Dynamic-Mechanical Study of the Secondary Transition of Poly(vinyl Chloride)

G. PEZZIN, *Società Montecatini-Edison and Istituto di Chimica Fisica, Universita' di Padova*, and G. AJROLDI and C. GARBUGLIO, *Società Montecatini-Edison, Istituto Ricerche di Bollate, Milano, Italy*

Synopsis

The influence of crystallinity, thermal history, plasticization, copolymerization, and chemical modifications on the dynamic-mechanical properties of poly(vinyl chloride) has been studied by means of a free-oscillation torsional pendulum. It was found that the secondary dispersion maximum is not affected by free volume, crystallinity, or head-to-head microstructure, but is modified by post-chlorination, copolymerization, and plasticization. These results show that the molecular motions responsible for the PVC β peak are not influenced by local differences in the distribution of the Cl atoms along the chain, so that they seem to be largely of a cooperative type.

INTRODUCTION

In the glassy state below the glass transition temperature T_g, most linear polymers exhibit one or more secondary dispersion regions. These are attributed to the relaxation of particular molecular motions, such as the movements of side groups or of small groups within the main chain. The secondary transitions are usually investigated by dynamic-mechanical[1-5] or dielectric[5-9] measurements and by nuclear magnetic resonance (NMR) spectroscopy.[10,11] It is generally agreed that the dynamic-mechanical and dielectric-dispersion peaks have a common origin,[8-12] and it has been shown[11] also that the NMR data correlate satisfactorily with the results obtained from these techniques.

In comparison with the main transition or α peak, which is associated with T_g and is attributed to the cooperative motion of long segments of the main chain, the secondary transitions or β peaks are generally weak and broad and change very rapidly their temperature of maximum loss with changing the frequency of test.

The study of secondary transitions can be of considerable importance in structural investigations, because of the correspondence between macroscopic relaxations and molecular motions.[10-13]

Moreover, it has been shown that the secondary transitions influence strongly the physical properties (e.g., the impact strength) of glassy polymers.[13-17]

At frequencies below about 10^5 cps, two dispersion peaks are found in

the relaxation spectrum of poly(vinyl chloride) (PVC). At 1 cps the principal or α peak lies at 85°C. and the secondary or β peak at about -50°C.

The β peak was first reported in the dielectric-absorption spectrum by Fuoss[6] and in the dynamic-mechanical spectrum by Schmieder and Wolf.[1] Recently it has been observed by dielectric[7,9] and dynamic-mechanical[16-18] measurements as well as by dilatometric[19,20] techniques. It can be shown that the position of the β transition on a frequency–temperature map is the same for the dielectric and mechanical peaks; this indicates that the same molecular motions are concerned in both processes. Furthermore, the intensities of the dielectric and mechanical β peaks are comparable.[10] The activation energy of the β transition is about 15 cal./mole,[7,21] which represents only a small fraction of the activation energy of the α transition.

The broadness of the β peak, as measured by the half-peak width on the logarithmic frequency axis, is about twice that of the α peak.[9,22] On the temperature axis, it is spread over about 150°C. at 1 cps.[21]

The β peak of PVC has been tentatively attributed to impurities, to small crystalline regions of the polymer,[23] and to the endgroups.[24] Ishida[25] showed that the molecular weight, hence the endgroup content, does not affect the dielectric loss peak. Since PVC has no side chains (with the exception of a small number of branches), the process should arise from a main-chain motion, which is different from the cooperative microbrownian motions of the main chain responsible for the α peak. According to McCall,[10] the motion should be a hindered rotation of the chains about their long axes. Sauer and Woodward[26] attribute the β peak to rotational oscillations of the methylene groups of the main chain. According to Boyer[13] the β peak of PVC, as well as the β peaks of most linear amorphous polymers, should originate from the hindered rotation of short chain segments about two colinear bonds, in the manner of a crankshaft. Finally, Yamafuji[27] interprets the dielectric β peak of PVC on the basis of a theory which postulates local twisting motions of the main chain to which the rigid C—Cl dipoles are attached.

It is the purpose of this paper to report the results obtained in the course of an investigation of the factors affecting the dynamic-mechanical secondary transition of PVC. This work deals with the influence of crystallinity, thermal history, plasticization, copolymerization, and chemical modifications on the dynamic-mechanical properties of PVC polymers.

