

Properties of PVC. II. Properties of PVC Compounds with Solvents

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Synopsis

It was the aim of this paper to study the influence of the solvent residues in PVC compounds on physical and mechanical properties of samples prepared from them as well as the rheologic properties of their melts. Besides tetrahydrofuran other solvents are also partly retained in PVC even after processing at higher temperatures. The properties of samples prepared from PVC compounds containing solvents depend on the solubility parameter of the solvent used. Solvents with a solubility close to that of PVC have the same effect as plasticizers. Solvents with very high solubility parameters, e.g., water, influence the flow and dynamic properties in just the opposite way than plasticizers and behave rather like fillers. A mechanism for influencing the properties of PVC by the presence of solvent residues is suggested.

INTRODUCTION

The possibilities of processing plastic materials depend in the first place on their rheologic properties. The regulation of rheologic properties of the processed compounds is done normally by adding small quantities of plasticizers or lubricants.¹

It has been proved² that mutual interaction between polymer and solvent can cause tetrahydrofuran to be partially retained in PVC even after treatment at higher temperatures and after extremely long periods, although the boiling point of tetrahydrofuran itself is 65°C. It is, therefore, very likely that the remnants of the solvent (e.g., tetrahydrofuran) would act in PVC compounds in a way like plasticizers and lubricants and thus influence their rheologic properties.

Contrary to solvents, plasticizers and lubricants have a substantially higher boiling point than the temperature at which molding is done and their choice is made in such a way as to have minimum losses by evaporation on prolonged heating.

The aim of this paper is to evaluate the properties of samples prepared from PVC compounds with solvents and to study the rheologic properties of their melts.

EXPERIMENTAL

Determination of Physical and Mechanical Properties

Preparation of Samples

A compound was prepared of 300 g Halvic 223 (suspension PVC $[\eta] = 0.63$ dl/g) with 3 cc Advastab D 671 (stabilizer) and 60 cc solvent. This compound was thoroughly mixed and milled for 5 min at 160°C to sheets ca. 2.2 mm thick. From the sheets, plates of 2 and 4 mm were molded in a small frame under pressure of 120 kp/cm² and at a temperature of 190°C and which, after 3 hr of tempering at 85°C, were used for determination of properties.

To investigate the properties of samples containing a solvent of different solubility parameter than that of PVC, a mixture of 300 g PVC with 100 ml of distilled water or gasoline was taken and thoroughly mixed. The mixture was put into the autoclave and heated for 1 hr at 150°C. The autoclave was decompressed under heat and the content was cooled down freely in the air. From the PVC thus processed samples were milled, molded, and tempered as described in the preceding paragraph. For these samples the following properties were determined: density, tensile strength, notch impact strength, embrittlement temperature, and dynamic properties. Their determination has been described previously.²

Rheologic Properties

The rheologic properties were determined by the Brabender plastograph with a Banbury chamber and a pressing bar. Velocity was 30 rpm, chamber volume, 30 cc, temperature of the tempering fluid, 150°C. The compound for determining rheologic properties was prepared from 30 g Halvic 223 with 0.3 cc Advastab D 671 plus 5 cc solvent.

RESULTS AND DISCUSSION

Several solvents of increasing solubility parameter were used for the compounds. Solubility parameters according to Tobolsky,³ boiling points, and densities of single solvents are indicated in Table I.

Chlorine Content in Samples at Determination of Physical and Mechanical Properties

The chlorine content determined by elemental analysis in samples chosen for measuring physical and mechanical properties in relation to solubility parameter of the solvent used in the compound is indicated in Figure 1. Sample numbers throughout this paper correspond with the numbers of the solvents given in Table I.

