

Antiplasticization and Transition to Marked Nonlinear Viscoelasticity in Poly(vinyl Chloride)/Acrylonitrile-Butadiene Copolymer Blends

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Synopsis

A series of PVC/NBR blends with varying acrylonitrile (AN) content in the NBR has been studied in uniaxial tension creep tests. The tests have been carried out at $21.5 \pm 0.5^\circ\text{C}$ covering creep times from 10 to 1000 sec. NBR with low AN content, having poor compatibility with PVC, gives the blends with higher compliance and increased time dependence of the compliance. A higher AN content in the NBR gives the blends with the opposite properties when the NBR is added in small amounts. NBR with 40 wt-% AN is found to act as an antiplasticizer giving minimal creep compliance when 7 wt-% NBR is added. The antiplasticization reveals a considerably increased stress level at which the transition from approximately linear to marked nonlinear viscoelasticity occurs and a decreased stress dependence of the creep compliance in the nonlinear viscoelastic range. Since the antiplasticization is also associated with a suppression of the β -transition mechanism, the results provide a demonstration of the importance of β -mechanism in the stress activated processes responsible for the appearance of nonlinear viscoelasticity in solid polymers.

INTRODUCTION

It is common practice to mix existing polymers in such a way that the resulting material has certain properties superior to those of the individual components. In this way, commercially successful high-impact thermoplastics based on brittle poly(vinyl chloride) (PVC) and polystyrene are being produced by addition of a small amount of a rubber.

The most common ways to characterize the materials have been dynamic mechanical investigations, fracture studies, and examinations of the fine structure with electron microscopy. The results from such investigations have given much information concerning the compatibility of the rubber with PVC.

In most polymer blends, incompatibility is thermodynamically true and is mainly evidenced by two damping maxima representing the parent polymers. However, PVC/NBR blends were reported to form a compatible system when the acrylonitrile (AN) content in NBR is larger than 40 wt-%.¹ Many studies have been carried out to characterize the poly(vinyl chloride)/acrylonitrile-butadiene copolymer (PVC/NBR) blends, e.g., dynamic mechanical property,¹⁻⁵

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impact strength,^{2,6,7} morphology,¹ and gas transport.⁸ However, no available data on the creep property of the blend were reported, although it is of significant importance in engineering applications.

Tensile creep tests on several stress levels over a limited time scale provide a good characterization of the engineering properties as well as a basis for a physical examination of materials.⁹ If creep measurements are carried out over many stress levels, the results give information on (a) the transition from the approximatively linear to the marked nonlinear viscoelasticity of the material, and (b) the tendency of increasing the nonlinearity with increasing applied stress.

The present work explores such properties of the PVC/NBR blends as the AN content in the NBR of the blends is varied. The results are discussed with relation to the compatibility of the blends.

MICROSTRUCTURES OF PVC/NBR BLENDS

The morphologic structures of PVC/NBR blends have been examined by Matsuo et al.¹ using contrast electron microscope and the results correlated with dynamic mechanical measurements. The AN content in the NBR was found to significantly affect the compatibility of the blends. NBR with 8 wt-% AN was found to form an incompatible system with PVC, and only slightly smoother phase boundaries were observed as compared to completely incompatible PVC/polybutadiene blends. As the AN level of the NBR was increased to 20 wt-%, there was a continuous rubber network extending throughout the PVC matrix, even in the blends with low rubber content. The rubber particles were also observed to be finer. Dynamic mechanical measurements of this blend showed that the location of the α -transition peak of the rubber phase was not changed with changing rubber content in the blends. However, the corresponding peak for the PVC phase was shifted to lower temperature with increasing rubber content. Such a system, according to Matsuo et al.,¹ is called a semicompatible system and was also observed in PVC/ethylene-vinyl acetate copolymer (EVA) blends with a vinyl acetate content of 65 wt-% and milled at 160°C.¹⁰

With 30 wt-% AN in the rubber, a fine dispersion of the rubber particles in the PVC matrix appeared together with a continuous rubber network. A relatively compatible system was achieved with 40 wt-% AN in the NBR. Microheterogeneity was still observable, but rubber particles could not be identified, at least not exceeding 100 Å.

