

Antiplasticization and Transition to Marked Nonlinear Viscoelasticity in Poly(vinyl Chloride) (PVC)/Poly- ϵ -caprolactone (PCL) Blends

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Synopsis

Measurements of mechanical damping ($\tan \delta$) in the temperature range of -120° to $+120^\circ\text{C}$ at 110 Hz, of uniaxial tensile creep at $25.0^\circ \pm 0.5^\circ\text{C}$ covering creep times from 10 to 1000 sec, and of impact strength at 21°C have been carried out for a series of physical PVC/PCL blends in the composition range of 0%–12% by weight of PCL in the blend. With increasing PCL content in the blend, the α -peak of PVC was shifted to lower temperatures and became broadened. The β -peak of PVC was also shifted to lower temperatures and was markedly suppressed. The tensile creep compliance of approximately linear viscoelasticity showed a maximum decrease of 10%, and the impact resistance was reduced 3.5 times when 5% and 12% by weight of PCL, respectively, was blended with PVC. There was also a considerable increase (25%) in stress level at which the transition from approximately linear to markedly nonlinear viscoelasticity occurred when up to 5% by weight of PCL was added to the PVC. These results are attributed to the antiplasticizing effect of PCL on PVC. They support the importance of β -mechanism in the stress-activated processes proposed to be responsible for the appearance of nonlinear viscoelasticity in glassy polymers, and they are in agreement with the pseudocrosslinking concept of antiplasticization. By comparing the antiplasticization behavior of PVC/PCL blends with that of PVC/DOA and PVC/DOS from reported data, it was possible to obtain an idea of the level of compatibility in the PVC/PCL blends. The results suggest that PCL is partially compatible with PVC.

INTRODUCTION

Most polymers show, within the limits of experimental accuracy, a linear viscoelastic behavior for small stresses and strains. For amorphous polymers in the glassy state it has been observed that the uniaxial tensile strain limit of linear viscoelasticity is about 1.0%. For highly crystalline polymers the strain limit of linearity is much lower, roughly 0.1%–0.4%.¹ In engineering applications, however, thermoplastics are often used at higher strain levels where their viscoelastic response is nonlinear.

From a plastic material design point of view this fact introduces difficulties since the useful theory of linear viscoelasticity is not applicable. Moreover, the transition from linear to marked nonlinear viscoelasticity is associated with effects that from a material physics point of view are undesirable since they involve a decreased load-bearing capacity of the material. The following are some of the phenomena that have been reported to be associated with the transition to nonlinear viscoelasticity: (1) a shift of relaxation times to shorter time scales and a broadening of the relaxation time spectrum^{2–4}; (2) a marked change in the IR-dichroic ratio, indicating a marked onset of segmental motions, has been

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observed in glassy polycarbonate above a certain strain level (0.7%)⁵; (3) the existence of a certain strain level below which crazing at a given time is unable to develop⁶; for amorphous glassy polymers this strain level is approximately the same as the strain limit of linear viscoelasticity; (4) a deviation from linear stress dilatation around the region of transition from linear to nonlinear viscoelasticity has been observed for poly(methyl methacrylate)⁷ and poly(vinyl chloride)⁸ in uniaxial tensile creep experiments.

Furthermore, it is evident from the results of Benham and Hutchinson,⁹ who studied the cyclic creep and fracture of PVC, that the fatigue resistance was markedly reduced under stresses around the region of transition to nonlinear viscoelastic behavior. Although the transition from linear to nonlinear viscoelasticity is so important from a material physics and design point of view, very little work has been done to study the phenomenologic character of the transition and explain its molecular origin. Yannas¹ and Bertilsson and Jansson¹⁰ give an outline of this subject in their recent papers.

