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Antiplasticization and Crystallinity in Poly(vinyl chloride)

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ABSTRACT: The rise in tensile modulus observed in formulations of poly(vinyl chloride) (PVC) at low concentrations of tricresyl phosphate (TCP) can be influenced and even eliminated according to the way the sample is prepared or treated prior to measurement. All pretreatments that were found to eliminate crystallinity in the sample (quenching, chlorination of the polymer) also produced samples that failed to show the rise in modulus associated with antiplasticization. Formulations where the plasticizer was introduced at room temperature rather than by heating also showed a lack of an antiplasticization effect. Wide-angle X-ray diffraction measurements cannot be analyzed in a straightforward manner, since orientation effects are detected. In spite of this, the experimental data as a whole point to a strong correlation between the rise in modulus and the presence of a crystalline phase at low levels of TCP in PVC formulations.

Introduction

Among the questions that still remain to be answered regarding PVC's unique response to plasticizers, one aspect that has received intermittent attention is the unexpected phenomenon of antiplasticization. The apparently anomalous increase in modulus and tensile strength, together with a decrease in elongation, at low concentrations of plasticizers has been known for many years. This unforeseen change in mechanical properties was first assigned to possible experimental difficulties in preparing homogeneous samples for testing.[1] There was no inmediate explanation as to why small quantities of plasticizer (a liquid at room temperature) should lead to higher values of modulus and tensile strength. A straightforward application of any law of mixtures would predict a steady decrease in those properties with increasing plasticizer content, which is exactly what occurs once a threshold or critical plasticizer concentration has been passed.

Since later studies have shown that this effect is observed consistently though with different intensity according to the plasticizer, two lines of reasoning have been proposed. Horsley in 1957 carried out one of the few studies to date that have tried to correlate changes in crystallinity with the antiplasticization effect.[2] Though the X-ray evidence presented is limited by the state of knowledge on PVC crystallinity at the time, he presents semiquantitative data based on WAXD flat-plate transmission photographs. The three haloes he refers to are taken to be, in order of increasing diameter, the 200 reflection, the 110 reflection, and the unresolved group of the 210, 201, and 111 reflections. All three haloes are superimposed on the two broad amorphous background reflections. He reports a sharpening and increase in intensity of the two outermost haloes with respect to the innermost one, this effect being more prominent in the plasticizer concentration range where the maximum in modulus is observed. He also found that quenching of the samples prior to mechanical testing eliminates the rise in modulus associated with antiplasticization. Later work reported by Lebedev et al.[3] studied basically the same phenomenon, this time using WAXD diffractometer traces, with corrections for the scatter of the plasticizer. They report that the intensity of the reflection at $2\theta = 17°$ (that is, the 110 reflection) goes through a maximum in the concentration range of plasticizer where also a maximum in strength and modulus is measured.

The other line of explanation that has been proposed involves polymer–plasticizer associations that are believed to have a stiffening effect on the chain at low concentrations of plasticizer, therefore acting as cross-links in the structure. Ghersa was the first to propose this, together with a possible crystallization effect concurring, depending on the type of plasticizer.[4] Pezzin et al.[5] propose that this sort of association could explain the disappearance of the PVC β peak, as evidenced from dynamic mechanical studies on slightly plasticized PVC. The loss in mobility would explain, according to this model, the observed rise in tensile modulus. Kinjo and Nakagawa[6] carried out further studies using a wide range of plasticizers and arrived at a similar explanation.

In light of present knowledge regarding the crystallizing capability of PVC in the presence of solvents (including plasticizers)[7] a new look will be taken at the possible relation between changes in physical structure and its effect

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on the rise in modulus of plasticized PVC associated with the phenomenon of antiplasticization.

Experimental Section

Materials. Suspension-polymerized PVC was supplied by Plasticos Petroquímica C.A. (Petroplas). The PP-150 grade used in this study has a *K* value of 70–74, apparent density of 0.52 g/cm^3 and a porosity of 0.27 cm^3/g.

