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# Dynamic-Mechanical and Tensile Properties of Poly(vinyl Chloride). Influence of Thermal History and Crystallinity*

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## Synopsis

The dynamic-mechanical properties as a function of temperature and the low- and high-speed tensile properties at 23°C have been determined on specimens of conventional suspension-polymerized PVC and of low-temperature-polymerized PVC roll milled and then compression molded at different temperatures. It has been found that the main transition $\alpha$ and the shear modulus above $T_\alpha$ depend on the thermal history and are strongly affected by crystallinity, whereas the dynamic-mechanical spectrum below $T_\alpha$ is not influenced by these parameters. Room-temperature tensile modulus and yield properties are very little affected by processing history and crystallinity. The elongation at break and the fracture energy, on the contrary, increase, at any fixed strain rate, for conventional PVC with milling temperature. The same trend has been found for low-temperature PVC, but the elongation at break-versus-temperature curve is shifted, as a whole, toward higher temperatures by approximately 50°C. Such results are discussed in terms of homogeneity of the specimens, which is controlled by the melting process of the crystallites. Stereoscanning electron micrographs of fracture surfaces appear to substantiate these conclusions.

## INTRODUCTION

Some attempts have been made in recent years to correlate the dynamic-mechanical spectrum with the fracture properties of PVC. After the pioneering paper by Oberst[1] and Bohn[2] in 1963, in which the transition from brittle to tough fracture is related to the presence of a secondary damping maximum (see also refs. 3 and 4), Retting[5] in a series of papers has given a complete description of the relationship between the dynamic-mechanical properties of the polymer and both falling-weight impact strength and tensile impact strength.

On the other hand, it is well known that the impact strength of PVC depends quite strongly on the processing history. According to Hyndman,[6] the brittle temperature of PVC is strongly affected by the extrusion

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conditions. Berens and Folt[7] showed that the impact strength of strip-die extrudates of emulsion PVC increases from three to seven times with increasing the extrusion temperature from 160°C to 190°C. Melt spinning above 200°C substantially increases the elongation at break of PVC filaments, according to de Vries et al.[8] All these data have to be interpreted as evidence that, with the increasing of the processing temperature, the PVC particles disappear giving gradually a homogeneous melt.

However, other results show a different trend: no influence of roll-milling temperature on the Izod impact strength was found by Trautvetter[9]; and a "decrease" of the impact strength with milling temperature was found by Gross and co-workers[10] for modified PVC compounds. A decrease of the impact strength of sheets with the molding temperature is reported by Malac.[11] The impact strength is affected also by thermal treatments of the polymer after processing,[11] as shown by Phillips and co-workers[12] and by Illers.[13] Annealing of the sample decreases usually the elongation at break, and therefore the impact strength, owing possibly to an increase of crystallinity and/or a decrease of free volume.[14] It seems interesting therefore to investigate what changes, if any, are found in the dynamic-mechanical spectrum and in the tensile properties of PVC when the thermal and processing history of the samples are modified. Since often the physical properties of this polymer are severely changed by changes of crystallinity, parallel investigations on samples of conventional PVC and of "crystalline," or syndiotactic, PVC have been carried out.

## EXPERIMENTAL

### Polymers

The samples investigated are:

1. A commercial PVC, polymerized in suspension at about 50°C, whose intrinsic viscosity (cyclohexanone, 25°C) is 105 ml/g. The crystallinity of this polymer is of the order of 10%.[15,16]
2. A sample of syndiotactic PVC (called SPVC for sake of simplicity), polymerized in bulk at −30°C, whose intrinsic viscosity is 125 ml/g and whose crystallinity is of the order of 20%.[15,16]

### Preparation of Samples

Dry-blends of the samples were prepared by thoroughly mixing the powdery resins with 4 phr of a barium–cadium stabilizer and 1 phr of a liquid additive (Chel 210). The dry-blends were then roll milled for 5 min at various temperatures, namely between 140° and 210°C for the conventional PVC compound and between 180° and 220°C for the SPVC compound. Compression molding of the samples was carried out at the same temperatures, and the molded sheets were cooled in the mold, down to 40°C, in about 9 min. The sheet thickness was 2.0 mm for the specimens for the impact tests and 1.0 mm for the specimens for dynamic-mechanical measurements. Conditioning of the molded samples was performed at 23°C and 50% R.H. for seven days.

