

Properties of PVC. III. Influence of the Way of Processing on the Properties of PVC Samples

J. MALÁČ, *Department of Rubber and Plastics Technology Technical University, Prague, Czechoslovakia*

Synopsis

The work shows PVC qualitative dependence under the conditions for the preparation of samples and some of their properties. The different ways of preparation influences the differences of residual stress and the free volume of samples, which is apparent even on properties, the measuring of which is not sufficiently precise, and therefore the differentiating ability is small (as, e.g., the notch impact strength).

INTRODUCTION

Polyvinylchloride crystallizes to a very small extent. Its properties are therefore determined substantially by the properties of the amorphous phase, e.g., mainly by the changes of the free volume and residual stress of the sample. In view of the high rigidity of the chains of PVC molecules, the time-dependent changes of the free-volume are very slow, and therefore the resulting free-volume is strongly influenced by the conditions of the sample preparations.

The effect of preparation methods of PVC samples on (a) the IR spectrum¹⁻³ on the diffraction of x-rays^{4,5}; (b) on the specific heat⁶⁻⁸; (c) on the DTA process⁹; (d) on density^{10,11}; and (e) on the embrittlement temperature¹² was investigated. Sommer¹³ pointed out that for achieving reproducible results of dynamic measurements of PVC samples, it is necessary to maintain a constant procedure when preparing the samples. Pezzin and his colleagues¹⁴ investigated the dynamic properties dependence on the conditions of the preparation in more detail.

The work is to show the qualitative connection between the condition of the samples and density (as value connected with the free volume) and between some selected physical and mechanical properties.

Experimental

From the PVC polymer of the Halvic type 223 $[\eta] = 0.63$ dl/g we got:
(a) Films (ca. 0.1 thick) were prepared by milling (for a different period of time at different temperatures) or compression molding between polished aluminum sheets (at different temperatures for 3 min, 200 kp/cm²) were

then cut to samples of $2 \times 2 \times 0.1$ mm, tempered for 3 hr at 85°C and used for measuring density.

(b) From the compound containing 1% of Advastab D 671 (stabilizer) sheets, 2.2 mm thick were prepared by 5 min milling at 160°C , and were compressed in a small frame for 3 min, 120 kp/cm^2 .

(1) Sheets of 4 mm thick at temperatures from $160^\circ\text{--}200^\circ\text{C}$ (scale grades 10°C) were used without further tempering for the determination of the influence of compression temperature on properties.

(2) Sheets of 2 and 4 mm thick, at 190°C were used for determination of properties as follows:

- I. After 3 hr tempering at 85°C and slow cooling (cca $30^\circ/\text{hr}$).
- II. After 30 min of heating at 140°C and fast cooling (sheets 2 mm thick cooled by dipping into cooling mixture to -75°C , sheets 4 mm thick water cooled to $+15^\circ\text{C}$).

Determined were: density, tensile strength (corresponding to the upper yield strength), notch impact strength, embrittlement temperature, and dynamic properties. The description of determination of these properties is in the work.¹⁵

RESULTS AND DISCUSSION

PVC Without Additives (compounding ingredients)

Density of the Milled Films

Results of the density measuring of samples in dependence on time and temperature of milling are shown on Figure 1. It is obvious from this figure, that the density of the sample depends on the time of milling only at 120°C , when the value after 2 min is substantially lower than other values, which is clearly caused by deficient plastification. At all temperatures shear forces in the polymer cause quick leveling (establishing a certain

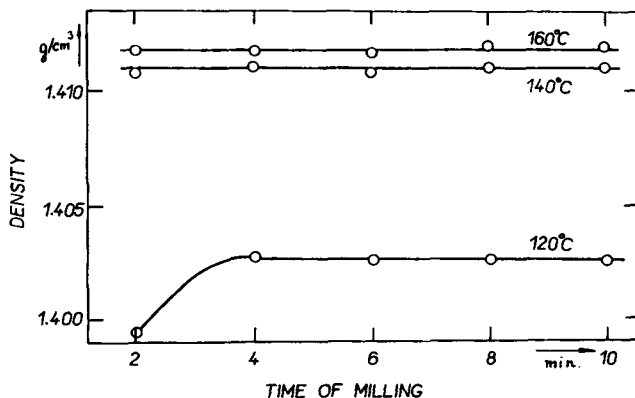


Fig. 1. Dependence of the density of films on the time of milling (samples tempered for 3 hr at 85°C and slowly cooled).

equilibrium), depending on the temperature given for milling characteristics.