EXPERIMENTAL

Polymers

Polymer A. This was a commercial PVC (Sicron 548) having intrinsic viscosity $[\eta] = 105$ ml./g., number-average molecular weight $\bar{M}_n = 53,000$, weight-average molecular weight $\bar{M}_w = 130,000$, and glass transition temperature $T_g = 78$°C. Two different series of samples were prepared with polymer A. In the first series, several samples (A-1 to A-4) were dry-blended (see Table I), calendered at 170°C., compression-molded at

TABLE I
Formulation and Treatment of Samples

Sample no.	Stabilizers and lubricants	Parts used	DOP, phr	Calendering temperature, °C.	Molding temperature, °C.
A-1 A-2 A-3 A-4	Tribase E[a] DS 207[a] Lead phosphite	3 2 1		170	180
A-5 A-6 A-7 A-8 A-9	Advastab X 28 M[b]	1	0 3 6 9 12	173	175
B-1 B-2 B-3	Advastab X 28 M[b]	1	0 3 9	215	215
C-1 C-2	R 672[c]	3		190 150	190 180
D-1 D-2	R 672[c]	3		200 200	200 200
E-1 E-2	Ferro 1827[d] Ferro 904[d]	4 1		— —	140 140

[a] National Lead Company.
[b] Deutsche Advance Produktion.
[c] Reagents.
[d] Ferro Chemicals.

180°C. and subjected to the following treatments: A-1, annealing at 120°C. and slow cooling from 120 to 40°C. at a rate of 1°C./hr.; A-2, annealing at 120°C. and slow cooling from 120 to 40°C. at a rate of 20°C./hr.; A-3, quenching from 120°C. to liquid nitrogen temperature; A-4, cold drawing at 23°C. at a draw ratio of 2.1 (110% of strain) by means of an Instron Tensile Tester.

In the second series, several samples were dry-blended with variable

TABLE II
Density of Plasticized Samples

Sample	Density (23°C.), g./ml.	Theoretical density, g./ml.[a]	Volume change, %	Free volume carried by the plasticizer, %[b]
A-5	1.4050	1.4050	—	0
A-6	1.3850	1.3881	+0.22	+0.23
A-7	1.3754	1.3723	−0.22	+0.46
A-8	1.3654	1.3580	−0.54	+0.68
A-9	1.3555	1.3443	−0.83	+0.89
DOP	0.9865	—	—	—

[a] Density calculated on the basis of volume additivity.
[b] Calculated by assuming for the DOP $T_g = 190°K.$ and $\alpha = 8 \times 10^{-4}$ deg.$^{-1}$.

amounts of diethylhexyl phthalate (DOP). These polymers are labeled as samples A-5 to A-9 (see Table I). The densities measured at 23°C. are reported in Table II, together with the corresponding theoretical densities calculated on the basis of volume additivity.

Polymer B. A sample of crystallizable PVC, polymerized at −40°C.[28] and having $[\eta] = 120$ ml./g. was dry-blended with variable amounts of DOP, calendered and compression-molded at 215°C. (samples B-1, B-2, and B-3, see Table I).

Polymer C. Two samples of copolymers of vinyl chloride and ethylene containing 5 and 13% of ethylene on a molar basis, had intrinsic viscosities $[\eta] = 75$ and 45 ml./g., respectively (samples C-1 and C-2).

Polymer D. Two samples of chlorinated PVC, had a chlorine content of 61.5 and 67.6% (corresponding to approximately 21 and 56% of chlorinated monomeric units, respectively) and intrinsic viscosity $[\eta]$ of 103 and 104 ml./g., respectively. The chlorination was carried out by bubbling chlorine gas through a dispersion of swollen PVC particles. The microstructure of the samples has been shown by NMR measurements, to be mainly 1,2 in agreement with the results of other workers.[29-31] The glass transition temperature of the chlorinated samples, measured by differential thermal analysis (DTA) is 97 and 105°C., respectively (samples D-1 and D-2).

Polymer E. Two samples of head-to-head PVC were prepared by chlorination of a sample of polybutadiene. The microstructure of the latter was 92% *cis*, 4% *trans*, and 4% vinyl as determined by infrared analysis. The chlorination was performed at 50°C. by dissolving the polybutadiene sample in CHCl$_3$ at a concentration of 0.7 g./l. and bubbling chlorine gas in 4.2 liters of the solution at approximately 1 l./min. Sample E-1 was chlorinated for 15 min. and sample E-2 for 90 min. The resulting polymers were precipitated in methanol, washed, and dried at 50°C. under high vacuum. The chlorine content of sample E-2 was 54.3%, and the intrinsic viscosity was 210 ml./g. The head-to-head structure of the polymers was checked by infrared analysis.[32]

Preparation of Samples

The preparation of samples for the dynamic-mechanical testing consisted of the following steps: (1) dry-blending with stabilizers (and plasticizer); (2) calendering; (3) compression molding.

The composition of the compounds and the processing conditions are reported in Table I.