The increase in chlorine content in the sample with carbon tetrachloride (sample 2, Table I) is due to the fact that CCl₄ has a higher chlorine content than PVC and the presence of CCl₄ in the sample tends to increase

TABLE I
Properties of Solvents

Sample no.	Solubility parameter,	Solvent	Grade used	Boiling point, °C	Density at 20°C, g/cc
0	(sample without solvent)				
1	7.3	n-hexane	gasoline pure	68	0.659
2	8.6	{ CCl ₄	technical grade	77	1.594
3	8.9	toluene	pure	110	0.867
4	9.2	benzene	technical	80	0.875
5	9.9	tetrahydrofuran	purified	65	0.888
6	10.0	acetone	p.a.	56	0.791
7	12.7	ethanol	plus 1% gasoline	77	0.780
8	24.2	water	distilled	100	0.998

the total chlorine content. The remaining solvents do not contain chlorine. Their presence in the sample will consequently result in a decrease of chlorine content. The differences in chlorine content make possible the rough determination of the quantity of solvent retained in the sample after milling and molding.

The samples from Table I, together with their respective chlorine contents, the differences in chlorine content as compared with a sample without solvent, and the approximate quantity of solvent retained in the sample are given in Table II. The approximate solvent content for samples 1, 7, and 8 was not calculated, as the difference in chlorine content is within the limits of measurement accuracy.

It is evident from Figure 1 and Table II that the quantity of solvent retained in a sample after milling and molding depends on the solubility

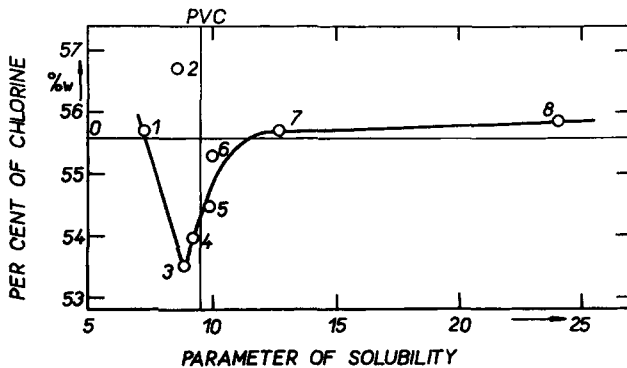


Fig. 1. Dependence of chlorine content on solubility parameter of solvent used in the PVC compound. Numbers (1) to (8) refer to sample numbers as described in Table I.

TABLE II
Chlorine Contents of Samples

Sample no.	Chlorine content, wt-%	Difference in chlorine content, wt-%	Approximate quantity of solvent retained, wt-%
0	55.66	0	0
1	55.71	+0.05	—
2	56.72	+1.06	2.90
3	53.55	-2.11	3.79
4	53.97	-1.69	3.04
5	54.46	-1.20	2.16
6	55.30	-0.36	0.65
7	55.70	+0.04	—
8	55.85	+0.19	—

parameter. In the region where the solubility parameter of a solvent is close to that of PVC, this quantity is relatively high.

Density of PVC-Solvent Compounds

The density of samples from PVC compounds in relation to the solubility parameter of the solvent used is given in Figure 2. The greatest decrease of density is caused by the addition of a solvent having a solubility near that of PVC. The exception from this rule is the sample with carbon tetrachloride (sample 2). The essentially higher density of the sample containing CCl_4 is due to the fact that the density of CCl_4 is roughly double that of other solvents, being even higher than the density of PVC. The presence of CCl_4 in the sample thus tends to increase the density instead of decreasing it as a solvent normally would.

The dependence of density on the solubility of the solvent used (Fig. 2) is similar to that of the chlorine content (Fig. 1). The density depends, therefore, on the quantity of solvent retained in a milled and molded sample and on its properties.