An applied macroscopic stress on a polymer sample is heterogeneously distributed among the polymer chains. A certain fraction of the material can be considered to be subjected to a higher stress level than the mean macroscopic stress. Therefore, the transition to nonlinear viscoelasticity is gradual. Moreover, the polymer chains in a glassy state are not in conformational equilibrium. It has been shown that the metastable state of a glass changes with time,¹¹ often called aging, and that this aging can be enhanced by mechanical stresses and strains.¹² Such changes will of course be in disagreement with the time invariance criterion of linear viscoelasticity. It is, however, possible to study the transition from approximately linear to nonlinear viscoelasticity as long as the experimental effects are significant and provided that time invariance is observed within the limits of experimental uncertainty.

Bertilsson and Jansson¹⁰ have studied the transition from approximately linear to nonlinear viscoelasticity for poly(methyl methacrylate) and poly(ethyl methacrylate) by uniaxial tensile creep experiments. They have found the β -mechanisms of the polymers to be of importance for the stress range of linear viscoelasticity, and they have presented a hypothesis that explains the transition to nonlinear viscoelasticity of the studied polymers as being due to stress activation of coupled α - and β -transition mechanisms. In this context it is evidently of interest to study antiplasticizing systems. Antiplasticization can occur when a small amount of a polar plasticizer or polar polymer is added to a polymer with a pronounced β -transition. The phenomenon is associated with a gradual suppression of the β -peak with an increasing amount of additive. Antiplasticization is therefore a valuable tool for studying the importance of the β -mechanism in the molecular mechanisms responsible for the appearance of nonlinear viscoelasticity.

In a previous report¹³ it was shown for the antiplasticizing system PVC/acrylonitrile-butadiene copolymer NBR-40 (acrylonitrile content 40% by weight) that the suppression of the β -peak of PVC was associated with a marked increase in the stress range of linear viscoelasticity. This result supports the hypothesis regarding the appearance of nonlinear viscoelasticity presented by Bertilsson and Jansson.¹⁰

Since antiplasticization seems to be one way of extending the approximately linear viscoelastic region of a polymer and also leads to an increase of the mod-

ulus, further investigations of such systems ought to be made. Antiplasticization is unfortunately also associated with a decrease in impact strength, and this fact may mean that antiplasticizing systems lack commercial interest.

Antiplasticization caused by a small amount of polar polymer is of special interest since (a) in contrast to low molecular weight plasticizers there are no migration effects associated with the added polymer and (b) such systems may give further information about the level of compatibility of the blended polymers.

Poly- ϵ -caprolactone (PCL) is reported to be compatible with PVC by dynamic mechanical measurement¹⁴ and gas diffusion measurement.¹⁵ Recently, however, Khambatta et al.,¹⁶ who studied the morphology in PVC/PCL blends by low-angle x-ray and light scattering, have found that PCL is only partially compatible with PVC and that the phase morphology of the blend is consistent with a model of lamellar structure consisting of PCL lamellae (amorphous below 40% by weight of PCL in the blend) separated by amorphous regions containing PCL and PVC. It is, however, expected that the ester groups of PCL are able to form pseudocrosslinks between the PVC chains and thereby suppress the β -mechanism of PVC in a manner similar to the action of ester plasticizers such as DOS and DOA.

The aim of this work has been to study the antiplasticizing effect of PCL on PVC with regard to changes in the dynamic mechanical loss factor spectrum, the creep compliance, the stress range of linear viscoelasticity, and the impact strength, in line with our previous work on PVC/NBR and the new aspects mentioned.

EXPERIMENTAL

Materials

The materials studied were prepared by physical blending of PVC and PCL weight ratios of 100/0, 98/2, 96/4, 94/6, 92/8, 90/10, and 88/12. The PVC powder with the common thermal stabilizer additives (organic Sn salt and Ca stearate, totally 1.5 parts per 100 parts PVC + PCL) was first milled for 15 min at about 160°C to a continuous slab using a steam-heated calender mill. The PCL was then added and milled into the slab. Pieces of the slabs were thereafter pressed to sheets for 15 min at 170°C for the measurements.