Apparatus

The apparatus here employed was the free oscillations torsion pendulum described previously.[33] The storage shear modulus G' and the loss tangent tan δ were derived by well-known equations.[1]

The apparatus operates with polymer samples having dimensions of $10 \times 1 \times 0.1$ cm. at frequencies of 2.8–1.5 cps in the range of temperature from −180 to +50°C. and at frequencies of about 0.2 cps above T_α.

RESULTS AND DISCUSSION

The dynamic-mechanical data are plotted in Figures 1–9 where the shear modulus–temperature and the tan δ–temperature curves are reported for each material investigated.

All the samples show a well-defined β peak whose intensity, frequency, and position on the temperature axis are reported in Table III. These results will be examined in detail.

TABLE III
Temperature, Frequency and Intensity of the β Peak

Sample	T_β, °C.	f_β, cps	tan $\delta_\beta \times 10^2$
A-1	−40	2.7	3.6
A-2	−40	2.7	3.7
A-3	−45	2.8	3.9
A-4	−45	1.8	3.5
A-5	−40	2.2	3.8
A-6	−50	2.2	3.3
A-6	−55	2.1	2.7
A-8	−60	2.2	2.4
A-9	−65	2.2	2.2
B-1	−45	2.2	3.8
B-2	−50	2.2	3.0
B-3	−60	2.3	2.2
C-1	−50	2.1	3.5
C-2	−60	2.1	3.5
D-1	−5	2.0	4.0
D-2	+20	2.0	3.9
E-1	−47	2.1	3.7
E-2	−40	2.0	3.5

Thermal and Mechanical Treatments

The effects of the thermal and mechanical treatments on the dynamic-mechanical properties of samples A-1 to A-4 are shown in Figure 1.

It may be noted that the β peak of these samples is not sensibly affected by annealing, quenching, and cold drawing (see Table III), even though the densities at 23°C. of undrawn and cold-drawn samples differ by as much as 3%, being 1.4465 for sample A-2 and 1.3998 for sample A-4. On the contrary, the tan δ minimum above 30°C. is influenced by the thermal or mechanical history of the sample. Cold drawing changes appreciably the free volume of the sample; in fact as far as the sample A-4 is concerned the sudden increase of tan δ, which indicates the beginning of the main transition, occurs at a temperature about 35°C. lower with respect to the other samples. From free volume considerations the fractional free volume of sample A-4 should be increased by $(\alpha_1 - \alpha_g) \Delta T$, where α_1 and α_g are the thermal expansion coefficients of PVC above and below T_g, respectively, and $(\alpha_1 - \alpha_g)$ is about 5×10^{-4} deg.$^{-1}$. For sample A-4, ΔT is 35°C., so that the increase of fractional free volume should be 0.017, which corre-
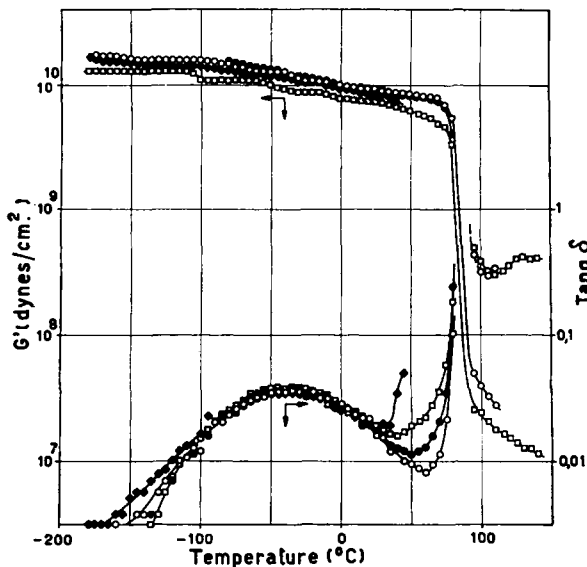
Fig. 1. Effect of thermal treatments and of cold drawing on the dynamic-mechanical properties of PVC: samples A-1 (O) and A-2 (●) annealed at 120°C. and cooled at 40°C. at a rate of 1°C./hr. and 20°C./hr.; samples A-3 (□) quenched from 120°C. to liquid nitrogen temperature; samples A-4 (■) cold-drawn at 110% strain at 23°C.

sponds to a decrease of density of about 2.4%, in good agreement with the experimental density change.

It is well known that the free volume influences strongly the α peak of polymers. For example, Koppelman[34] showed that with increasing the pressure from 1 to 10^3 kg./cm.², the α peak of PVC, at frequencies between 10^{-4} and 10^5 cps, was shifted about 18°C.

Koppelman[35] found that also the dielectric β peak of PVC, at high frequencies (10^4–10^5 cps), is affected by pressure, being displaced by approximately 10°C./1000 kg./cm.². The effect of pressure on the β peak is therefore, at high frequencies (i.e., at high temperatures), approximately half as strong as that on the α peak.

