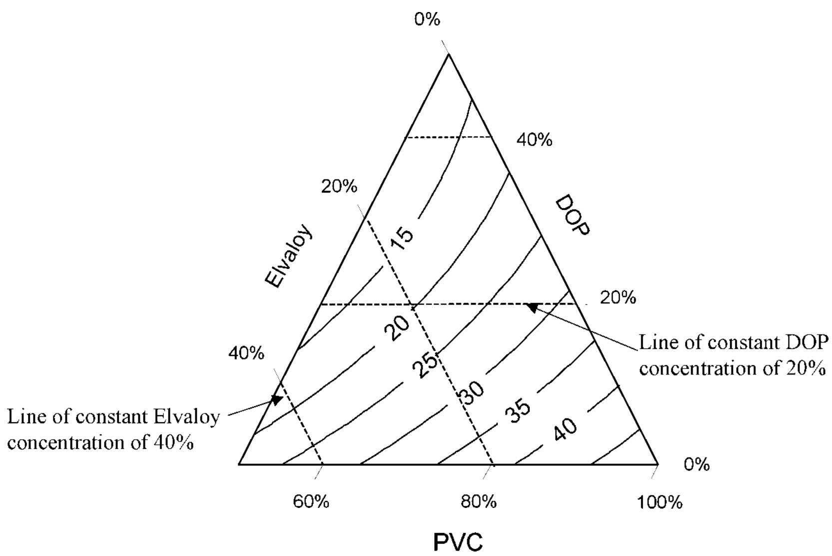

Figure 12 Two-dimensional contour plot of tensile strength (MPa) as a function of formulation ingredients. (Contour lines are lines of constant tensile strength.)

are no benefits to be gained in tensile properties from plasticizing with Elvaloy.

By using the mixtures design approach it is possible to model the results and thus map out the effects of a wide range of formulations (Figs. 2, 4, 6, 8, 10, and 12). This provides a much clearer picture than the conventional method of changing one variable while keeping the ratio of the other two constant (Figs. 1, 3, 5, 7, 9, and 11). It is also possible to solve the equations for several responses simultaneously and thus predict the optimum formulation that will give a particular combination of properties.

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