### Measurements

The dynamic-mechanical tests were carried out with the torsional pendulum of our own construction which operates at about 2 cps below the transition temperature[17] and at about 0.2 cps above it. The tensile tests were carried out at 23°C on ASTM 1822 type S specimen, for which we assumed (on the basis of the results of several comparative tests on specimen of various geometry) an effective initial gauge length $L_0 = 15$ mm.[18]

Four straining rates were explored, namely $\dot{\epsilon} = 1.1 \times 10^{-3}$ sec$^{-1}$ and $\dot{\epsilon} = 5.5 \times 10^{-1}$ sec$^{-1}$, obtained on the Instron tensile tester, and $\dot{\epsilon} = 90$ (or 117) sec$^{-1}$ and $\dot{\epsilon} = 230$ sec$^{-1}$, obtained on an autographic home-made apparatus.[18]

## RESULTS AND DISCUSSION

The dynamic-mechanical data obtained for conventional PVC for samples milled and molded at 140°C and at 210°C are reported in Figure 1. The measuring frequencies are very close to each other for these samples (2.15–2.30 cps on the $\beta$-peak maximum).

One may observe that the $\beta$-peak is not substantially influenced by the processing temperature, whereas the shear modulus above $T_\alpha$ is changed.

In a previous paper,[14] we have found that annealing, quenching, and cold drawing of PVC samples processed at a fixed temperature do influence the dynamic-mechanical properties only above the conditioning temperature (room temperature).

The results obtained for the SPVC samples processed at 180° and 200°C are similar (Fig. 2). Again, one may see that the shear modulus above

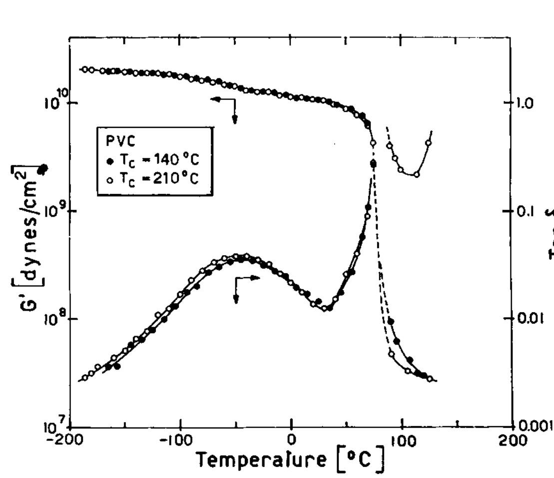


Fig. 1. Effect of milling temperature on the dynamic-mechanical properties of commercial PVC sample.

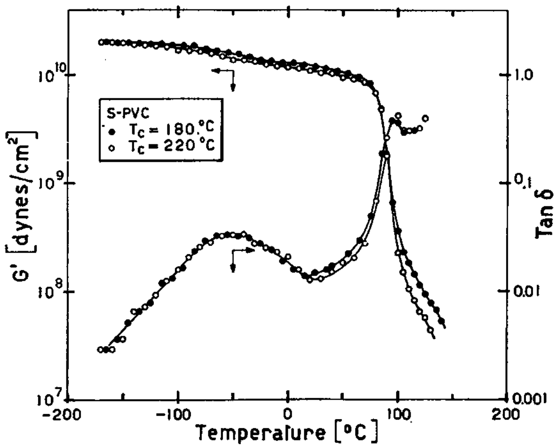


Fig. 2. Effect of milling temperature on the dynamic-mechanical properties of SPVC sample.