The PVC sample used was of suspension grade (supplied from Kema Nord AB, Sweden) with $\bar{M}_w = 74,000$ and a dilatometric glass transition temperature (T_g) $\sim +85^\circ\text{C}$. The PCL sample (PCL-700, Union Carbide Corp., U.S.A.) is highly crystalline, with $\bar{M}_n = 13,000$, $\bar{M}_w = 14,000$, and T_g around -60°C .¹⁷

From the pressed sheets, ordinary dumbbell-shaped specimens were machined out according to SIS 112116, approximately corresponding to ASTM D638 type II, for the uniaxial creep measurements. All specimens were annealed for 100 hr at about $+75^\circ\text{C}$ and then cooled very slowly. For the measurements of dynamic mechanical loss factor ($\tan \delta$), the sheets were further pressed for 15 min at 170°C. Thin strips with dimensions $60 \times 2.5 \times 0.04$ mm were cut from these sheets. The specimens for the impact test were machined out according to DIN 53504.

Measurements

Creep experiments in uniaxial tension were carried out for the blends at a temperature of $25.0^\circ \pm 0.5^\circ\text{C}$ over periods up to 1000 sec as previously described by Bertilsson and Jansson.¹⁰ From the recorded creep curves, the strains at 10, 100, and 1000 sec creep times were determined in order to enable isochronous stress-strain diagrams to be drawn. From the origin in the diagrams a straight line can be drawn through the points of low stress and strain. This line corresponds to approximately linear viscoelastic behavior. In this work we define the stress limit of linear viscoelasticity as the point where the experimental isochronous curve deviates from the straight line by more than 1% of the stress. This value is, of course, arbitrarily chosen but is of the same magnitude as the standard deviation of the experimental points. For each blend creep experiments at 10–15 different stress levels were carried out. The maximum stress level was chosen so as to give a clear nonlinear response within the experimental time range, roughly 1.2 times the limiting stress of linear viscoelasticity.

The measurements of the mechanical loss factor were carried out at 110 Hz in the temperature range of -120° to $+120^\circ\text{C}$, using a direct-reading viscoelastometer (Rheovibron, Model DDV II, Toyo Measuring Instrument Co., Japan).

High-speed tensile impact tests were carried out using a hydraulic machine in which the ramp input was a constant rate of elongation. The force and the elongation were measured by a force cell and electromechanical gauge, respectively, and they were registered on a storage oscilloscope.

The impact energy per unit volume was calculated from the area under the force-elongation curve and the dimension of the specimen (DIN 53504). The coefficient of variation of the values did not exceed 4%. In this work the elongation rate applied was 0.5 m/sec, and test was made for four specimens of each blend. The mean value of their impact energies was taken.

RESULTS AND DISCUSSION

α -Transition

With increasing amount of PCL in the blend, the α -peak is shifted to lower temperatures, its intensity is gradually reduced, and it becomes broader, as shown in Figure 1. The shift of the peak to lower temperatures is caused by the plasticizing effect of PCL. This effect is attributed to the fact that the PVC chains are separated from each other by the plasticizing additive causing an increase in free volume and a weakening of the cohesive forces between the PVC chains.

When an additive of plasticizing ability is mixed with a polymer, a broadening of its α -peak is usually apparent. In a study of antiplasticization of PVC by DOP, DOS, DBS, and TCP,^{18,19} Kinjo has observed that (a) the plasticizers caused different broadening of the α -transition region, (b) the suppression of the β -peak of PVC was almost the same for all plasticizers, and (c) the antiplasticizing ability of the additives, referred to modulus increase, was inversely related to their ability to broaden the α -peak.