In dynamic mechanical measurements of the compatible PVC/NBR blends (AN content 41.6 wt-% in NBR), the α -transition peak of PVC was shifted toward lower temperatures in proportion to the NBR content of the blends. However, the α -transition peak of the NBR was almost lost in the β -transition mechanism of PVC. A slight suppression of the β -transition peak of the PVC in proportion to the NBR content in the blend could be observed. It was also evident that for the blends containing less than 10 wt-% NBR, the dynamic modulus (E') values were larger than those of pure PVC over the temperature range between the α - and β -transitions of PVC. This may be due to the so-called *antiplasticizing effect*. It should be noted that this effect is not visible for the PVC/NBR blends with less than 20 wt-% AN in the NBR. According to the mechanism of the

antiplasticizing effect, this would be explained by the mutual interaction between the PVC and NBR.

ANTIPLASTICIZATION

It is well known that small amounts of common low molecular plasticizers, i.e., esters of phthalic acids, added to PVC make the PVC stiffer and slightly more brittle. This phenomenon was interpreted as the antiplasticizing effect of the plasticizers. Jackson and Caldwell¹¹ have studied the antiplasticizing effect of many substances on polycarbonates and found chlorinated biphenyls to be the most effective. The antiplasticized materials showed an increase in modulus as well as in tensile strength. Jackson and Caldwell have also found that poly-(methyl methacrylate) can be antiplasticized but not polystyrene. Robeson and Faucher¹² have reported that antiplasticization of polycarbonates and polysulfones was signified by the suppression of the β -transition process of the polymers. This was evident from the results that polymers showing an antiplasticizing effect show a decrease in impact strength and that polystyrene, having no pronounced β -transition, showed no antiplasticizing effect. The suppression of the β -transition mechanism as related to antiplasticization was further examined on PVC with small amounts of common phthalic acid ester plasticizers,^{13,14} on antiplasticized crosslinked epoxy,¹⁵ and on polycarbonates.¹⁶

Most of the reports on antiplasticized systems have also shown nonadditivity in specific volumes of the systems.^{13,16} The same results were reported for the compatible polymer blends such as PVC/NBR (AN \geq 30%)⁸ and PVC/EVA (vinyl acetate = 65 wt-%).⁹ Further evidence for antiplasticization in PVC/NBR with high AN content has been reported by Hidemaro¹⁷ who found increased tensile strength, decreased elongation to break in constant strain-rate tensile tests, and the nonadditivity in specific volumes of the blends.

The β -transition in PVC is due to local main-chain movements of a cooperative character.¹⁴ If a polar additive such as an ester-type plasticizer or a polymer having strong polar groups is added to PVC, the interaction will result in secondary bond crosslinks between PVC chains. This will then suppress the β -transition process of the PVC. The specific volume contraction observed when such an antiplasticizing substance is added is evidence of this strong interaction. Further evidence is the reported increase in the second moment (ΔH^2) in the NMR absorption line when small amounts of polar plasticizer are added to PVC.¹⁸ Depending on the type of plasticizer, the maximum antiplasticizing effect on PVC seems to be observed at 5–10% plasticizer.

In line with aspects mentioned above, it is very possible that the antiplasticizing effect on PVC due to addition of highly polar NBR (AN = 40%) may take place, at least in the low composition range.

NONLINEAR VISCOELASTICITY

Most polymer materials exhibit an approximatively linear viscoelastic behavior at low strain levels when subjected to an uniaxial tensile stress. At a certain stress level, molecular mechanisms are activated to the extent that the material becomes significantly nonlinear. The appearance of nonlinear viscoelastic behavior in solid polymers has been reviewed by Yannas.¹⁹ The definition of the stress or

strain limit of linear viscoelasticity will naturally be arbitrarily chosen. In this work, we use a deviation from linear viscoelasticity exceeding 1% as a criterion for marked nonlinear viscoelasticity. It must be pointed out that for amorphous and crystalline polymers used in engineering applications, the strain limit of linear viscoelasticity lies between 0.005 to 0.01 uniaxial strain. Thus, the strain limit will be quite independent of the kind of definition of strain used.