From the approximate content of the solvent in a sample (Table II) and on the presumption of volume additivity of PVC and solvent it is possible to calculate the theoretical density of a given sample prepared from a PVC-

TABLE III
Densities of Samples

Sample no.	Density, g/cc		
	Actual	Calculated	Calculated Minus Actual
0	1.4055	—	—
2	1.4190	1.4102	-0.0088
3	1.3826	1.3732	-0.0094
4	1.3910	1.3801	-0.0109
5	1.3985	1.3881	-0.0104
6	1.4018	1.3984	-0.0034

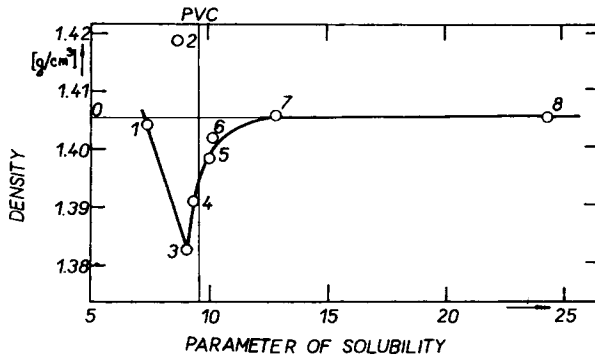


Fig. 2. Dependence of sample density on solubility parameter of solvent used in the PVC compound.

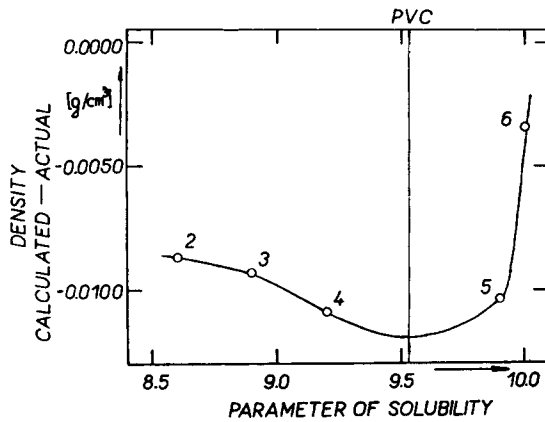


Fig. 3. Dependence of difference between calculated and actual density on solubility parameter of solvent used in the PVC compound.

solvent compound. The samples, their actual and calculated densities, and the difference between the two are given in Table III.

Dependence on solubility of the difference between calculated and actual density (Fig. 3) is at its minimum in a region where the solubility parameter of solvent and that of PVC are identical.

Tensile Strength of PVC-Solvent Compounds

The changes of tensile strength caused by the presence of solvent in the compound are shown in Figure 4. We again get a curve similar to that showing the dependence of density on the solubility parameter. The minimum value of this curve is again for the compound containing toluene (Sample 3).

There is another anomaly for samples containing CCl_4 : "br" at sample 2 (Fig. 4) means that this case does not indicate the tensile strength corresponding to the upper limit of yield strength, but shows that the samples

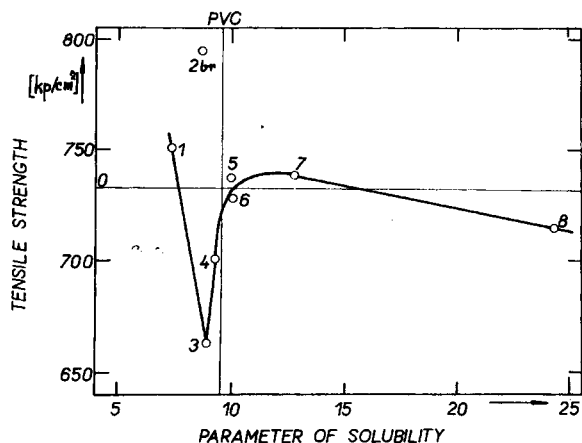


Fig. 4. Dependence of tensile strength on solubility parameter of solvent used in the PVC compound.

containing CCl_4 broke brittly, i.e., before reaching the upper yield strength limit. The shift in upper yield strength limit was, therefore, due to the presence of CCl_4 in the sample to such an extent that it lies above the brittleness strength of the sample at the velocity of deformation (50 mm/min). It was necessary to decide whether the increase in yield strength originated in new chemical bonds (crosslinking) or in an increase in intermolecular forces of a physical nature.