The broadening of the α -transition region was considered to be a consequence of the multiplicity of molecular conformations which plasticizer molecules can

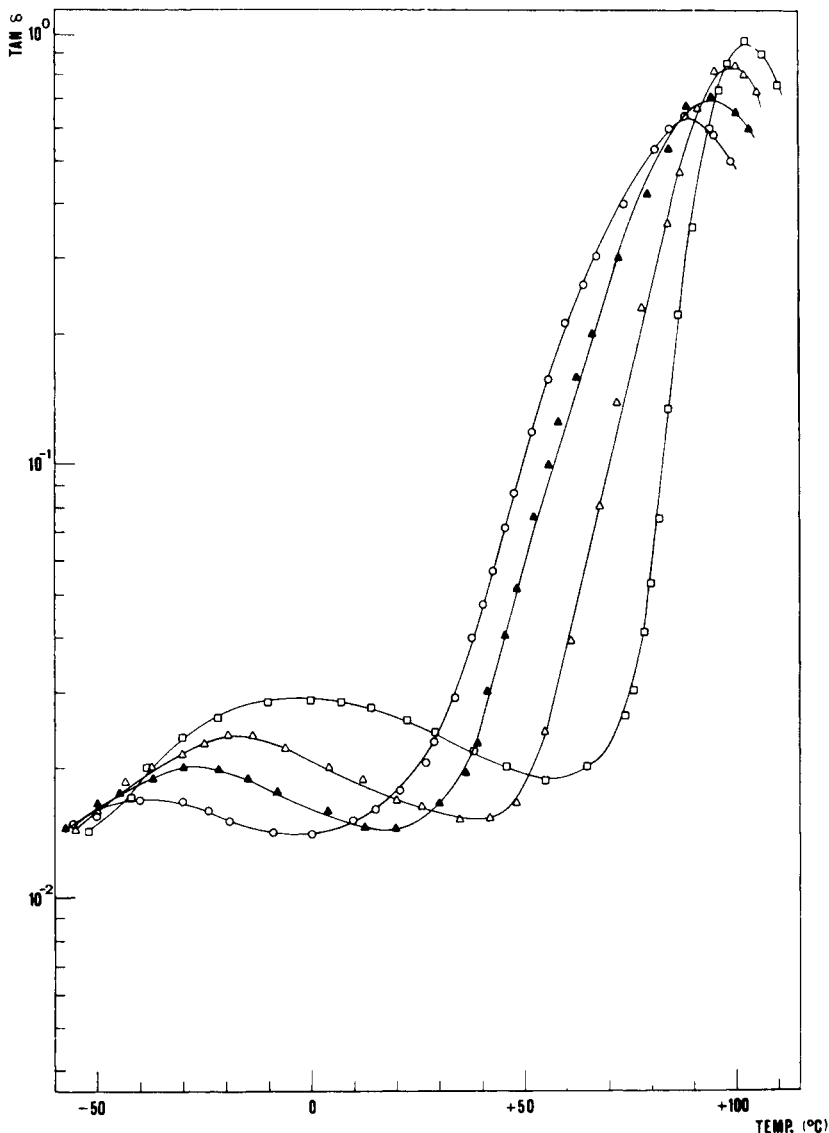


Fig. 1. Loss tangent as function of temperature for PVC/PCL blends: (\square) 100/0; (Δ) 96/4; (\blacktriangle) 92/8; (\circ) 88/12.

form, resulting in multiple ways of causing the separation of PVC chains from each other by each plasticizer molecule. Thus, plasticizers with long, flexible alkyl groups (DOS and DBS) caused a relatively larger broadening of the α -peak compared with those which have a more rigid molecular structure (TCP and BBP).

It must also be pointed out that the processed PVC material is believed to have a heterogeneous phase structure: (1) there are density fluctuations in the amorphous regions due to variations in chain packing,^{20,21} (2) PVC has a certain degree of crystallinity, and (3) regions of unmelted primary particles of the PVC (particle structure) may exist.²⁰ Incorporation of a plasticizer in PVC will therefore result in microheterogeneous plasticization, i.e., some regions in the

PVC phase will become more plasticized than others. Such an effect, we believe, is the major reason for the broadening of the α -transition region of PVC. Compared with low molecular weight plasticizers such as DBS and DOS,¹⁸ PCL is less able to shift the α -peak of PVC to lower temperatures, but the tendency to broaden the peak is rather similar.