Two types of chlorinated PVC were tested: (i) A suspension-chlorinated PVC commercial sample, supplied by B.F. Goodrich, with a stated chlorine content of 63%. This sample will be referred to as sample J. (ii) Solution-chlorinated samples prepared in the laboratory. Chlorine gas was bubbled through a 5% solution of PVC Petroplas PP-150 in tetrachloroethane, at 125 °C. The rate of flow was approximately 0.5 g/min. The chlorinated polymer was recovered according to the procedure reported in ref 8. The reaction time was 5 h, achieving a final chlorine content of 65%. This sample will be referred to as sample F. Technical grade tricresyl phosphate (TCP) was used as plasticizer. Diethyl ether (analytical grade) as used as received. Tetrahydrofurane (THF) was freshly distilled before use. Irganox 1010 antioxidant and Irgastab 17 MOK heat stabilizer, supplied by BASF Venezuela, were added to the formulations.

Preparation of the Film Samples. To prepare the films, all the ingredients of the fomulation were dissolved in THF. Sufficient stabilizer was added to ensure a final concentration in the dried film of 1 pph Irganox 1010 and 2 pph Irgastab 17 MOK.

Films were then cast from these solutions. It is well-known that THF is a very difficult solvent to eliminate completely from PVC. Various treatments were tried, monitoring via T_g measurements the last traces of solvent. The procedure adopted in this study consisted of air-drying the films during 48 h and then placing them in a circulation oven at 190 °C for 9 min, in the case of commercial PVC. Oven temperature for sample J could be only 180 °C, while sample F showed signs of evident degradation at temperatures over 160 °C.

Since the heat treatment also caused a loss in TCP, each sample subjected to mechanical testing was monitored for TCP content via IR spectroscopy. A ratio of the bands at 780 (TCP) and 680 cm^{-1} (PVC) was found to give a reasonably straight line when plotted against TCP concentration up to approximately 16 pph of TCP. The plot flattens out appreciably in the 18–25 pph range. In the case of chlorinated PVC, the bands used were those at 1490 (TCP) and 1435 cm^{-1} (PVC), with similar results.

In another type of test, unplasticized PVC films cast from THF solutions and dried as described previously were then inmersed for different periods in a mixture of diethyl ether/TCP, at room temperature. After the surface of the films was washed, IR spectroscopy was used in the manner described to determine the final TCP concentration.

Equipment. (i) Mechanical Testing. The tensile secant modulus at 1% strain was measured on dumbbell-shaped samples according to ASTM Norm D638 Type IV specifications. All measurements were carried out at room temperature (25 °C) on a JJ Lloyd tensile measuring machine fitted with a 50-N load cell. The samples were stretched at a cross-head speed of 10 mm/min. Each point plotted in the figures corresponds to the average of a minimum 6 and a maximum 15 measurements.

All samples, except where otherwise stated, were kept at room temperature for 48 h after the high-temperature removal of residual THF. In the case of samples inmersed in diethyl ether/TCP, films were left to dry in air for 7 days.

(ii) Wide-Angle X-ray Diffraction. A Philips PW 1730/10 generator fitted with a Cu tube was equipped with a vertical goniometer PW 1050/70. 1° receiving and scatter slits were used, together with a $^1/_2$° divergence slit. Measurements were carried out using counting times of 200 s at 0.2° (2θ) intervals. The Cu tube was operated at 40 kV and 30 mA. A Ni filter was used to obtain Cu Kα radiation. Data were stored and handled at an IBM Personal Computer connected to the interface of the Philips Channel Control Unit.

Samples were measured both in reflection and transmission modes. The greater resolution in reflection mode determined its preferential use when recording the definitive WAXD profiles. The range usually scanned was from 10° to 35° (2θ), though certain scans were taken up to 60° (2θ).

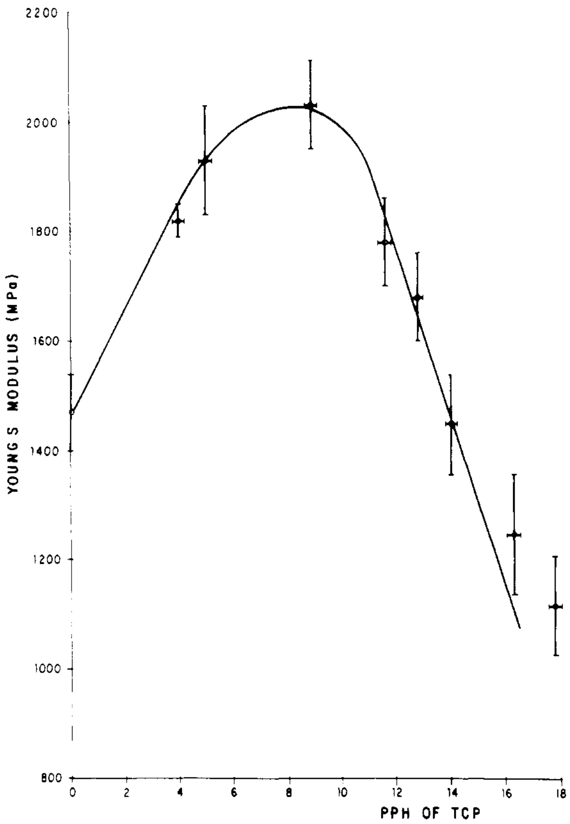

Figure 1. Rise in Young's modulus observed in slightly plasticized PVC films. Samples were prepared and then stored at room temperature for 2 days.