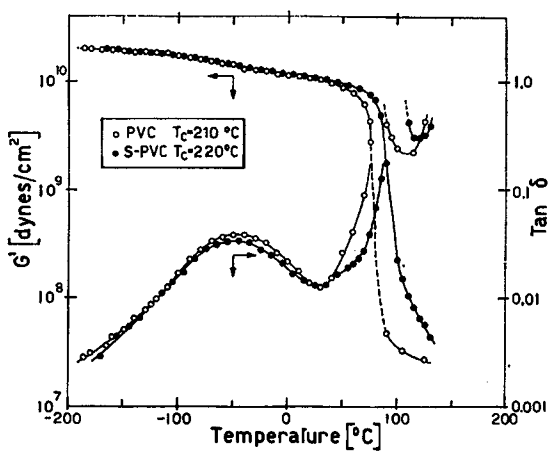


Fig. 3. Effect of crystallinity on the dynamic-mechanical properties of PVC.

$T_\alpha$ is affected quite strongly by the processing history owing presumably to changes of crystallinity, that is, to the gradual melting of crystallites with increasing processing temperature.[19]

A comparison between the PVC samples processed at 210°C and the SPVC sample processed at 220°C (Fig. 3) shows that the $\beta$-peak is largely independent of crystallinity, whereas the $\alpha$-peak and the modulus above $T_\alpha$ differ considerably. The modulus of PVC at high temperatures is lower than that of SPVC due to its lower crystallinity.[15]

The influence of the processing temperature on the tensile stress–strain curves is strong both for the conventional PVC specimens (Fig. 4) and for the SPVC samples (Fig. 5).

PVC specimens processed at 140°C undergo a brittle fracture at small elongations ($\epsilon \cong 5\%$), which should be related to an imperfect melting

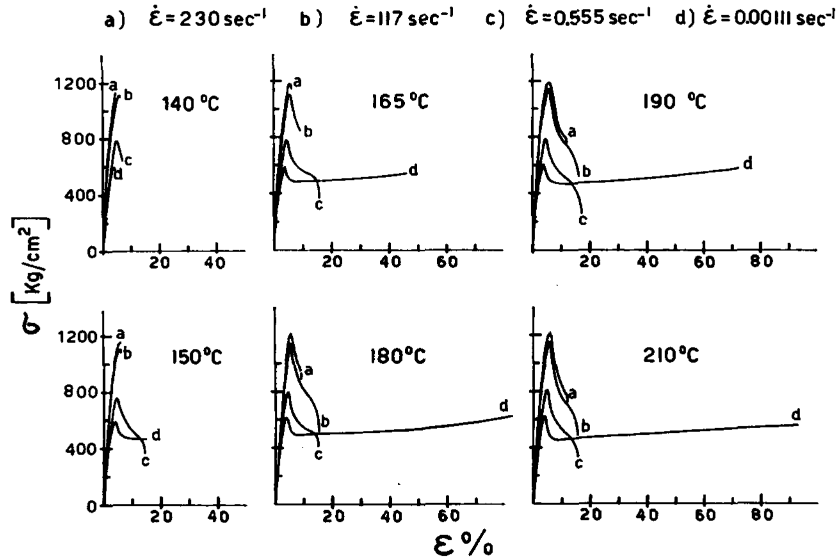


Fig. 4. Stress–strain curves of the commercial PVC samples measured as a function of milling temperature and at four strain rates: (a) $\dot{\epsilon}$ = 230 sec; (b) $\dot{\epsilon}$ = 117 $sec^{-1}$; (c) $\dot{\epsilon}$ = 0.555 $sec^{-1}$; (d) $\dot{\epsilon}$ = 0.00111 $sec^{-1}$.