The origin in new chemical bonds would lead to an increase in limit viscosity number of the sample with CCl_4 content as compared with the values of samples from the original PVC, or it would even lead to the formation of an insoluble portion. As no such change was observed, we must presume the action of some forces of a physical nature.

Notch Impact Strength of PVC-Solvent Compounds

The dependence of notch impact strength on the solubility of the solvent is plotted in Figure 5. It is obvious that the dependence of the notch

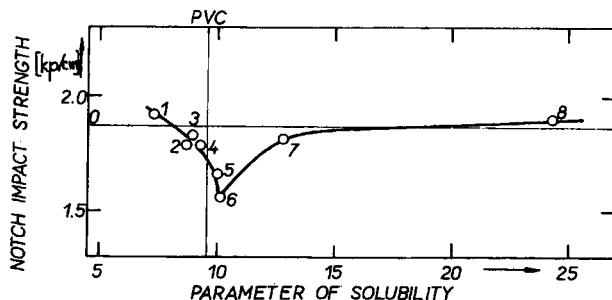


Fig. 5. Dependence of notch impact strength on solubility parameter of solvent used in the PVC compound.

impact strength on solubility differs somewhat from the two previous dependencies (tensile strength and density). This dependence has its minimum value for the sample of PVC compound containing acetone (sample 6), contrary to the previous dependencies (Figs. 1, 2, 4) showing a minimum with toluene (sample 3).

Properties of PVC-Solvent Compounds Heated for Long Periods Under Pressure

It is obvious from Figures 1 to 5 that the maximal change of a property under observation, in comparison with the polymer without solvent, lies near the solubility value 9.53, when the solubility of the solvent used and that of PVC are identical.^{3,4} This result is in accordance with the current hypothesis that such solvents are best for PVC.

The solvents whose solubilities differ widely from that of PVC do not influence the properties of samples of PVC compounds. This is probably due to the fact that they fail to dissolve in PVC in a comparatively short time and therefore evaporate freely.

Both marginal cases with solubility showing maximal distance from the PVC solubility are represented in our series of solvents by gasoline at one end (solubility parameter 7.3) and water on the other (solubility parameter 24.2).

If the partial water or gasoline pressure is increased by an increase in temperature, while at the same time the periods of contact of PVC with the solvent (or with the solvent vapor, to be exact) are prolonged, it is even possible to prepare a PVC sample containing a solvent with a solubility distant from that of PVC. The procedure of preparing these samples is described in the experimental part.

Density, yield strength, brittleness temperature, and the notch impact strength for the samples containing water or gasoline as compared with samples of original polymer without solvent are shown in Table IV.

It is obvious from Table IV that the presence of incompatible solvents (gasoline and water) decreases density, tensile strength, and notch impact

TABLE IV
Properties of PVC Samples Processed at 150°C

	Original PVC	Gasoline-PVC	Water-PVC
Tensile strength, kp/cm ²	733	713	728
Notch impact strength, kp/cm	1.9	1.6	1.6
Embrittlement temperature, °C	+15	+3	-5
Density at 20°C, g/cc	1.4055	1.4042	1.4049
T _α from dynam. measurement, °C	88	86	94

strength, which is in accordance with the effect of compatible solvents (with solubility near that of PVC) as can be deduced by comparing Figures 2, 4, and 5.

Thermographic investigation of the effect of moisture on PVC has already shown that besides water retained by mechanical means in the pores of PVC powder (released at about 100°C) and adsorbed water (released at 100°–120°C) there exist further small quantities of strongly adsorbed, eventually bonded water in a polymer the presence of which influences the hardness, thus having the same effect on this property as a plasticizer.⁵

Small quantities of compatible solvent increase very substantially the embrittlement temperature and decrease T_{α} , as has been shown previously.² With incompatible solvents, the decrease of T_{α} for a compound with gasoline is within the limits of experimental error, while it is on the increase with the compound containing water. The embrittlement temperature has dropped both for compounds with water and gasoline. To clarify the differences between the influence of compatible and incompatible solvents we will deal further with samples from compounds containing tetrahydrofuran (a solvent with solubility close to that of PVC) and samples containing gasoline and water, whose solubility parameters differ widely from that of PVC.