Table I
Young's Modulus of Unplasticized PVC Samples Cast from THF Solution, after Ageing at 70 °C

ageing time, days	Young's modulus,[b] MPa
0[a]	1710 ± 150
7	1720 ± 80
14	1630 ± 110

[a] Corresponds to a sample measured 1 h after film preparation. [b] Absolute modulus values have been found to vary according to film batch and cooling rate. All values reported in this table correspond to the same film batch and cooling rate. This value is higher than the values reported in the figures for comparable samples.

(iii) IR Spectroscopy. A Perkin-Elmer 1320 IR spectrophotometer was used to record the spectra of the film samples in the 4000–600-cm^{-1} range.

(iv) Differential Scanning Calorimetry. Thermograms were obtained by using a Perkin-Elmer DSC II equipped with a data station. Heating rates in all cases were 20 °C/min.

Results

Figure 1 indicates the rise in modulus observed in slightly plasticized PVC formulations. The modulus rises some 30% in value in the concentration range of 8–10 pph TCP. To identify the possible causes of such a rise, various sets of measurements were carried out so as to determine the effect of physical ageing, solvent–polymer interaction, and crystallinity on the type of curve observed.

Physical Ageing. Figure 2 shows that even when the moduli are measured just 15 min after cooling the films from the oven, there is an evident antiplasticization effect. Related to this finding is the fact than unplasticized PVC films did not show appreciable changes in modulus after being aged at 70 °C, even though the samples evidenced a pronounced ageing endotherm in their DSC thermo-

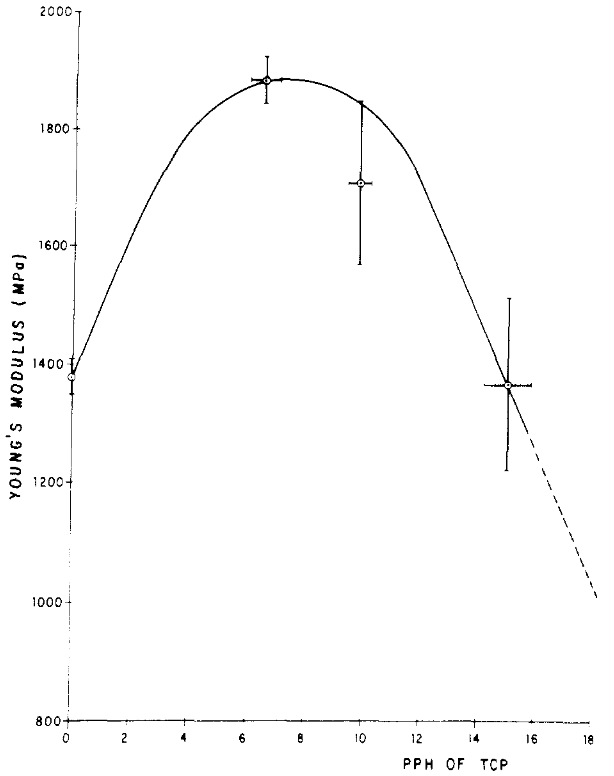

Figure 2. Rise in Young's modulus observed in slightly plasticized PVC films. Measurements were carried out 15 min after films were prepared.