Our results seem to indicate that at low frequencies the β peak is not affected by a change of density (that is of free volume) caused by thermal treatments or by cold stretching.

This is in agreement with the results of Hellwege and co-workers[19] who found that cold drawing does not influence the low-temperature transition of PVC determined by linear expansion measurements. Some intensity data reported by Koppelman[36] indicate that the effect of pressure on the height of the dielectric β peak tends to vanish when the peak is located at lower temperatures, that is, when it is examined at lower frequencies (see Fig. 11 of ref. 36). It may be concluded that changes of free volume influence the β peak only if it is located at temperatures not too far from the main transition (about 50°C. below T_g).

Crystallinity

The PVC sample B-1 polymerized at −40°C. has a crystallizable content of approximately 20%,[28] twice as high as that of the standard samples of the A series. As shown in Figure 2 and Table III there are no strong effects of the crystallinity on the secondary peak, at least in the crystallinity
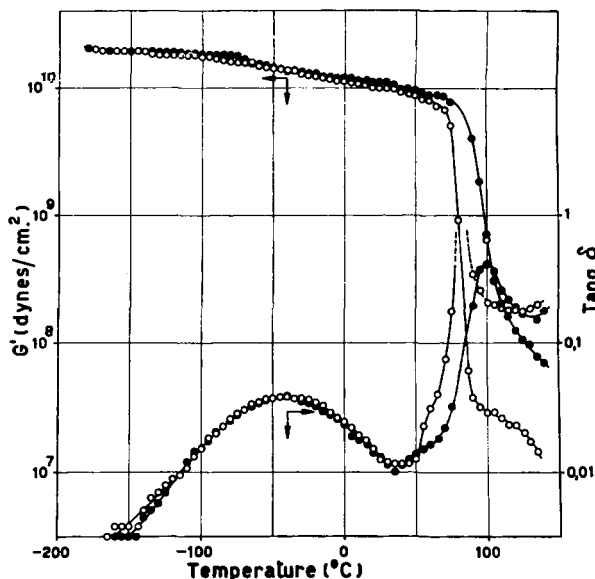

Fig. 2. Effect of crystallinity: sample A-5 (O) is a standard PVC sample; sample B-1 (●) is a crystallizable PVC polymerized at −40°C.

range here investigated, while the principal peak is displaced at higher temperatures. On the other hand, it is known that PVC polymerized at −40°C. is not appreciably branched, so that the results of Figure 2 indicate that the β peak cannot be attributed to the motion of side chains.

Plasticization

The influence of plasticization is shown in Figures 3 and 4 on logarithmic and linear plots, respectively, for samples A-5 to A-9, and in Figures 5 and 6 for samples B-1, B-2, and B-3. The effect of plasticizer on the α peak (Figs. 3 and 5) is well known.[1,9]

The β peak is shifted to lower temperatures and its intensity is decreased gradually with increasing the plasticizer content from zero to 12 phr.

The decrease of intensity cannot be accounted for by the small decrease of PVC concentration in the plasticized compounds. Both the tan δ maximum and the peak area are decreased by a factor of 2 or more, while the PVC concentration is lowered only by 10% (Fig. 4). It may be noted that there are no differences, in this respect, between the standard PVC

samples and the samples of crystalline PVC, within the limits of experimental accuracy.

The dielectric results of Fuoss[37] on PVC–diphenyl mixtures are in qualitative agreement with those shown in Figures 3–6.   Saito[9] found that the intensity of the dielectric β peak decreases, at constant temperature, with
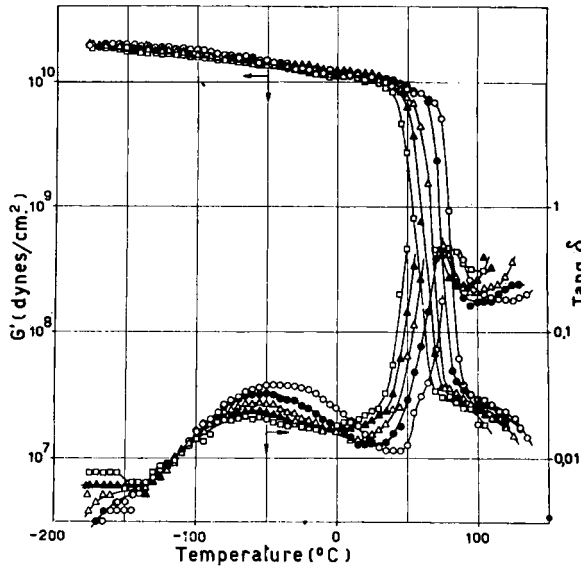