β -Transition

The β -peak of PVC is markedly suppressed and shifted to lower temperatures with increasing amount of PCL in the blends, as shown in Figure 2. In part, antiplasticization of a polymer is evident as a suppression of its β -peak. For PVC the suppression is considered to be due to a pseudocrosslinking effect caused by a strong interaction between the polar groups of the additive and the PVC chains. The pseudocrosslinks will hinder the β -mechanism motions and thereby stiffen the chains. In Figure 2 it can be clearly seen that the suppression starts from the higher temperature side corresponding to motions with relatively longer relaxation times. When the PCL content in the blend is increased, motions with progressively shorter relaxation times are hindered. This phenomenon has also been observed by Kinjo¹⁸ and Pizzoli et al.²² in studying antiplasticization of PVC by low molecular weight plasticizers.

Pizzoli et al.²² have suggested that the β -peak of PVC is due not to local mode motions of the main chain but rather to a kind of cooperative motion. By plotting the height and area of the β -peak versus the content of additive (DOP, DBP, or diphenyl plasticizer) and extrapolating to zero, they estimated that 1 mole

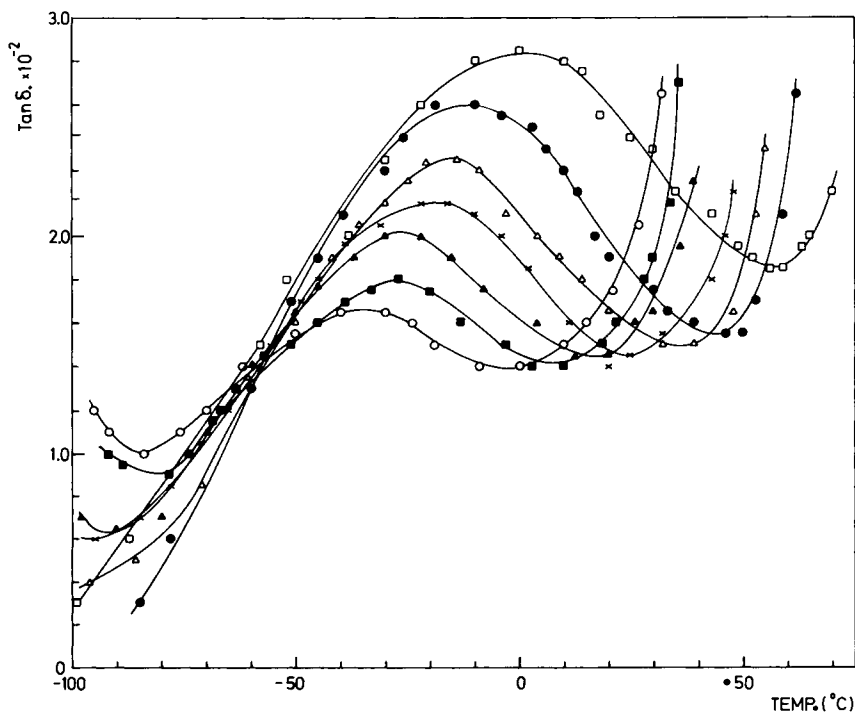


Fig. 2. Loss tangent as function of temperature over the β -transition range for PVC/PCL blends: (\square) 100/0; (\bullet) 98/2; (\blacktriangle) 96/4; (\times) 94/6; (\blacktriangle) 92/8; (\blacksquare) 90/10; (\circ) 88/12.

plasticizer per 20 repeat units of PVC ought to be sufficient for complete suppression of the β -peak of PVC. They have concluded that this mole ratio is too low to hinder a local mode relaxation. This method used by Pizzoli et al.²² is rather uncertain because at high plasticizer content the β -peak will be overlapped by the α -transition peak. We believe, however, that valuable information, such as a qualitative picture of the antiplasticizing effect, can be obtained by using such a method. It should also be pointed out that the decrease in β -peak intensity and area with decreasing PVC concentration in the blend is of minor importance compared with the decrease caused by the antiplasticizing effect.