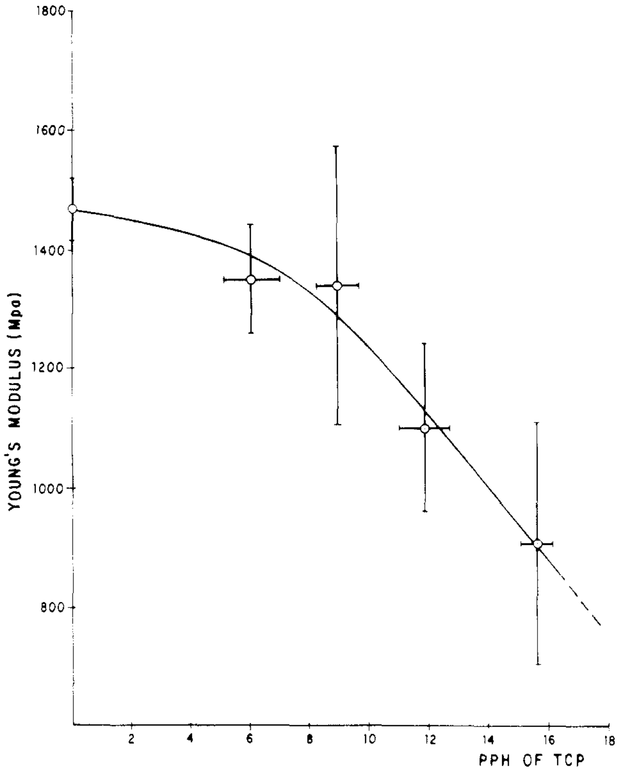

Figure 3. Steady decrease of Young's modulus observed in slightly plasticized PVC films. In contrast with Figure 2, these samples were prepared by inmersion of unplasticized PVC film in an ether/TCP solution at room temperature. Films were then left to dry at room temperature for 5 days to eliminate the greater part of their residual diethyl ether.

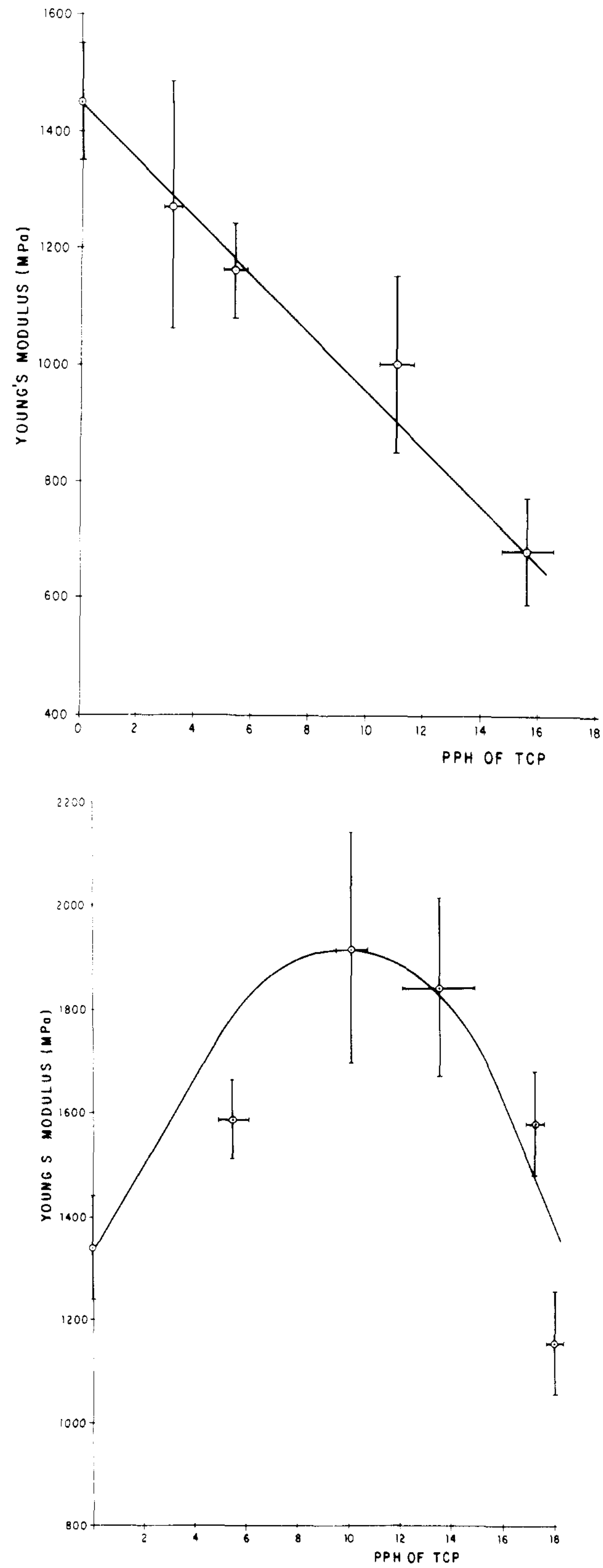

Figure 4. Variation of Young's modulus in slightly plasticized films that were quenched into liquid nitrogen immediately after being heated to remove residual THF. Top: Measured 15 min after being removed from liquid nitrogen and stored at room temperature. Bottom: measured 12 h after removal from liquid nitrogen and storage at room temperature.

grams. Table I reports the modulus data for the aged samples.