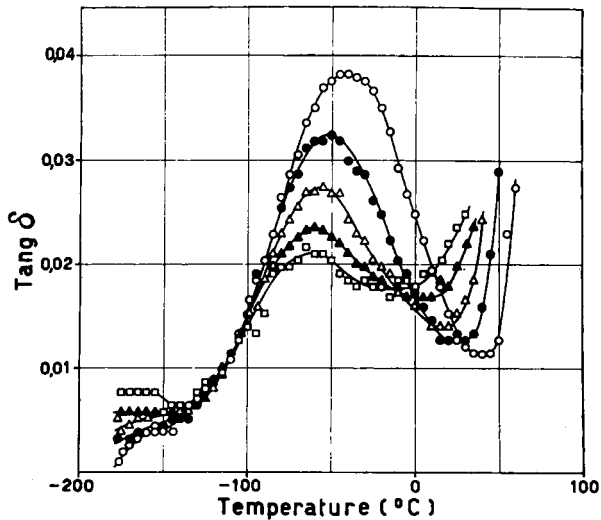Fig. 3. Effect of plasticization.   Samples A-5 to A-9 contain increasing amounts of DOP, up to 12 phr.

Fig. 4. Effect of plasticization.   Linear plot of tan δ vs. temperature for samples A-5 to A-9.

the DOP concentration in the range between zero and 9% DOP, while the maximum frequency does not change.

From Figures 3–6 it can be seen that on the low temperature side the curves are superimposed and the plasticizer modifies only the right-hand part of the β peak. The tan δ of the minimum above T_β increases gradually, and T_β decreases accordingly with increasing plasticizer content. The overall effect of the plasticizer on the β peak seems to be that of
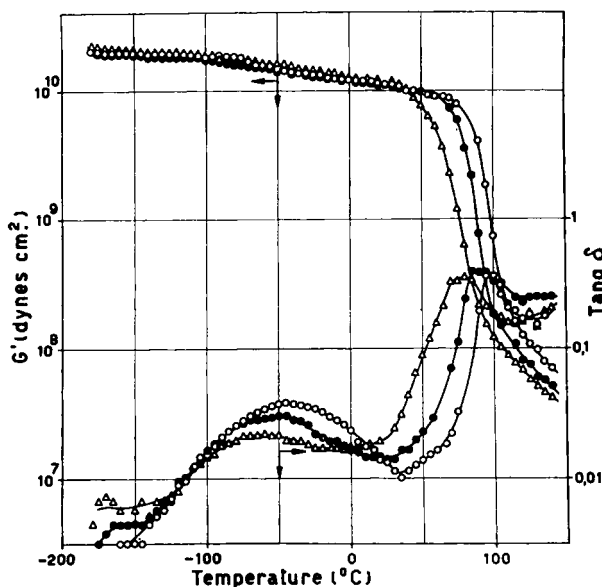

Fig. 5. Effect of plasticization on the dynamic mechanical properties of crystallizable PVC. Samples B-1, B-2, and B-3 contain zero, 3, and 9 phr of DOP, respectively.
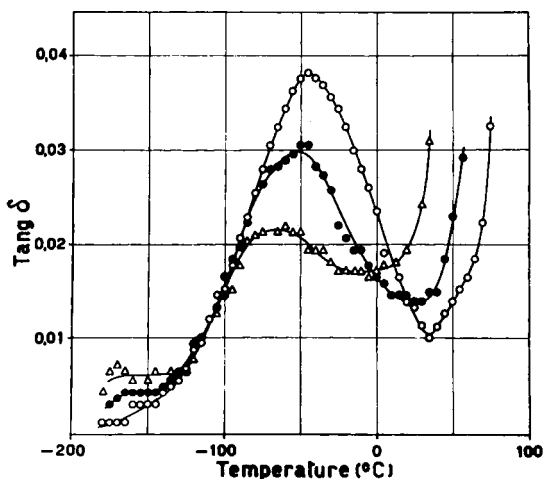

Fig. 6. Linear plots of tan δ vs. temperature for same samples as in Fig. 5.

reducing the motions of the chain segments responsible for the mechanical absorptions between approximately −80 and +20°C. (at a frequency of 2 cps). It is difficult to attribute these effects to changes of free volume due to the plasticization.[9] In fact, from the density data, it can be seen that the additional free volume carried by the plasticizer is practically equal to the measured volume contraction (Table II).

On the other hand, as shown previously on the basis of quenching and cold-drawing results, it seems that the β peak is not influenced by free volume changes.

Therefore it seems reasonable to attribute the decrease of the β peak to an interaction between the plasticizer molecules and the PVC chains (for example through polar interactions) so that the motions responsible for the β peak are hindered.