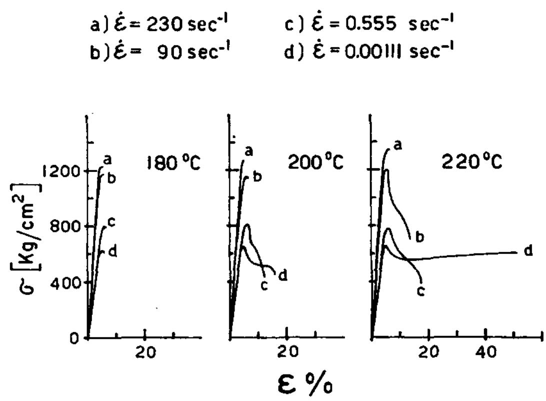


Fig. 5. Stress–strain curves of SPVC sample measured as a function of milling temperature and at four strain rates: (a) $\dot{\epsilon}$ = 230 $sec^{-1}$; (b) $\dot{\epsilon}$ = 90 $sec^{-1}$; (c) $\dot{\epsilon}$ = 0.555 $sec^{-1}$; (d) $\dot{\epsilon}$ = 0.00111 $sec^{-1}$.

of the resin particles. Pictures taken with the Cambridge stereoscanning electron microscope of the fracture surfaces of this sample (specimen fractured at −180°C) give evidence (Fig. 6) for the persistence of particles. A gradual melting of the particles with increasing temperature is shown in the other pictures (Figs. 7 and 8).

With increasing the processing temperature, the elongation at break $\epsilon_r$, at any given strain rate, increases gradually toward asymptotic values which depend on the straining rate (Fig. 9).

Fig. 6. Fracture surface stereoscanning electron photomicrograph (×8,300) of commercial PVC sample milled at 140°C.

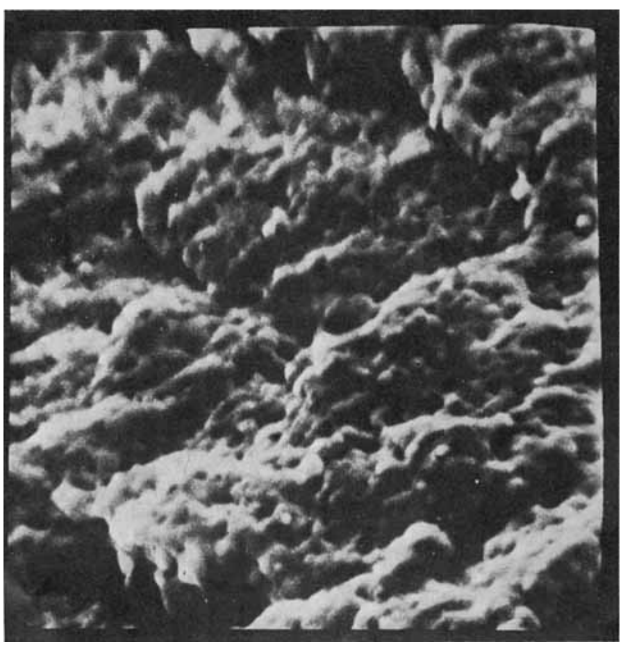

Fig. 7. Fracture surface stereoscanning electron photomicrograph (×8,000) of commercial PVC sample milled at 165°C.

