

The Secondary Relaxation Process of Poly(vinyl Chloride) and its Derivatives*

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Synopsis

The temperature dependence of the shear modulus G' and of the damping $\tan \delta$ of poly(vinyl chloride), poly(vinylidene chloride), copolymers of vinyl chloride–vinylidene chloride, PVC chlorinated in solution and suspension, and chlorinated polyethylene was measured. Secondary relaxation process of PVC and its derivatives are being explained as vibration of methylene groups polarized by neighboring CCl dipoles. This process, being suppressed by lowering the concentration of the methylene groups in the PVC chain (e.g., by chlorination), remains, however, unaffected by the growth of crystalline content. The achieved results show that in the α -transition region there occurs, in accordance with Andrews' theory, a loosening of the bonds between the CCl dipoles, whereas in the β -transition region a loosening of the weaker bonds among the dipoles of the polarized methylene.

INTRODUCTION

The secondary relaxation process of poly(vinyl chloride) is most often explained by the motion of short-chain sections by the so-called crankshaft motion. It was Schatzki¹ and Boyer² who proposed the mechanism of this motion. It is primarily the rotation of four-carbon chain sections around two colinear bonds. Another explanation combines the β -process with the rotational oscillations of methylene groups.³ It is also possible to interpret the secondary process of poly(vinyl chloride) according to Andrews^{4,5} as a process of loosening of the intermolecular cohesive forces, e.g., of dipolar bonds.

From the extensive study of Pezzin and co-workers,⁶ it becomes evident that the shape, intensity, and position of the β -process is not affected by the free volume, the 20% of crystallinity, nor by local changes in the distribution of chlorine atoms, for instance, by head-to-head structure. The decrease in the β -maximum is caused by adding a small quantity of plasticizer whereby at the same time the β -peak is slightly shifted to lower temperatures.^{6,7} A conspicuous change of shape and position of the β -peak is

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brought about by the heterogeneous chlorination of poly(vinyl chloride).^{6,8,9} In this case, the secondary peak is broadened and shifted to higher temperatures. Changes of the β -peak are also caused by the copolymerization of vinyl chloride with ethylene which results in an inconspicuous change of the shape and a small shift to lower temperatures.⁶ All measurements carried out so far have been essentially explained both by the crankshaft and the Andrews theory.^{6,10}

It is the aim of this paper to offer an explanation for the mechanism of the secondary relaxation process of PVC. This interpretation is based on the dynamic-mechanical properties of copolymers of PVC, chlorinated PVC, and of crystalline PVC.

EXPERIMENTAL

Polymers

Sample No. 1. Suspension poly(vinyl chloride), $[\eta] = 105$ ml/g.

Sample No. 2. Copolymer vinyl chloride-vinylidene chloride, containing 44% VDC.

Sample No. 3. Copolymer vinyl chloride-vinylidene chloride, containing 72% VDC.

Sample 4. Poly(vinylidene chloride).

Sample No. 5. Copolymer vinyl chloride-propylene, containing 6% of propylene.

Sample No. 6. Chlorinated polyethylene containing 57% Cl. Polyethylene (Hostalen GS) was chlorinated at 120°C in a tetrachlorethane solution.

Sample No. 7. Chlorinated PVC containing 63% Cl. It was prepared by the chlorination of a PVC solution in tetrachlorethane at 120°C.

Sample No. 8. Chlorinated PVC containing 61.5% Cl. It was prepared by the chlorination of PVC in water suspension at 50°C. As swelling agent, CHCl_3 was used.

Sample No. 9. Chlorinated PVC containing 70% Cl. It was prepared the same way as sample no. 8.

Sample No. 10. Chlorinated copolymer VC-VDC. Polymer no. 2 was chlorinated in water suspension at 50°C. It contains 67% Cl.

Sample No. 11. Crystalline PVC. It was prepared by polymerization in a urea complex at -60°C. It contained 6% of urea.

Specimen Preparation

All samples, with the exception of the samples no. 4 and 11, were stabilized by a 2% organotin stabilizer, Meister Z 10. Samples no. 2, 3, and 5 were milled for 5 min at 150°C and pressed for 5 min at 170°C. Samples no. 1, 6, 7, 8, and 9 were milled for 5 min at 170°-190°C (according to chlorine content) and pressed for 5 min at 185°-200°C. Then they were conditioned for 15 hr at 100°C.

Sample no. 11 was pressed in a special mold at 195°C directly from powder and was conditioned for 110 hr at 100°C. During this time the density increased from its original value of 1.407 g/ml to 1.422 g/ml (after urea deduction) and remained unchanged thereafter.

Measuring Methods

The real parts of the shear modulus G' and the damping $\tan \delta$ were measured on a torsion pendulum of the current type. The temperature of the maximum damping in the main transition region has been designated as T_α while the temperature of the maximum damping at the secondary peak is described as T_β . The minimum temperature between the α - and β -maximum has been designated with T_{\min} and the corresponding value of damping, by $\tan \delta_{\min}$ (Table I).