Polymer–Solvent Interaction. If TCP is incorporated into PVC films without prior heating, by immersing unplasticized films in a diethyl ether/TCP mixture, the resulting films fail to show an antiplasticization effect, as shown in Figure 3. This result indicates that the presence of solvent or plasticizer is not sufficient to produce the expected rise in modulus.

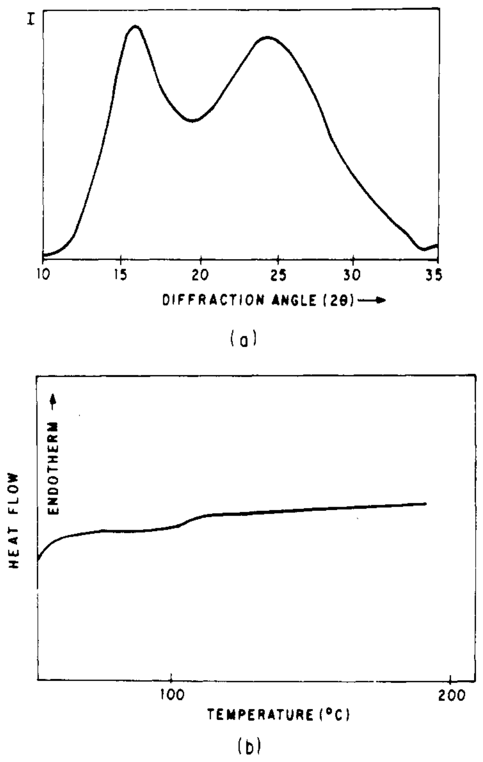

Figure 5. (a) WAXD profile of a solution chlorinated PVC. (b) DSC thermogram of a solution chlorinated PVC.

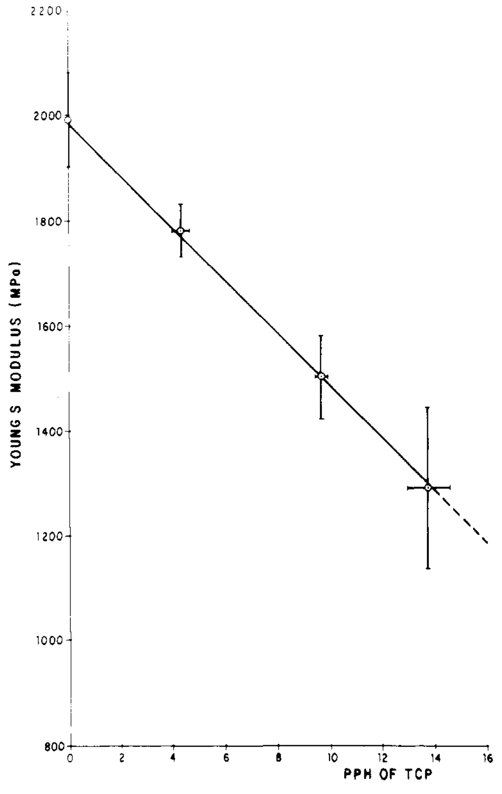

Figure 6. Steady decrease of Young's modulus observed in a slightly plasticized solution-chlorinated PVC sample.