Dynamic Properties

Tracing the dependence on temperature of dynamic properties, i.e., the real component of dynamic modulus in torsion, G' , and mechanical damping, $\tan \delta$, is very valuable, as it gives some basic information on the interaction between polymer and solvent.

Comparison of dynamic properties of samples of polymer without solvent (Fig. 6) with those of samples of PVC compound with tetrahydrofuran (Fig. 7) shows that the presence of the residue of a good-quality solvent such as tetrahydrofuran causes the lowering and even disappearance of the β -maximum on the curve tracing the dependence of mechanical damping

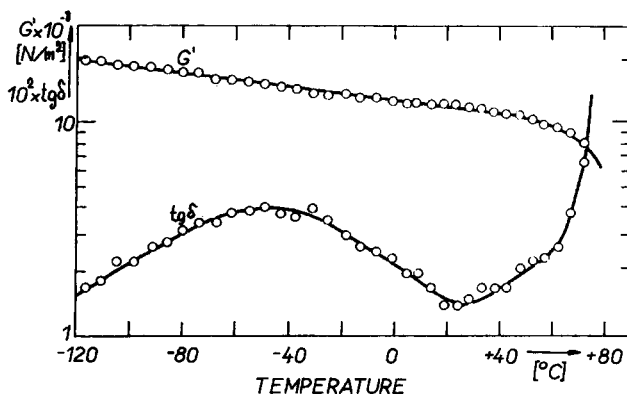


Fig. 6. Dependence of G' and $\text{tg} \delta$ on temperature of a PVC sample without solvent.

tan δ on temperature, as already described,² and which corresponds with the action of the addition of plasticizers on dynamic properties of PVC, interpreted by Bohn⁶ as a result of the restriction or even complete blocking of motion in chain sections. Pezzin et al.⁷ also ascribe the decrease of the β -peak to an interaction between plasticizer molecules and PVC chains (for example, through polar interactions) so that the motions responsible for the β -peak are hindered.

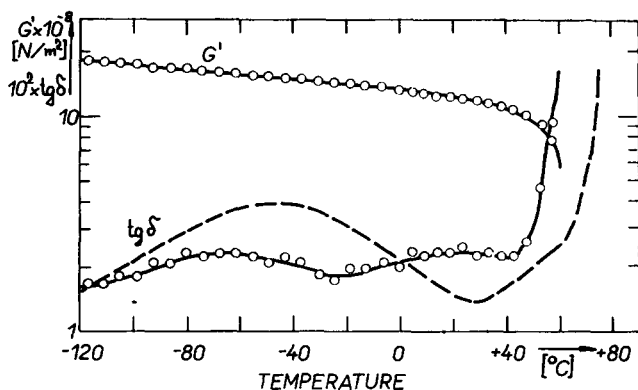


Fig. 7. Dependence of G' and $\text{tg } \delta$ on temperature: (O) PVC sample containing tetrahydrofuran; (---) $\text{tg } \delta$ for PVC sample without solvent.

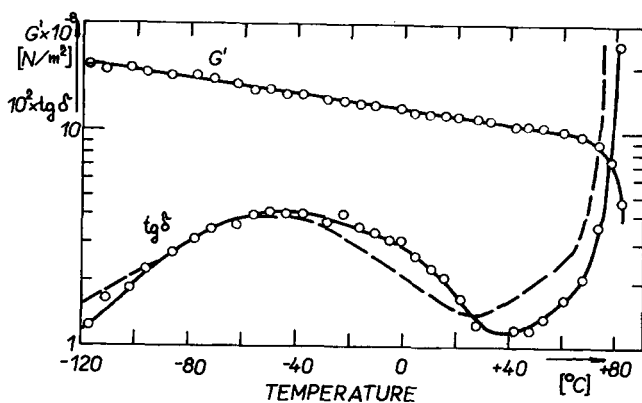


Fig. 8. Dependence of G' and $\text{tg } \delta$ on temperature: (O) PVC sample containing water; (---) $\text{tg } \delta$ for PVC sample without solvent.