According to the observed shift in the relaxation time spectrum around the transition to marked nonlinear viscoelasticity, it is proposed that the stress-activated mechanism causing the considerable nonlinearity is of a highly cooperative nature. In a study of the limits of linear viscoelasticity in poly(methyl methacrylate) and poly(ethyl methacrylate), it has been proposed that the appearance of nonlinearity was due to a coupling effect between the α - and β -transition mechanisms.²⁰ Thus, if the β -transition mechanism of a polymer is suppressed, this will eventually lead to a suppression of the mechanisms responsible to the appearance of nonlinear viscoelasticity. If this is true, the stress limit for the occurrence of marked nonlinear viscoelasticity should be increased by addition of a substance providing an antiplasticizing effect on the polymer.

EXPERIMENTAL

Materials and Specimens

The materials investigated were prepared by physical blending of PVC and NBR at weight ratios of 100/0, 94/4, 93/7, 90/10, and 85/15, using a steam-heated calender mill for 15 min at 160°C, and thereafter by pressing for 10 min at 170°C to a 2-mm-thick sheet.

The PVC powder and the common stabilizing additives used (organic Ba–Cd salts and Pb stearate, totally 3 parts per 100 parts of PVC + NBR) were first milled to a continuous slab. The NBR was then added and milled into the slab.

The PVC used was of suspension grade with $\overline{M}_w = 74,000$. The NBR samples were of three grades with different AN contents (see Table I).

From the pressed sheets, ordinary dumbbell-shaped specimens were machined out according to SIS 112116 (approximately corresponding to ASTM D638 Type II). Before being subjected to creep measurements, each specimen was annealed 100 hr at 75°C and then cooled very slowly.

Measurements

Uniaxial creep measurements during periods up to 1000 sec were made for the blends at a temperature $21.5^\circ \pm 0.5^\circ\text{C}$. The number of stress levels chosen varied between 10 and 20, depending on the blend. The maximum stress level was chosen so as to give a clear nonlinear response within the experimental time range, approximately 1.2 times the limiting stress of linear viscoelasticity. The creep equipment used and the measurement procedures have been described by Bertilsson et al.²⁰

Isochronous stress–strain diagrams were determined from the recorded creep curves by measuring the strain after 10, 100, and 1000 sec. From the diagrams,

TABLE I
Polymers Used in the Blends

Polymers	Commercial name	Manufacturer
PVC	Pevikon S 655	KemaNord AB, Sweden
NBR-1	Hycar 1024 (AN = 21.7%) ^a	B. F. Goodrich Chem. Co., U.S.A.
NBR-2	Hycar 1043 (AN = 29.6%)	B. F. Goodrich Chem. Co., U.S.A.
NBR-3	Hycar 1041 (AN = 41.6%)	B. F. Goodrich Chem. Co., U.S.A.

^a AN contents determined by Jorgensen et al.²¹

it was possible to determine the extent of the linear viscoelastic range. A best-fit straight line was drawn through the points of the lowest stress levels to origin. The linear viscoelastic limit is defined as the point where the best-fit curve for all stress levels deviates from the straight line by more than 1%.

RESULTS AND DISCUSSION

From the factors discussed in the introduction, it was expected that a variation of AN content in the NBR would give quite different levels of creep compliance. However, differences in the stress dependence of the creep compliance are also quite apparent. In Figure 1, the creep compliance is plotted as a function of creep stress for the blends with 10 wt-% NBR of three different types, respectively.