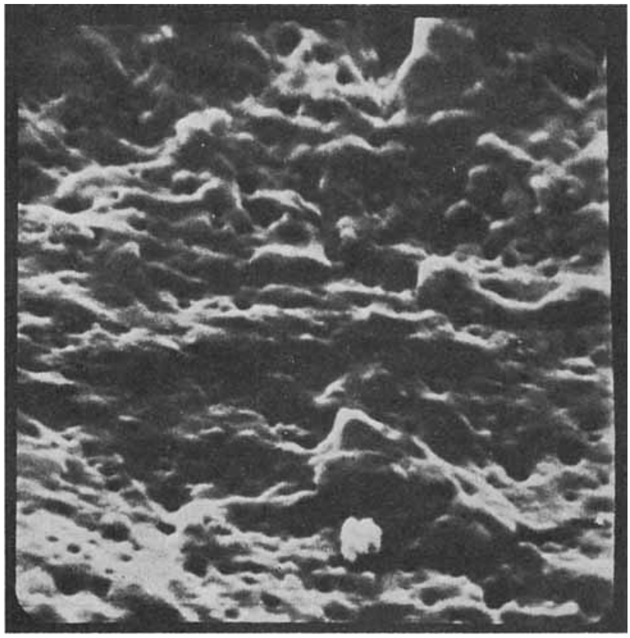

Fig. 8. Fracture surface stereoscanning electron photomicrograph (×8,000) of commercial PVC sample milled at 210°C.

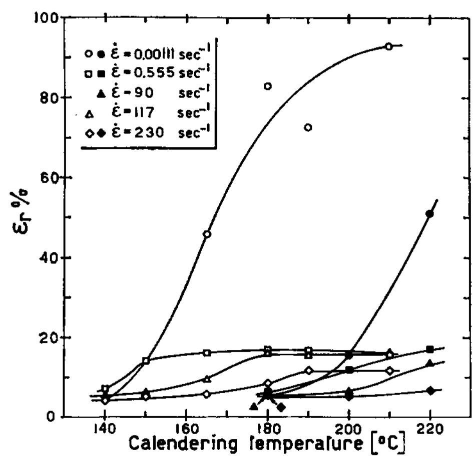


Fig. 9. Influence of milling temperature and strain rate on the apparent strain at rupture $\epsilon_R$. Open points: commercial PVC sample; black points: SPVC sample.

Similar results are found also for the crystalline PVC samples, whose $\epsilon_r$, however, increases only when the processing temperatures are about 50°C higher than those used for conventional PVC. Stereoscanning electron microscope pictures of SPVC fracture surface (Figs. 10 and 11) confirm the above-mentioned results.

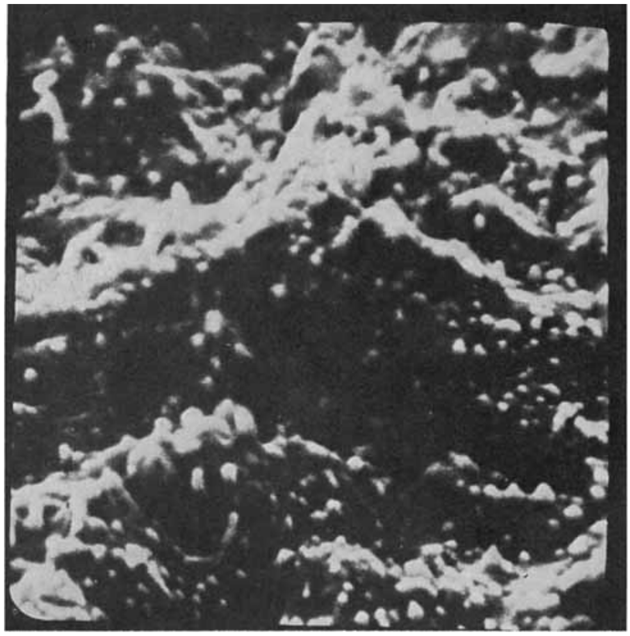

Fig. 10. Fracture surface stereoscanning electron micrograph (×8,300) of SPVC sample milled at 180°C.

Fig. 11. Fracture surface stereoscanning electron micrograph (×9,300) of SPVC sample milled at 220°C.