The minimum amount of PCL in the blend necessary for complete suppression of the β -peak of PVC was estimated using the procedure applied by Pizzoli et al.²² This was also done for PVC/DOS (data taken from Kinjo¹⁹) and PVC/DOA (data taken from Bertilsson²³). The corresponding ester group concentrations in the systems were also calculated. The results are given in Table I.

For PVC/DOA and PVC/DOS, about one ester group per 20 vinyl chloride (VC) units of PVC is required for the β -peak to disappear. This ester group concentration is half the value reported by Pizzoli et al.²² for the PVC/DOP, PVC/DBP, and PVC/diphenyl plasticizer systems. From the point of view of an antiplasticizing pseudocrosslinking theory, such a result is to be expected because in each case one of the two ester groups of DOP, DBP, and diphenyl plasticizer is sterically greatly hindered by the aromatic ring structure from interacting with PVC and forming secondary bonding.

For PVC/PCL, one ester group per 10 VC units of PVC was estimated to give a complete suppression of the β -peak of PVC. The difference in ester group concentration, compared with the PVC/DOA and PVC/DOS systems, is mainly to be regarded as being due to the difference in molecular size. The steric conditions for the ester groups along the PCL chains to form pseudocrosslinking between the PVC chains ought to be approximately the same as for ester groups of a low molecular weight plasticizer with long alkyl groups, such as DOA and DOS, because the methylene groups in the PCL chains provide high chain flexibility. DOA and DOS can be regarded as fully compatible with PVC. The relatively higher ester group concentration estimated for the PVC/PCL blend is, therefore, mainly attributed to a lower miscibility of PCL with PVC.

TABLE I
Minimum Concentration of Additive (Percent by Weight) and Corresponding Ester Group Concentration Necessary for Complete Suppression of the β -Peak of PVC

System	Additive, ^a % by weight	Mole ester groups per repeat unit of PVC	Number of ester group per number of repeat units of PVC
PVC/PCL	16	0.10	1/10
PVC/DOA ^b	14	0.055	1/18
PVC/DOS ^c	14	0.049	1/20

^a Values were obtained by the procedure of Pizzoli et al.²²

^b Data taken from reference 23.

^c Data taken from reference 19.

Creep Properties

Other indications of the antiplasticizing effect of PCL on PVC are shown in Figures 3 and 4. Figure 3 shows the uniaxial creep compliance in the linear viscoelastic range after creep times of 10, 100, and 1000 sec as a function of PCL content in the blend. There are minima in the compliances, with a decrease of 10%–12%, and they are located at about 5% by weight of PCL. It also shows that the time dependence of the compliance increases with increasing PCL content in the blend. This fact is consistent with the observed broadening of the α -peak (see Fig. 1).

It should also be pointed out that the antiplasticizing effect is more pronounced at a lower testing temperature because the antiplasticization behavior is related to the difference between T_g and the testing temperature.¹⁹ In this work, the antiplasticizing effect was studied only at room temperature.

Figure 4 shows the limiting stress of approximately linear viscoelasticity as a function of PCL content in the blend for creep times of 10 and 1000 sec. In all creep experiments, the lateral contraction of the specimens was also recorded simultaneously with the axial extension. Nonlinear viscoelastic responses were found to occur at about the same stress levels according to both axial extension and lateral contraction data. The data from the contraction measurements have been used to augment the extension data in the determination of limiting stresses.

The general character of the curves in Figure 4 is rather similar to that of the linear viscoelastic compliance curves (Fig. 3). The antiplasticizing effect is, however, more pronounced. Up to 5.5% by weight PCL, the stress limit (10-sec curve) is increased by about 25%. Thus, in the antiplasticizing region, PCL affects the molecular mechanisms responsible for the nonlinear viscoelastic behavior of PVC more than it affects those in the approximately linear viscoelastic region. This behavior has also been observed in the antiplasticizing systems such as PVC/NBR-40,¹³ PVC/DOA, and PVC/DOP.²³ Some experimental results regarding the effects of PCL and DOA on the creep properties of PVC are listed in Table II.