TABLE I
Transition Temperatures and Damping Properties

Sample no.	T_α , °C	T_β , °C	T_{\min} , °C	$\tan \delta_{\min}$	Change in β -peak shape
1	90	-56	32	0.014	—
2	47	-48	15	0.023	no change
3	35	-32	18	0.045	no minimum between peaks
4	31	-32	—	—	both maxima are shifted together
5	76	-54	32	0.014	no change
6	60	-49	18	0.017	enlargement of the left side of the β -peak
7	101	-40	30	0.020	enlargement of the right side of the β -peak
8	107	-30	30	0.030	enlargement of the right side of the β -peak
9	121	—	—	—	no β -peak
10	59	-39	20	0.030	enlargement of the right side of the β -peak
11	114	-55	42	0.023	enlargement of the right side of the β -peak

RESULTS

The results of measuring the temperature dependence of the mechanical damping $\tan \delta$ of the various polymers are summarized in Table I. It follows from this table that the chlorine increase in polymers in an arbitrary way results as a rule in a shift of the β -peak to higher temperatures. In the case of copolymer vinyl chloride-vinylidene chloride 56/44 (sample 2), this shift is not accompanied by a change in β -peak shape. With copolymer vinyl chloride-vinylidene chloride 28/72 (sample 3), the basic β -peak shape remains unchanged; there occurs, however, a shift to higher temperatures, and, owing to the lowering in T_α , the minima between the α - and β -maxima

are being levelled off. Only with poly(vinylidene chloride) (sample 4), the β -maximum loses its typical shape; it is most likely shifted to higher temperatures, which is manifested by an unobvious indication of the maximum on the left part of the α -maximum.

The position and shape of the β -peak remain unchanged with copolymers of vinyl chloride-propylene (sample 5). This result differs somewhat from that achieved by Pezzin's measurements carried out on copolymer vinyl chloride-ethylene.⁶

Polyethylene chlorinated to the same chlorine content as PVC (sample 6) is showing the characteristic β -maximum. The lower T_α as well as the enlargement of the left part of the β -peak, however, give evidence of the presence of unchlorinated polyethylene sequences.

In the case of chlorinated PVC, there occurs a change in the shape of the β -peak, manifested originally by a levelling of the minima between both peaks. This process is especially conspicuous with PVC chlorinated in suspension, where the minimum has almost disappeared (sample 8).

PVC chlorinated in solution (sample 7) tends, at the same chlorine content, to have a lower T_α and a more regular β -peak than PVC chlorinated in suspension. It was ascertained by the chlorination of α -deuterated PVC that chlorine does not enter into CHCl groups, which means, no vinylidene chloride units are being generated.¹¹ Chlorinated PVC may therefore be regarded as a terpolymer of vinyl chloride, 1,2-dichloroethylene, and 1,1,2-trichloroethylene. The difference between sample 7 and sample 8 is likely to be connected with the representation of the mentioned structural units. With a sufficiently high chlorine content, the original β -peak of PVC is entirely suppressed (sample 9).

This comparison implies that a growing chlorine content results in a shift in β -peak to higher temperatures, the more so the more the concentration of methylene groups is suppressed, i.e., the greater the number of various types of structural units contained in the polymer. This fact is rather well demonstrated in sample 10.

With crystalline PVC there occurs no change in T_β . The density of sample 11 corresponds to about 68% of the crystallinity, calculated according to Nakajima.¹³ The enlargement of the right side of the β -peak of crystalline PVC is obviously due to the urea content acting as a filler and exerting the same influence on the shape of the β -peak of PVC.¹²

DISCUSSION

The reported measurements indicate that the α -process is very sensitive to any change in the chlorine content. In accordance with Andrews' theory we can state, therefore, that the α -process and the T_α are connected with the interaction of the CCl dipoles, which incidentally had been already anticipated by Schmieder and Wolf¹⁵ and elaborately expounded by Niklas.¹⁶ The secondary process tends to be less sensitive to structural changes and is

changing according to the procedure by which further chlorine atoms are introduced into the chain or had been replaced in it. To be more precise, it can be said that the β -peak does not change substantially, provided the content of the methylene groups remains constant and the predominant constituent of polymer is to be vinyl chloride and is located in such a way that the methylene group is in the vicinity of at least one CHCl group. Vice versa, that is to say, if the content of the methylene groups is being decreased by chlorination, an increase in the T_α and a deformation of the β -peak follows.

The relative insensibility of the β -process to the content of crystallinity determined by Pezzin⁶ and by us implies that this process is not connected with the amorphous or the crystalline phases only, but that it occurs both in amorphous as well as in crystalline regions. Since it is difficult to imagine an equivalent motion of the crankshaft type both in the amorphous as well as in the crystalline phase, we may assume that the crankshaft theory does not offer a satisfactory explanation of the mechanism causing the β -process of poly(vinyl chloride). A justification of this claim can be found, for instance, in Flocke's data on polypropylene.¹⁴ The γ -peak (-70°C) to be attributed to the crankshaft motion was found in this case to be conspicuously influenced by the degree of crystallinity.

This is why, in explaining the β -PVC process, we have to take into consideration only such a motion which might occur in the amorphous as well as in the crystalline phases.

This requirement is fully met by the vibration of the methylene groups. It is, however, a known fact that the β -process is characterized by its polarity since it can be ascertained by measuring the temperature dependence of the dielectric loss factor.

Let us now try to interpret the β -process on the basis of Andrews' theory by taking into account all known facts. Although the insulated methylene group is electrically neutral, we may anticipate that it can be polarized by the field of the adjoining CCl dipoles. Providing this assumption is correct, then we have two kinds of physical bonds between the PVC chains. These are, firstly, bonds between the CCl dipoles which are rather strong and tend to dissociate in the T_α region, and, secondly, there are these between the polarized methylene groups which are naturally much weaker and tend to dissociate owing to the loosening of the vibrations of the methylene groups already in the T_β region.

The changes of the β -peak caused by the chlorination are due to the decrease in methylene group content and change in the inductive influence of CCl dipoles and quadrupoles. The decrease in β -peak intensity and the T_β shift to lower temperatures caused by the small quantity of plasticizer can be explained by a partial liquidation of these secondary bonds by their screening off, or, which is more likely, by the change in character of the quadrupoles, since CCl dipoles can form bonds with the plasticizer. In a similar way, the T_α decrease by plasticizers can also be explained.

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