The behavior of the rupture energy curves is substantially identical to that of the rupture strain curves (Fig. 12), whereas the yield parameters, yield stress $\sigma_y$ and yield strain $\epsilon_y$, are very little affected by the processing history (Fig. 13). The same is true for the tangent modulus $E$, obtained

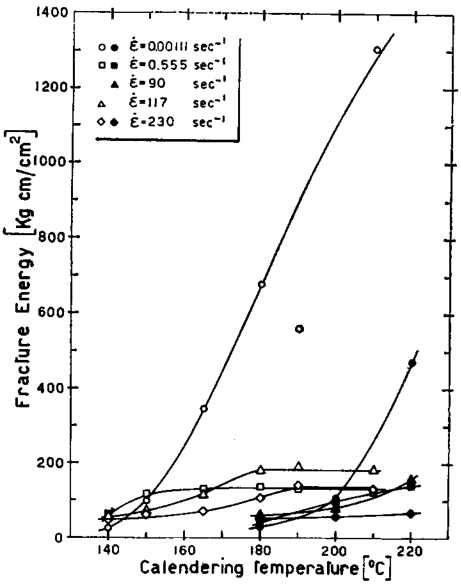


Fig. 12. Influence of milling temperature and strain rate on the tensile fracture energy. Open points: commercial PVC sample; black points: SPVC sample.

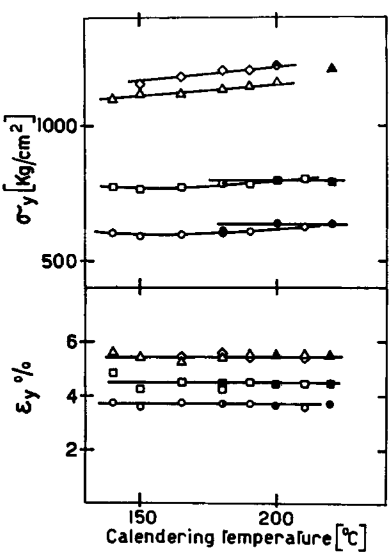


Fig. 13. Influence of milling temperature and strain rate on the yield strength $\sigma_y$ and yield strain $\epsilon_y$. Key as in Fig. 12.

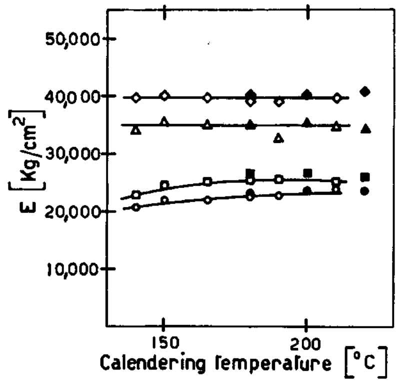


Fig. 14. Influence of milling temperature and strain rate on the tangent Young modulus. Key as in Fig. 12.

from the $\sigma$–$\epsilon$ curves (Fig. 14). The moduli and the yield parameters are substantially independent of the crystallinity as well, but they all are influenced by the straining rate, as normally found for polymers.

## CONCLUSIONS

Summing up the above results, one may say that:

1. The $\alpha$-transition, i.e., the dynamic-mechanical properties above approximately 25°C, is substantially affected by the processing temperature, the thermal history, and the crystallinity of the sample.

2. The $\beta$-transition, at 2 cps, does not depend on the above-mentioned parameters. It has been found that even at higher frequencies (1000 cps), the $\beta$-peaks of PVC and SPVC are similar, at least for temperatures below 0°C.[20]

3. The yield process does not depend on processing history and crystallinity, which suggests that it depends only on molecular relaxation processes.[21–23]

4. The room-temperature impact strength is controlled only by the elongation at break $\epsilon_r$ (as reported by Oberst and Retting[24]) and therefore by the cold-flow process, which follows the initial yielding of the sample. This process appears to depend strongly on the degree of homogeneity of the sample, which in turn depends on the crystallite melting process that takes places during the processing and molding cycles. The more crystalline the polymer, the higher must be the processing temperature in order to melt the resin particles.[20] Only when the system is sufficiently homogeneous, a flow process can take place after yield. Its actual extent could be limited, not only by the sample homogeneity, but even by molecular flow processes.

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