Density of Compression Molded Films

The results of density measuring in dependence on the temperature of compression molding are on Figure 2. The compression molding temperature curve of 140°C reached its highest value, which will not change by further increase of the compression molding temperature.

When comparing Figure 1 and 2 we see that the resulting density depends to a great degree not only on temperature, but also on the way of processing.

Densities of samples, received by milling are higher than the maximal densities achieved by compression molding. The assumption that from the point of view of processing, the effect of the shear forces is far higher by milling than by compression molding is correct.

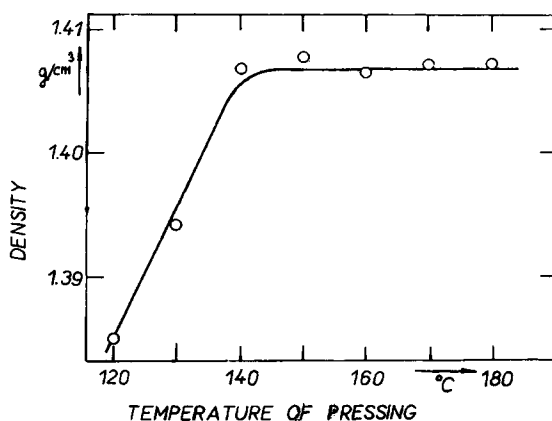


Fig. 2. Dependence of the density of films on the temperature of compression molding (samples tempered for 3 hr at 85°C and slowly cooled).

PVC Containing 1% Advastab D 671

The Influence of Compression Molding Temperature on the Properties of PVC

For the sheets compressed at 160–200°C the density and notch impact strength was measured. The dependence of density on the compression molding temperature is shown on Figure 3.

The density decreases by the increase of compression-molding temperature. The point for 200°C was not plotted, because the compression molded sample at this temperature already degraded.

In the previous paragraph it was shown for PVC that the density increases with increasing temperature of compression molding and reaches a certain constant value. The inconsistency is only illusory because the films were tempered in the previous paragraph before taking measurements.

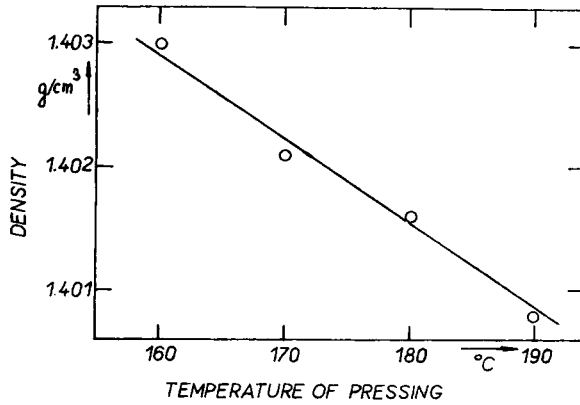


Fig. 3. Dependence of the density of sheets on the temperature of compression molding (samples containing 1% Advastab D 671, without tempering).

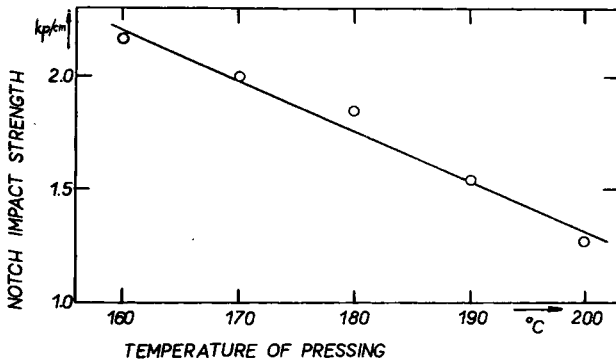


Fig. 4. Dependence of the notch impact strength of sheets on the temperature of compression molding (samples containing 1% of Advastab D 671, without tempering).

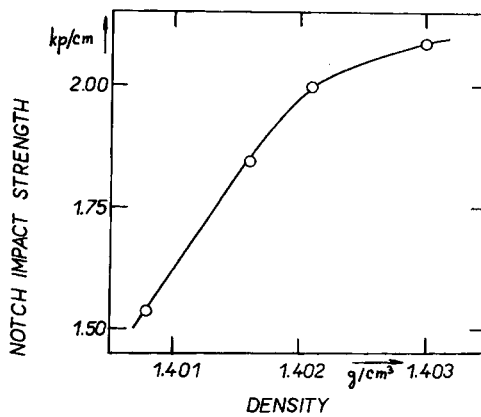


Fig. 5. Dependence of the notch impact strength on the density of sheets without tempering, compression molded at different temperatures.