The disappearance of the β -peak is accompanied by a simultaneous disappearance of the minimum between the α - and β -peaks. Comparison of dynamic properties of a sample without solvent (Fig. 6) with a sample containing water (Fig. 8) indicates that the presence of water lowers the minimum between α - and β -peaks on the curve of the dependence of tan δ on temperature and shifts it toward higher temperatures, increasing T_α at the same time.

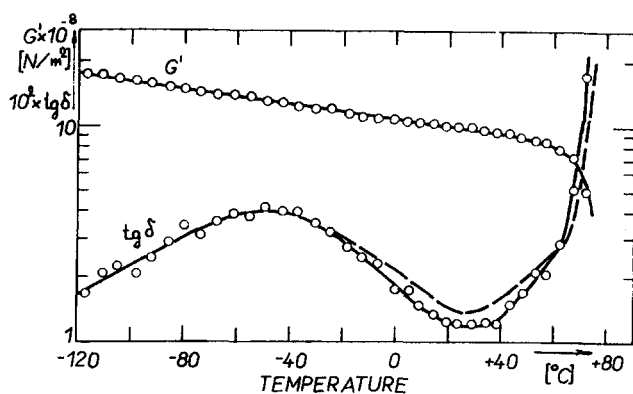


Fig. 9. Dependence of G' and $tg\delta$ on temperature: PVC sample containing gasoline; (---) $tg\delta$ for PVC sample without solvent.

This is just the opposite effect to that of plasticizers and resembles rather the effect of fillers on dynamic properties of PVC, as has been found by Heideingsfeld and Zelinger.⁸ The dependence of mechanical damping, $\tan \delta$, on temperature for a PVC sample without solvent (Fig. 6) is affected by the presence of gasoline (Fig. 9) only in the region of the minimum between α - and β -peaks. The minimum in this case is somewhat lowered, without being shifted.

Rheologic Properties

Mathematical evaluation of rheologic properties of materials, based on measuring the moment required for Brabender mixing, has not been carried out in view of the complexity of the flow conditions. We have only compared the torsion moments necessary for mixing of PVC compounds containing different solvents. Greater torsional moment also means a higher viscosity of the melt.

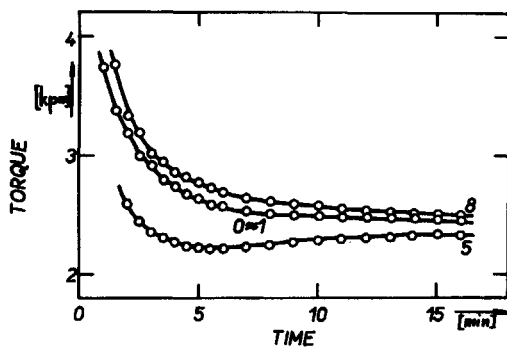


Fig. 10. Dependence of torsion moment on processing time: (0) compound without solvent; (1) compound with gasoline; (5) compound with tetrahydrofuran; (8) compound with water.

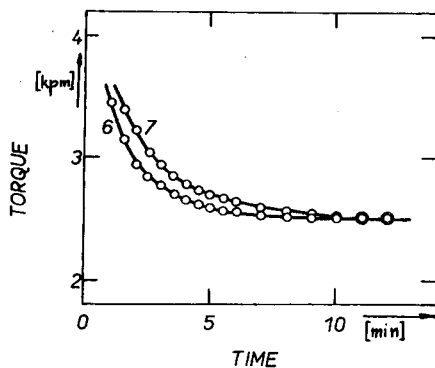


Fig. 11. Dependence of torsion moment on processing time: (6) compound with acetone; (7) compound with ethanol.