The decrease of the height of the β peak of plasticized PVC can explain the well known decrease of some physical properties (e.g., impact strength) of the polymer at low levels of plasticizer in the composition.[17,38] In fact it is well known that the low-temperature mechanical absorption of polymers is related to their impact strength.[13,16]

Chemical Modifications

The tan δ–temperature curves for samples C-1 and C-2 are shown in Figure 7. The β peak is slightly displaced at lower temperatures, whereas its intensity is not decreased appreciably. For sample C-2 there is an evident shoulder at −160°C. which can be attributed to the motion of
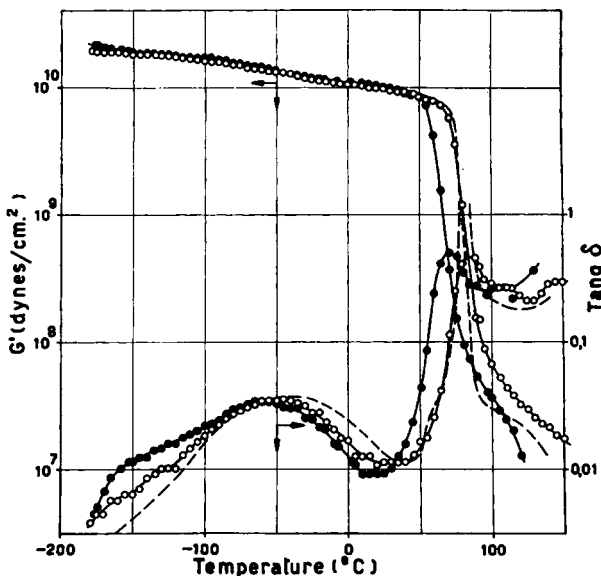

Fig. 7. Effect of copolymerization: Samples of vinyl chloride–ethylene copolymers C-1 (O) and C-2 (●) compared with (- - -) standard PVC (sample A-5).

$(CH_2)_n$ groups, where $n > 3$.[13]   Similar results were found for copolymers of vinyl chloride and ethylhexyl acrylate.   The introduction of the flexible polymethylenic units in the PVC chains also lowers the position of the α peak on the temperature scale.
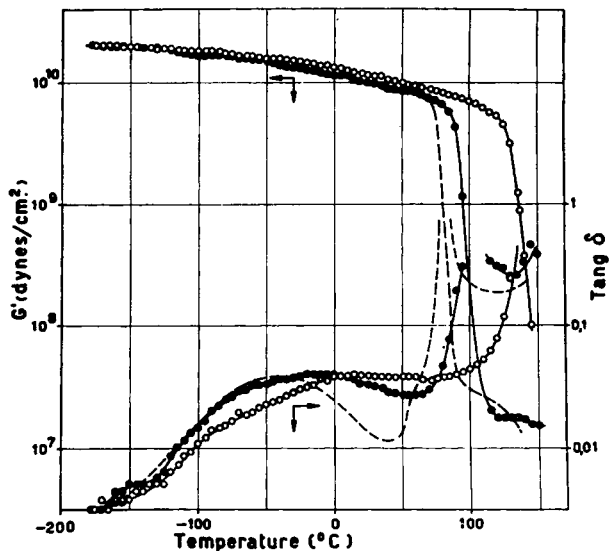

Fig. 8. Effect of post-chlorination: samples D-1 (●) and D-2 (○) containing 61.5 and 67.6% of chlorine, respectively, as compared with (- - -) standard PVC (sample A-5).
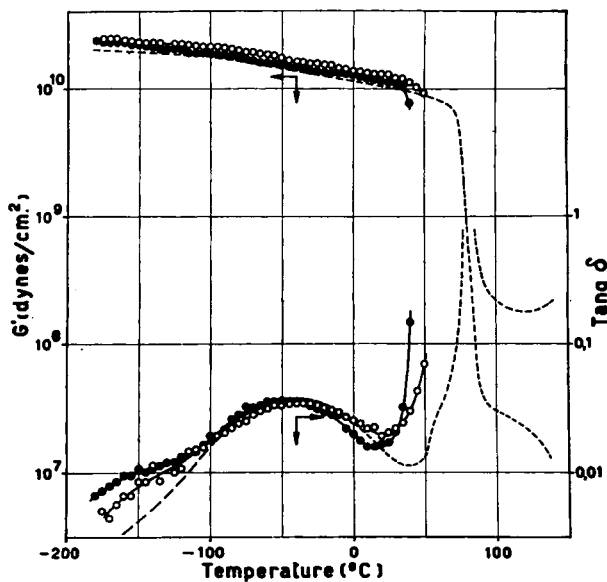

Fig. 9. Dynamic-mechanical properties of head-to-head PVC: samples E-1 (○) and E-2 (●) obtained from polybutadiene by chlorination for 15 and 90 min., respectively, compared with (- - -) standard PVC.