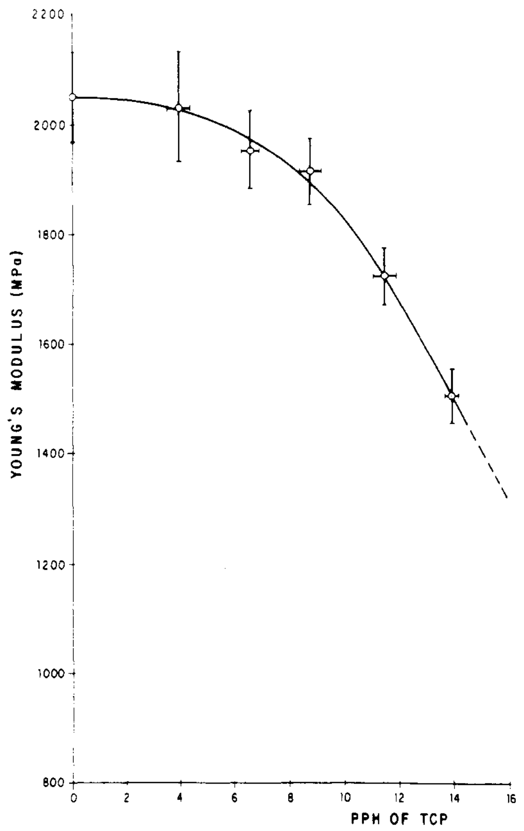

Figure 7. Decrease in Young's modulus observed in slightly plasticized suspension-chlorinated PVC film samples.

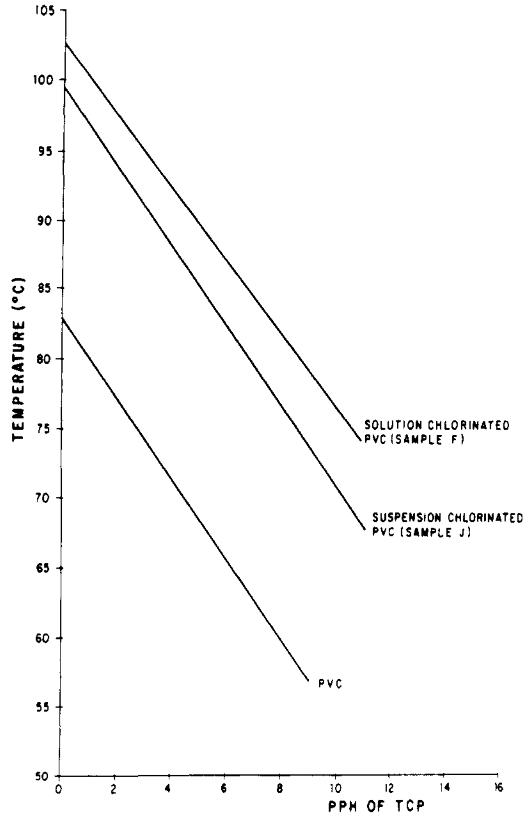

Figure 8. Decrease of T_g values as a function of TCP content in formulations of PVC and solution- and suspension-chlorinated PVC.

Crystallinity. It is known that quenching eliminates the rise in modulus at low concentrations of TCP (see, for example, Figure 4, top). What has not been reported is that on standing at room temperature after the quenching treatment, the films again show the expected antiplasticization behavior (Figure 4, bottom).

Chlorination of PVC eliminates all the usually accepted evidence for crystallinity in the commercial polymer (see Figure 5). Plasticized solution-chlorinated PVC (Figure 6) or plasticized suspension-chlorinated PVC (Figure 7) both fail to evidence an antiplasticization effect. Chlorination does not alter to a great extent the solubility pa-

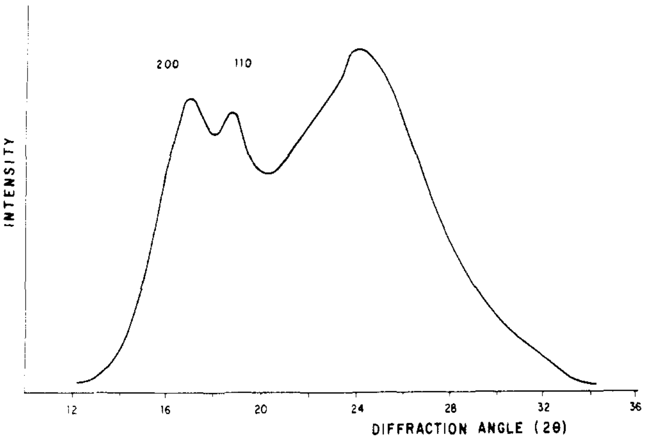

Figure 9. WAXD profile of PVC film with 0 pph of TCP.