Now we measured the density of samples without tempering. In such samples at cooling the free volume corresponding to higher temperature "is frozen" and simultaneously, also the stress corresponding to the compression pressure "freezes" in them. The increased free volume manifests itself by decrease of density with the temperature of compression molding.

Increasing stress with temperature is shown by the decrease of the notch impact strength with increasing temperature of compression molding (Fig. 4) and by increasing of the notch impact strength with density (Fig. 5).

The increase of the notch impact strength with density is an anomaly explained by stress, as the notch impact strength usually increases with decreasing density due to the increase of the free volume.

If we partially remove the stress in the sample by tempering it for 3 hr at 85°C, the density of the compression molded samples, at different temperatures, increases in all cases to the same value 1.4055 g/cm³, which is only imperceptibly lower than the value for milled and compression-molded films in the previous paragraph.

The difference is caused by the fact, that the density of Advastab D 671 is lower than the density of PVC. The notch impact strength increased after tempering the compression-molded sample at 190°C to 1.9 kp/cm.

Influence of Sheet Tempering Methods on Properties

From the comparison of slow and fast-cooled samples (see Table I) we see that fast cooling affects the decrease of the tensile strength (which corresponds to the upper yield strength), the increase of the notch impact strength and the decrease of the embrittlement temperature. The change of T_{α} is in the limits of experimental errors.

These changes can be explained by the increase of the free volume at fast-cooled samples, which is perceptible, from the decrease of density in comparison with the density of the slowly cooled sample. The increase of the free volume accompanied by higher stress facilitates easier cross movement of chains.

TABLE I
Properties of Slow- and Fast-cooled Sheets

	Cooling	
	Slow	Fast
Tensile strength, kp/cm ²	733	541
Notch impact strength, kp/cm	1.9	2.4
Embrittlement temperature, °C	+15	-15
Density at 20°C, g/cm ³	1.4055	Thick 2 mm 1.4017 4 mm 1.4020
T_{α} from dynamic measurement, °C	88	87

The consequence of easier cross movement are the noticed changes of properties.

Dynamic Properties Dependent on Tempering Procedures

The dependence of real constituent of the dynamic torsion modulus G' and of mechanical damping $\operatorname{tg} \delta$ on the temperature for the slowly cooled sample is shown in Figure 6, and for the fast cooled sample in Figure 7.

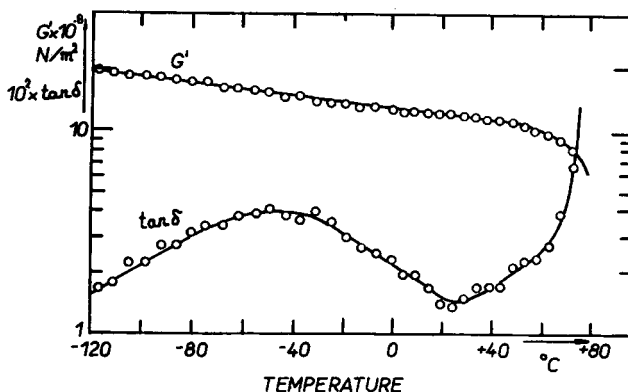


Fig. 6. Dependence G' and $\operatorname{tg} \delta$ on the temperature for the sample of sheet, tempered for 3 hr at 85°C and slowly cooled.

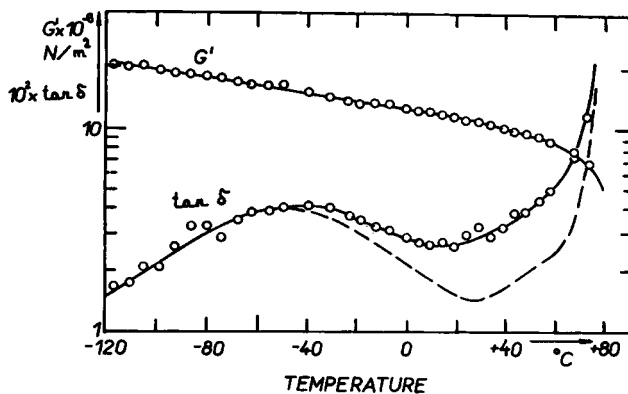


Fig. 7. Dependence G' and $\operatorname{tg} \delta$ on the temperature for the fast cooled sample; (—) values $\operatorname{tg} \delta$ from Figure 6.