The results for samples D-1 and D-2 are plotted in Figure 8. The chlorination causes substantial changes in the absorption spectrum. The α peak is shifted at higher temperatures[39] and the β peak is severely broadened and displaced at higher temperatures. It is known that the chlorination of PVC gives mainly 1,2 substitution,[29-31] so that the chemical composition should be predominantly that of a copolymer of vinyl chloride and 1,2-dichloroethylene. The chain flexibility should be decreased and the absorption spectrum shifted at higher temperatures, in agreement with the results of Figure 8.

The tan δ-temperature curves for samples E-1 and E-2 are shown in Figure 9. No differences are found in the β peak of this polymer with respect to the standard PVC sample.

Only the α peak and the minimum between the β peak and the α peak are changed. The shoulder at −170°C. in sample E-1 can be attributed to residual polybutadiene units. It is surprising that the substitution of the PVC repeating unit (I)

$$-CH_2-CH-CH_2-CH-$$
$$\quad\quad\quad | \quad\quad\quad |$$
$$\quad\quad\quad Cl \quad\quad\quad Cl$$

I
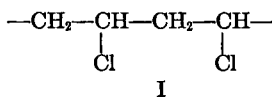
with the unit of the head-to-head poly(vinyl chloride) (II)

$$-CH_2-CH-CH-CH_2-$$
$$\quad\quad\quad | \quad | $$
$$\quad\quad\quad Cl \quad Cl$$

II
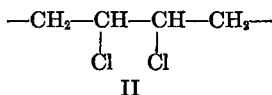
does not influence the β peak, considering that the secondary transitions of polymers having no side groups are attributed usually to the motion of very short segments of the main chain. On the contrary, the results shown in Figure 9 seem to indicate that the motions associated with the β peak of PVC are not influenced by local differences in the distribution of the Cl atoms along the chain, so that they seem to be largely of a cooperative type.

Some theories concerning the secondary transitions of polymers having no side groups have appeared recently.[27,40-42]

According to Yamafuji[27,40] the dielectric β peak of linear polymers of the rigid dipole type, is attributed to small vibrations of the dipoles, around their equilibrium position, in a viscoelastic field.

In the treatment of Kaestner[41] the β peak originates in the diffusional transposition ("Umlagerung") of a monomeric unit of the chain.

Following Andrews[42] the secondary transitions of polymers can be interpreted as due to reversible association–dissociation processes in which secondary bonds (e.g., dipolar or hydrogen bonds) are loosened.

The results found in the present work show that the β peak of PVC must be due either to a cooperative motion or to an association–dissociation process which is strongly affected by intermolecular interactions and which

depends more on the total number of C—Cl groups present in the chain than on their succession along the chain (Figs. 8 and 9).

These features could possibly be interpreted by the Andrews[42] theory, considering as association–dissociation process the breakdown of intermolecular bonding between the C—Cl dipoles.