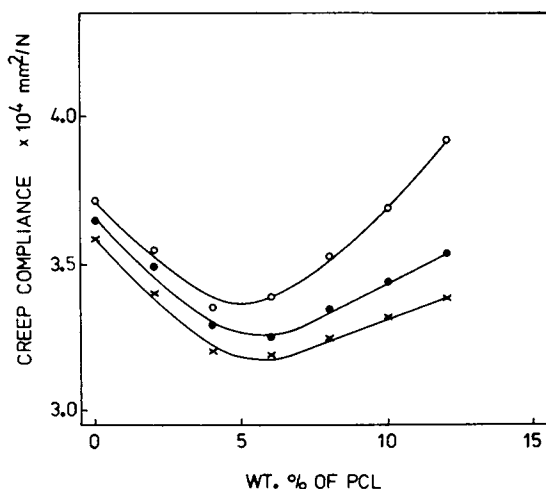


Fig. 3. Tensile creep compliance in the linear viscoelastic range vs PCL content in the PVC/PCL blends. Creep time: (x) 10 sec; (●) 100 sec; (○) 1000 sec.

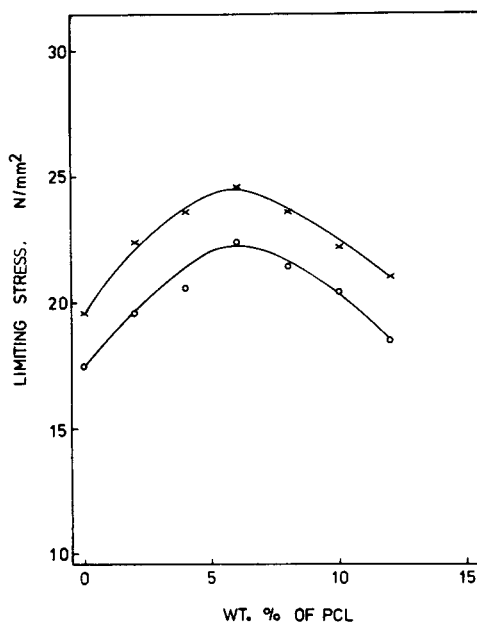


Fig. 4. Stress limit of approximately linear viscoelasticity vs PCL content in the PVC/PCL blends. Creep time: (X) 10 sec; (O) 1000 sec.

TABLE II
Antiplasticizing Effects of PCL and DOA on PVC from Uniaxial Creep Experiments

System	Increase in stress limit of linear viscoelasticity, ^a %	Decrease in linear visco-elastic creep compliance, ^a %	Mole ester groups per repeat unit of PVC ^a
PVC/PCL	25	12%	0.035
PVC/DOA ^b	40	12%	0.018

^a Values correspond to the maximum antiplasticizing effect of the additives observed at 10 sec creep time and at room temperature.

^b Data taken from reference 23.

The magnitude of the minimum in creep compliance, at 10 sec creep time and room temperature, is the same for both PVC/PCL and PVC/DOA (12%) in the linear viscoelastic range. The stress limit of approximately linear viscoelasticity is, however, increased by 25% for PVC/PCL but 40% for PVC/DOA. Moreover, the minimum of the linear viscoelastic compliance or the corresponding maximum of the stress limit of linear viscoelasticity is not observed at the same ester group concentration. For PVC/PCL, the maximum antiplasticizing effect occurs at approximately twice the amount of added ester groups per same number of repeat units of PVC. This result is consistent with the results in Table I, which were estimated from the β -peak suppression.

The results of Tables I and II indicate that only about half the added PCL is able to penetrate and interact within small segments of PVC chains and take part in the mechanism of antiplasticization. Such a result is in agreement with the results of Khambatta et al.,¹⁶ who have found that PCL is only partially miscible with PVC.