From the comparison of both graphs it is perceptible, that the fast cooling does not influence β -maximum on the dependence curve of mechanical damping on the temperature, but affects only considerable increase of mechanic damping in the zone of minimum between α and β -maximums. This phenomena at PVC was recently described by Pezzin et al.¹⁴ and interpreted as the consequence of the change of the free volume. Our results correspond to Pezzin's results.

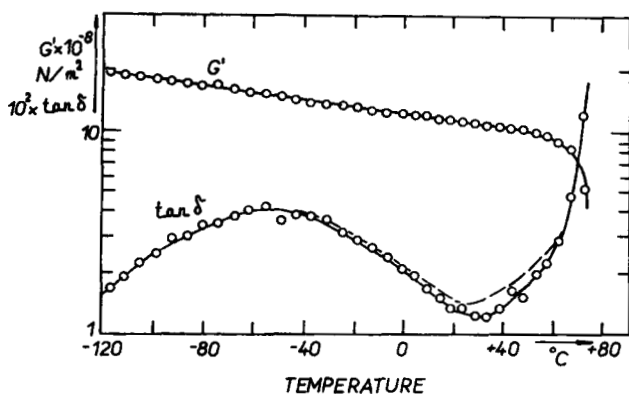


Fig. 8. Dependence G' and $\text{tg}\delta$ on the temperature for the sample of sheet, heated for 1 hr at 150°C, then tempered for 3 hr at 85°C and slowly cooled; (—) values $\text{tg}\delta$ from Figure 6.

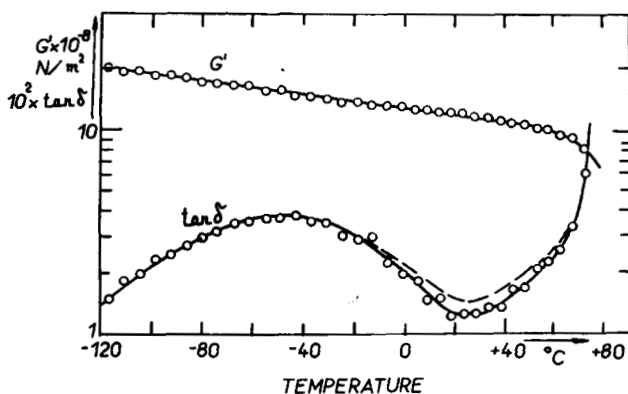


Fig. 9. Dependence G' and $\text{tg}\delta$ on the temperature for the sheet sample, heated for 4 hr at 100°C, then tempered for 3 hr at 85°C and slowly cooled; (—) values $\text{tg}\delta$ from the Figure 6.

Looking at the same comparison of slowly and fast cooled samples from another point-of-view, the tempering and slow cooling means deepening of minimum between α and β -maximums. It is very probable that even after 3 hr tempering at 85°C the sample does not reach equilibrium. Further tempering of samples should therefore mean further deepening of minimum between α and β -maximums. A proof of the fact is in the comparison of Figure 6 with Figures 8 and 9 from which further deepening of minimum by further tempering is obvious.

When heating polymer pulver before milling for the same periods of time and at the same temperatures as we have heated the sheets, in the finished samples it results not only in the deepening of minimum on the course of mechanical attenuation of $\text{tg}\delta$ on the temperature, but also in its substantial shifting to higher temperatures. This finding is rather surprising. By

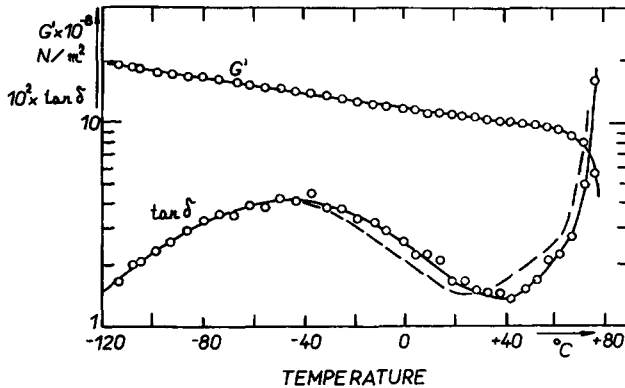


Fig. 10. Dependence G' and $\text{tg}\delta$ on temperature for the sheet sample prepared from PVC powder, heated before milling for 1 hr at 150°C . The finished sheet was tempered and cooled as the sheet from Figure 6; (—) values $\text{tg}\delta$ from the Figure 6.