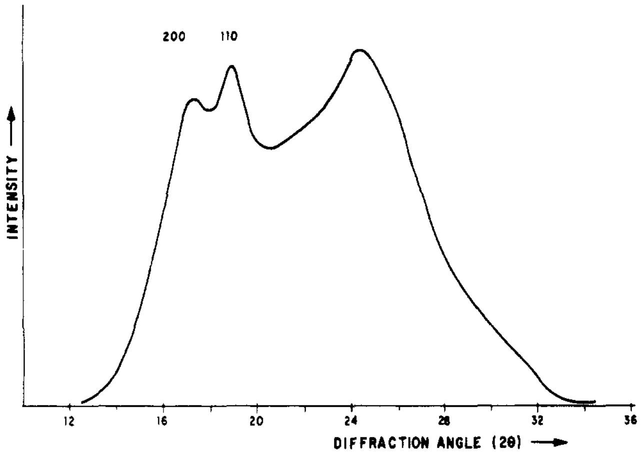

Figure 10. WAXD profile of PVC film with 10 pph of TCP.

rameter of the polymer,[9] and in fact both the chlorinated and virgin polymer show virtually the same rate of decrease of T_g with TCP concentration, as shown in Figure 8.

There is other evidence to the effect that heat treatments on unplasticized PVC influence the value of the tensile modulus. Annealing films at temperatures > 100 °C can produce up to a 30% increase in modulus. Slow cooling of the films after being heated to 190 °C to remove THF can also produce an overall 20% increase in absolute values of modulus.

While the evidence from mechanical properties is relatively straightforward, the analysis of the corresponding WAXD data is not. Figure 9 is the WAXD profile from an unplasticized PVC film cast from THF solution and dried at 190 °C. Figure 10 corresponds to a formulation containing 9 pph of TCP.

The overall problem of analyzing PVC WAXD curves has been treated in a separate paper.[10] Texture analysis of samples that give rise to profiles such as Figure 9 indicate an incipient crystal orientation in the plane of the film.[11] Unpublished data on slightly plasticized samples such as reported in Figure 10 also indicate nonrandom orientation. Therefore the increase in intensity of the 110 reflection cannot be interpreted per se as indicating an increase in crystallinity. It may simply be due to an orientation effect.

Since extraction with ether is known to reduce orientation in films,[10,11] crystallinity values using the Fourier transform method of ref 10 were calculated for extracted samples of plasticized PVC films. Because of limitations in the method, the most that can be said at the present time is that the crystallinity does not exceed 20% for extracted films with originally 10 and 18 pph of TCP. No firm value can be proposed for the nonplasticized sample, for reasons given in ref 10.

Discussion

The experimental results presented in the previous section serve as a guide in establishing the limits to the three most probable explanations to the phenomenon of antiplasticization in PVC. Each will now be analyzed in turn:

Physical Ageing of the Amorphous Fraction. Most of the reported mechanical measurements in the antiplasticization range of PVC have been carried out at a temperature below the range of T_g values of the formulations being studied. In this glassy state, it could be argued, any change in modulus is more likely to be influenced by the amorphous phase which makes up the majority of the structure. The rate and degree of physical ageing varies according to each formulation prior to mechanical testing, since they are all stored at room temperature irrespective of their individual T_g values. A correlation could be sought between the degree of physical ageing in each formulation prior to testing and the observed rise in modulus or other changes in mechanical properties.

The experimental evidence does not support this hypothesis, as far as tensile modulus is concerned. Antiplasticization has been observed as soon as 15 min after samples have started to age at room temperature. Long-term ageing, on the order of a month or more, was followed in a few experiments. Initial results show an overall absolute increase in modulus over the whole antiplasticization range, but no attempt was made to quantify the possible evolution in its crystalline phase. As to unplasticized PVC films, it has been shown that accelerated ageing at 70 °C fails to induce an increase in the measured tensile modulus.

Therefore, physical ageing of the amorphous phase cannot be taken to be the primary cause of antiplasticization in PVC. However, its effect on other mechanical properties, such as creep, fracture, etc., cannot be ruled out and may have to be taken into account in those cases.

Polymer–Solvent Associations. Plasticization and gelation of dilute PVC solutions are both solvent-induced processes where the nature of the polymer–solvent interaction plays a very important part in the type of physical structure that is finally obtained. While polymer–solvent associations have been used to explain the low creep of plasticized PVC, antiplasticization, the disappearance of the β transition in dynamical mechanical studies, and as a determining factor to explain the gelation of PVC,[4,5,12] there is not a great body of evidence available as to the exact nature and measured strength of associations capable of influencing to such a high degree the macroscopic mechanical properties of plasticized PVC.