The differences in stress limit of linear viscoelasticity may be due to less fa-

vorable kinetic conditions for PVC and PCL segments to interact, resulting in less influence on the mechanisms responsible for the occurrence of nonlinear viscoelasticity. It has been suggested that the appearance of nonlinear viscoelasticity in PVC is due to stress activation of a coupled α - and β -transition mechanism.¹³ Thus, if the β -mechanism of PVC is restrained due to a polar additive (antiplasticizer), the coupling mechanism will also be restrained in proportion to the amount of additive. A higher stress threshold for the appearance of nonlinear viscoelasticity will therefore arise.

It should be pointed out that it is unlikely that the antiplasticization in PVC is due to a decrease in free volume caused by "hole filling" by the additive. With such a concept it is very difficult to explain the observed suppression and the shift of β -peak of PVC to lower temperatures with increasing amount of the additive. The results of this work strongly support the proposed pseudo-crosslinking concept of antiplasticization.

One should ask whether PCL is able to form a crystalline phase in the blend studied. As Khambatta et al.^{15,16} have reported, the PVC/PCL blends are amorphous below 40% by weight PCL in the blend. This indicates that the changes in creep properties observed in this work can hardly be attributed to an increase in crystallinity.

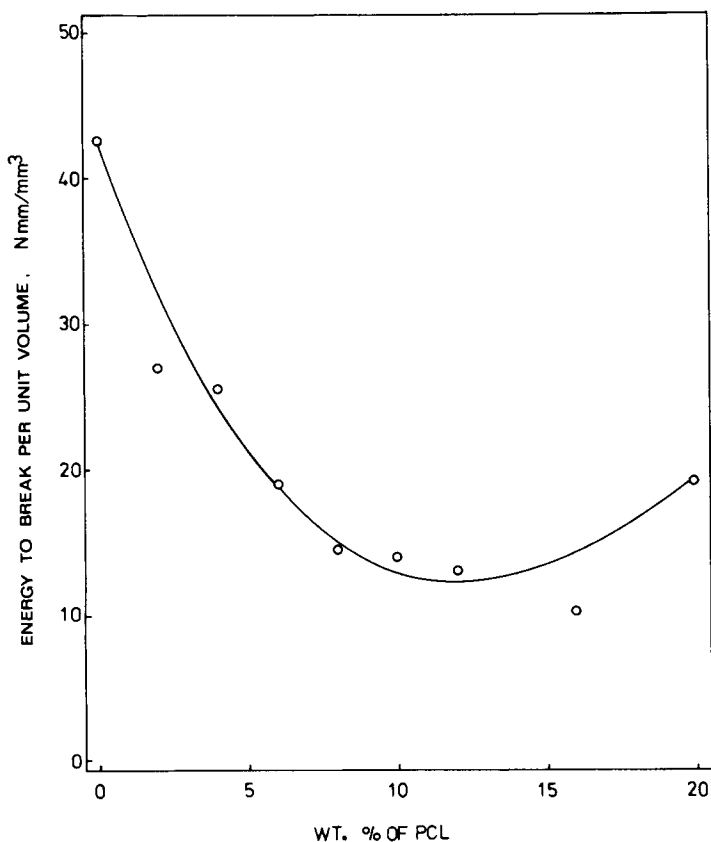


Fig. 5. Impact strength vs PCL content in the PVC/PCL blends.

Impact Properties

Figure 5 shows the impact strength, given as the energy to break per unit volume, as a function of PCL content in the blend. The impact resistance is reduced by a factor of 3.5 with increasing PCL content up to about 12% by weight and thereafter slowly increases. This impact behavior fits well into the pattern of antiplasticization. There is considerable evidence that impact strength is closely related to secondary transitions of a polymer. The polymers having a large β -peak usually exhibit a high impact strength.^{24,25} It is therefore to be expected that if the β -peak of PVC is suppressed due to antiplasticization, its impact resistance will also be decreased. The higher PCL content in the blend (about 12% by weight of PCL) at which maximum antiplasticization occurs, compared with the creep experiments, is attributed to the short time scale of loading in the impact tests.

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