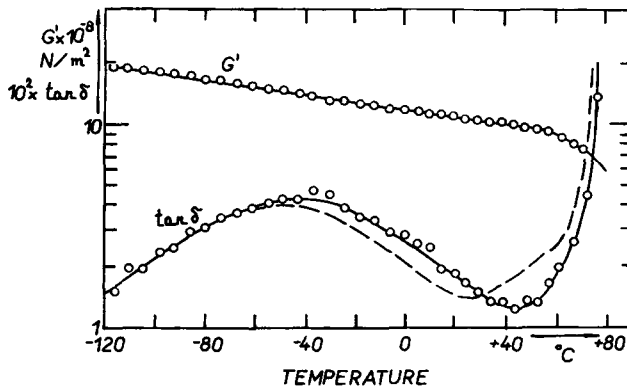


Fig. 11. Dependence G' and $\text{tg}\delta$ on the temperature for the sheet sample prepared from PVC powder, heated before milling for 4 hr at 100°C . The finished sheet was tempered and cooled as the sheet from Figure 6; (—) values $\text{tg}\delta$ from the Figure 6.

pulver heating a change was due, which was not eliminated by milling, compression moulding, or tempering.

The increase of crystallinity would not be eliminated because the temperature of melting PVC crystallites lies above 200°C .^{5,16} As far as the increase of crystallinity is concerned, the change caused by tempering the sheet should be approximately the same as the change caused by tempering the pulver, for the same period at the same temperature. By comparing the Figures 8 and 10 and 9 and 11, respectively, we see that this is not true.

The substance of the change caused by pulver tempering would be the moisture which evaporates quickly by direct processing on the mills, whereas at long time heating of pulver before milling it has the possibility, to defund partially into the polymer and influence its properties. This imagination is in good accordance with the influence of water on the shifting

of minimum between α and β -maximums toward higher temperatures which were noticed already.¹⁷

CONCLUSION

From the values for milled and compression-molded sheets we find that in the PVC samples the effect of external forces influences quickly the transformation of original polymer to the structure which does not change by further processing.

The properties of this structure depend to a great extent on the temperature and the way of processing.

From the values of the compression molded samples at different temperatures we find that the properties of samples are extremely sensitive also to residual stress in the sample after treatment.

On the dynamic properties, it was shown that the degree of residual stress in the samples after compression molding depends to a great extent upon the tempering of samples.

From the comparison of values for slow and fast cooled samples we find that the properties of samples depend not only on the way of processing and tempering, but also on the rate of cooling.

It was also shown that a preliminary tempering of PVC pulver before milling manifests itself in the properties of samples.

References

1. S. Krimm and S. Enomoto, *J. Polym. Sci. A*, **2**, 669 (1964).
2. J. Majer, *Chemický průmysl (Chem. Ind.)*, **17**, 141 (1967).
3. Yu. V. Glazkovskii, V. E. Zgaevskii, S. P. Ruchinskii, and N. M. Bakardijhiev, *Vys. Soed.*, **1472** (1966).
4. V. P. Lebedev, N. A. Okladnov, K. S. Minsker, and B. P. Shtarkman, *Vysokomolekul. Soedin.*, **7**, 655 (1965).
5. V. Nardi, G. Pisent, and M. Mammi, *Nuovo Cimento Suppl.*, **26**, 1 (1962).
6. H. Wilski, *Kunststoff-Rundschau*, **13**, 1 (1966).
7. H. Tautz, M. Glück, G. Hartmann, and R. Leuteritz, *Plaste Kautschuk*, **11**, 657 (1964).
8. H. Martin and F. H. Müller, *Kolloid Z.*, **191**, 1 (1963).
9. P. V. McKinney, C. R. Foltz, *J. Appl. Polym. Sci.*, **11**, 1189 (1967).
10. A. Kovacs, *Compt. Rend.*, **243**, 50 (1956).
11. L. A. Igonin and Yu. V. Ovchinnikov, *Vys. Soed.*, **3**, 1394 (1961).
12. J. R. Hyndman, *Polym. Eng. Sci.*, **6**, 169 (1966).
13. W. Sommer, *Kolloid Z.*, **167**, 97 (1959).
14. G. Pezzin, G. Ajroldi, and C. Garbuglio, *J. Appl. Polym. Sci.*, **11**, 2553 (1967).
15. J. Maláč, E. Šimůnková, and J. Zelinger, *Properties of PVC I.* (to be published).
16. A. Utsuo and R. S. Stein, *J. Polym. Sci. B* **3**, 49 (1965).
17. J. Maláč, V. Altmann, and J. Zelinger, *Properties of PVC II.* (to be published).

Received April 1, 1969

Revised June 3, 1969