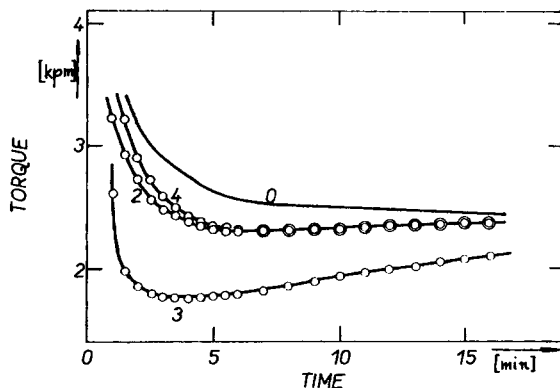


Fig. 12. Dependence of torsion moment on processing time: (0) compound without solvent; (2) compound with CCl₄; (3) compound with toluene; (4) compound with benzene.

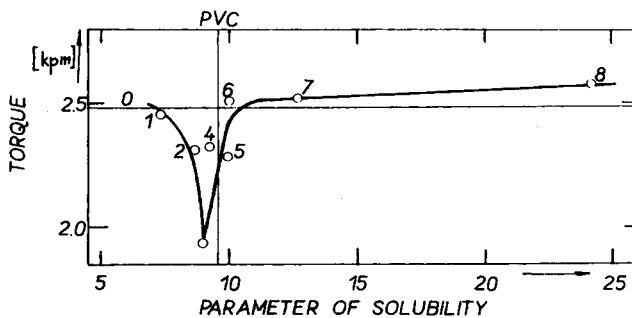


Fig. 13. Dependence of torsion moment after 10 min of processing on solubility parameter of solvent used in the compound. Number (1) to (8) refer to sample numbers as described in Table I.

The dependence of torsional moment on mixing time for compounds containing tetrahydrofuran, gasoline, and water and for the polymer without a solvent is apparent from Figure 10. Tetrahydrofuran in a compound behaves like a plasticizer (lowering the viscosity of the melt); gasoline on the other hand lowers the viscosity only very little (the decrease is within the limits of experimental errors). Water behaves just the contrary and shows its antiplasticizing effect similar to that demonstrated by dynamic measurements. Behavior similar to that of water can be found with the compounds containing ethanol and acetone (Fig. 11).

The action of CCl_4 , toluene, and benzene (Fig. 12) is similar to that of a plasticizer and tetrahydrofuran. The dependence of the torsional moment required for the kneading of PVC compound with a solvent on the solubility of solvent used is charted in Figure 13 for 10 min of mixing. The course of this dependence is similar to the course of physical-mechanical properties of samples from PVC compounds containing solvents and to that of the chlorine content, i.e., in the region where the solubility parameters of solvent and PVC are close, the curve running through the minimum.

CONCLUSIONS

Besides tetrahydrofuran there are other solvents that are partly retained in PVC even after processing at increased temperatures.

The properties of samples prepared from the compounds containing solvents depend on the solubility of the solvent used. Solvents with solubilities close to that of PVC have the same effect as plasticizers. Solvents with very high solubility parameters (e.g., water) influence the flow and dynamic properties in just the opposite way than plasticizers and behave rather like fillers.

The most probable mechanism by which solvent residues affect the properties of PVC is the following: On the one hand, molecules of solvent residues exert influence mechanically by their volume, i.e., they change the total free volume of a polymer and, on the other hand, by their field of force (characterized usually by CED), which is dependent on the chemical composition of the solvent. Both these factors can exert influence on the energy required for the rotation of polymer segments. The differences in segment mobility manifest themselves on a macroscopic scale by different properties such as notch impact strength, yield strength, rheologic properties of the melt, dynamic properties, embrittlement temperature, T_g , etc.

The increased interaction between polymer and solvent in the region where the solubility parameters are close to each other results in an increased quantity of solvent retained in the polymer.

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