References

1. K. Schmieder and K. Wolf, *Kolloid-Z.*, **127**, 66 (1952); *ibid.*, **134**, 149 (1953).
2. E. A. W. Hoff, D. W. Robinson, and A. H. Willbourn, *J. Polymer Sci.*, **18**, 161 (1955).
3. A. H. Willbourn, *Trans. Faraday Soc.*, **54**, 717 (1958).
4. A. E. Woodward and J. A. Sauer, *Fortschr. Hochpolymer.-Forsch.*, **1**, 114 (1958).
5. J. Heijboer, F. Schwarzl, and H. Thurn in *Kunststoffe*, Vol. I, R. Nitsche and K. Wolf, Eds., Springer, Berlin, 1962.
6. R. M. Fuoss, *J. Am. Chem. Soc.*, **63**, 369 (1941).
7. Y. Ishida, *Kolloid-Z.*, **168**, 29 (1960).
8. W. Reddish, *Pure Appl. Chem.*, **5**, 723 (1962).
9. S. Saito, Rept. Res. Electrotech. Lab. No. 648, Japan, 1964.
10. D. W. McCall, paper presented at Polymer Research Group Meeting, Moreton-hampstead, England, April 1964.
11. W. F. Slichter, paper presented at 150th American Chemical Society Meeting, Atlantic City, September 1965.
12. K. Deutsch, E. A. W. Hoff, and W. Reddish, *J. Polymer Sci.*, **13**, 565 (1954).
13. R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).
14. J. Heijboer, paper presented at IUPAC Symposium on Macromolecular Chemistry, Prague, 1965.
15. J. Bussink and J. Heijboer, in *Physics of Non-Crystalline Solids*, J. A. Prins, Ed., North Holland, Amsterdam, 1965.
16. H. Oberst, *Kunststoffe*, **53**, 4 (1963).
17. L. Bohn, *Kunststoffe*, **53**, 826 (1963).
18. P. Heydemann and A. Zozel, *Acustica*, **12**, 360 (1962).
19. K. H. Hellwege, J. Hennig, and W. Knappe, *Kolloid-Z.*, **188**, 121 (1963).
20. P. Heydemann and H. D. Guicking, *Kolloid-Z.*, **193**, 16 (1963).
21. G. Pezzin and A. Pagliari, *Chim. Ind. (Milan)*, **48**, 458 (1966).
22. W. Becker, *Kolloid-Z.*, **140**, 1 (1955).
23. F. Bueche, *Physical Properties of Polymers*, Interscience, New York, 1962, p. 292.
24. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962, p. 179.
25. Y. Ishida, *Kolloid-Z.*, **171**, 71 (1960).
26. J. A. Sauer and A. E. Woodward, *Rev. Mod. Phys.*, **32**, 88 (1960).
27. K. Yamafuji, *J. Phys. Soc., Japan*, **15**, 2295 (1960).
28. C. Garbuglio, A. Rodella, G. C. Borsini, E. Gallinella, *Chim. Ind. (Milan)*, **46**, 166 (1964).
29. J. Petersen and B. Ranby, *J. Polymer Sci.*, in press.
30. O. Frederiksen and J. A. Crowo, *Makromol. Chem.*, **100**, 231 (1967).
31. H. Kaltwasser and W. Klose, *Plaste-Kautschuk*, **13**, 515 (1966).
32. N. Murayama and Y. Amagy, *J. Polymer Sci. B*, **4**, 119 (1966).
33. G. Convalle, paper presented at 15th Intern. Congress on Plastics, Turin, 1963.
34. J. Koppelmann, in *Proceedings of the Fourth International Congress on Rheology*, E. H. Lee, Ed., Interscience, New York, 1965, p. 361.
35. J. Koppelman and J. Gielessen, *Z. Electrochem.*, **65**, 689 (1961).

36. J. Koppelman in *Physics of Non-Crystalline Solids*, J. A. Prins, Ed., North Holland, Amsterdam, 1965.

37. R. M. Fuoss, *J. Am. Chem. Soc.*, **63**, 378 (1941).

38. R. A. Horsley, *Plastics Progr. (London)*, **1957**, 77.

39. W. Reddish, in *Transitions and Relaxations in Polymers (J. Polymer Sci. C*, **14**), R. F. Boyer, Ed., Interscience, New York, 1966, p. 123.

40. K. Yamafuji and Y. Ishida, *Kolloid-Z.*, **183**, 15 (1962).

41. S. Kaestner, *Kolloid-Z.*, **204**, 77 (1965).

42. R. D. Andrews, in *Transitions and Relaxations in Polymers (J. Polymer Sci. C*, **14**), R. F. Boyer, Ed., Interscience, New York, 1966, p. 261.

Résumé

On a étudié par un pendule de torsion l'influence de la cristallinité, de l'histoire thermique, de la plastification et des modifications chimiques sur les propriétés dynamiques mécaniques du chlorure de polyvinyle. On a trouvé que le volume libre, la cristallinité et la structure tête-tête n'ont pas d'influence sur le maximum secondaire du facteur d'amortissement tandis qu'il est influencé par la post-chloruration, la copolymerisation et la plastification. Les résultats experimentaux démontrent que les mouvements moléculaires associés au maximum β du PVC ne sont pas influencés par les différences locales de distribution des atomes de chlore long de la chaîne: il semble donc que ces mouvements soient de type coopératif.

Zusammenfassung

Der Einfluss der Kristallinität, thermischen Geschichte, Plastizierung, Copolymerisation und chemischen Modifizierungen auf die dynamisch-mechanischen Rigenschaften von Poly(vinyl chlorid) ist mittels eines Torsionspendels untersucht worden. Es ist gefunden worden dass das sekundär Dämpfungsmaximum nicht von frei Volumen, Kristallinität und Kopf-Kopf Mikrostruktur beeinflusst wird sondern durch Nachchlorierung, Copolymerisation und Plastizierung modifiziert. Die Ergebnisse zeigen dass die Bewegungen die dem β-maximum von PVC assoziiert sind, nicht durch örtliche Unterschiede in der Verteilung del Cl Atome entlang der Kette beeinflusst werden, so dass sie hauptsachlich von kooperativ Typ zu sein scheinen.