The nature of the solvent has been known to influence the degree of antiplasticization.[6] Unpublished work by me has shown that the presence of low concentrations of a very good solvent, such as cyclohexanone, does not produce an antiplasticization effect. Equally relevant is the fact that the presence of TCP alone is not sufficient to induce a rise in modulus in PVC formulations. The evidence points to the fact that while a poor solvent such as a plasticizer can induce certain changes in the physical structure of the polymer, its presence alone cannot explain the antiplasticization effect.

Crystallization. The explanation for the antiplasticization effect in PVC on the basis of crystallinity is certainly not new and usually runs on the following lines: small quantities of plasticizer confer mobility to PVC chains, thus allowing the polymer to attain a greater degree of crystallinity, for the same thermal history, than the unplasticized polymer. The increase in crystallinity produces an increase in modulus. As the concentration in plasticizer keeps increasing, the modulus of the amorphous phase is lowered to such a degree that the overall modulus starts decreasing in value.

The experimental evidence presented in this paper clearly shows that any treatment that limits or eliminates crystallinity (quenching, chlorination) also limits or eliminates the rise in modulus associated with the antiplasticization effect.

Unfortunately the WAXD evidence is not as clear as would have been desirable. No conclusions can be drawn from relative increases in intensity of one reflection over another, since texture analysis shows signs of orientation in both 0 and 10 pph plasticized PVC films. A calculation of "crystallinity" of films of 10 and 18 pph TCP after extraction in ether (which will remove both TCP and incipient texture), using the method of ref 10, gives a maximum value below 20%. Is it possible to explain the observed rise in modulus in a material that is, after all, basically a glassy polymer?

To attempt to answer this, it has been necessary to simplify a complex situation. The incorporation of plasticizer poses the following problems: (a) It replaces a fraction of polymer with a fraction of solvent, which virtually does not contribute to the modulus. (b) It plasticizes a nonnegligible part of the remaining amorphous fraction, locally lowering the modulus of the glassy polymer. (c) Its presence may increase the relative concentration of the crystalline phase over the amorphous phase.

While it is possible to quantify the first parameter and approximate the third according to the partial WAXD results, the second has to be guessed at.

Whatever the macroscopic homogeneity of the plasticizer distribution may be, on a microdomain level there are certain to be areas where localized concentration of the plasticizer molecules will be such that the T_g of the microdomain is below ambient temperature. These microdomains will not contribute to the overall mechanical properties as will the rest of the material. To take an example, in a formulation with 10 pph plasticizer the amount of PVC that would have a "microdomain T_g" below room temperature could vary between 0 and approximately 20% of the polymer fraction.

If these assumptions are applied to a set of equations based on a simple law of mixtures, the modulus of the crystalline phase must be an order of magnitude greater than the modulus of the amorphous fraction to replicate the experimentally observed behavior. Since I am not aware of any experimental determinations of modulus of the very crystalline type of PVC (urea clathrate, for example), it is difficult to judge whether a more elaborate model should be attempted at the present time.

The second question that has to be answered is what kind of structure rearrangement is taking place that will restore the antiplasticization effect to quenched samples that are left at room temperature after quenching. That quenching should eliminate the effect is perfectly compatible with the explanation based on crystallinity. What was not so evident is that crystalline structures should re-form at room temperature in formulations where the T_g is still above 30 °C. None of the experimental evidence at present available can answer this. Unfortunately, the lack of adequate instrumentation made it imposible to measure the WAXD profile of quenched samples in a sufficiently short period of time without losing excessive resolution. Twelve hours after quenching, the WAXD profiles show not quite totally resolved but clearly identifiable the 110 and 200 reflections.

Independently of the validity of the calculation of crystallinity or crystalline modulus, the fact remains that on cooling PVC in the presence of TCP from high temperatures, a structure emerges that increases the modulus of the material at low plasticizer concentrations. This increase in crystallinity cannot be induced by the plasticizer by simply mixing the plasticizer and the polymer at room temperature, as shown by the films inmersed in TCP/diethyl ether mixtures. Present evidence points to the fact that plasticizer must be present in the critical stage during cooling when crystallization occurs, so that a material with enhanced crystallinity can be obtained. Whether or not an overall increase in modulus is observed will depend on the concentration of plasticizer. If the solvent present is too good a solvent, it may limit the crystallization to such a degree that no antiplasticization is observed.

Finally, it must be pointed out that this explanation in no way contradicts the clear evidence from dynamic mechanical studies.[4–6] The increased stiffness or lack of mobility of the amorphous chains can also be interpreted as the result of an increase in the number of cross-links (crystallites) in the structure.

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