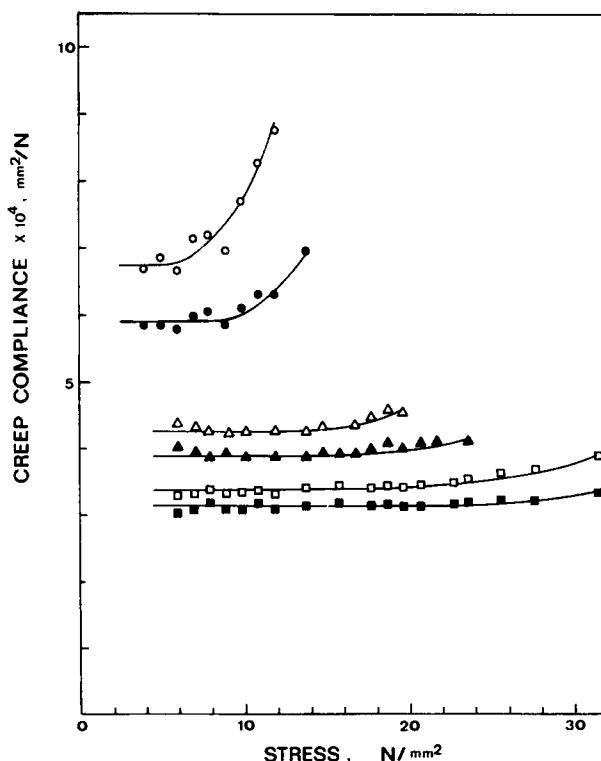


Fig. 1. Creep compliance vs. stress for PVC/NBR blends with NBR content 10 wt-%. PVC/NBR-1: (●) 10 sec; (○) 1000 sec. PVC/NBR-2: (▲) 10 sec; (△) 1000 sec. PVC/NBR-3: (■) 10 sec; (□) 1000 sec.

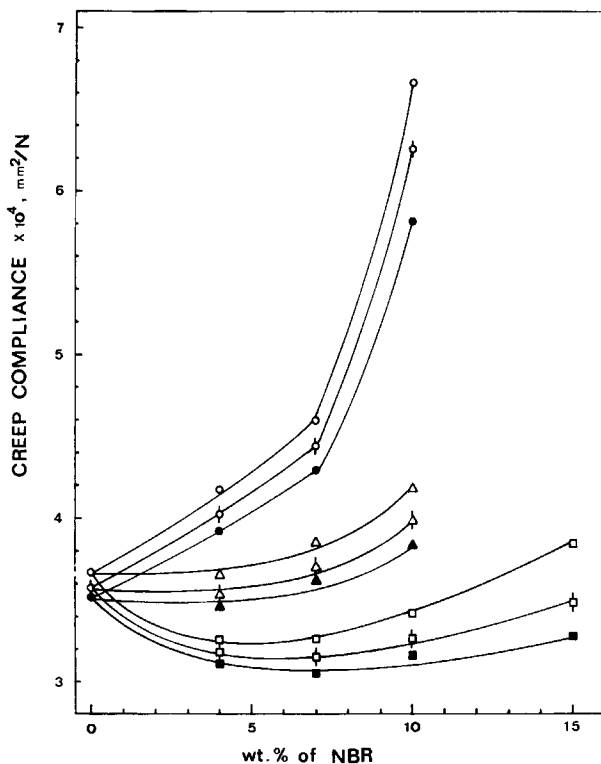


Fig. 2. Creep compliance vs. NBR content in the PVC/NBR blends. PVC/NBR-1: (●) 10 sec; (○) 100 sec; (○) 1000 sec. PVC/NBR-2: (▲) 10 sec; (△) 100 sec; (⬆) 1000 sec. PVC/NBR-3: (■) 10 sec; (◻) 100 sec; (◻) 1000 sec.

All the curves are isochronous, and the three samples are each represented by a 10- and a 1000-sec curve. The stress range of the approximately linear viscoelastic behavior is considerably decreased when the AN content in the NBR is decreased. There is also a marked difference in the expanding deviation from linear theory above the linear limit. Moreover, the time dependence of the linear viscoelastic compliance as well as the nonlinear viscoelastic compliance are more pronounced when the AN content in the NBR is decreased. The PVC/NBR-3 blends, which are most compatible, behave almost the same as the PVC with no additives, with the exception of a slightly lowered compliance level.

Figure 2 shows the creep compliance in the linear viscoelastic range versus NBR content. The antiplasticizing effect in the more compatible blends is evident. The plasticizing effect of NBR-1, with only 21.7% AN, may be operative at very low rubber content in the blends (<4%), although the analysis of the fine structure and the dynamic mechanical damping property classified the PVC/NBR-1 blends as a semicompatible system. With 29.6% AN in NBR, the linear viscoelastic creep properties of the blends seem to be unaffected up to about 5% NBR content. NBR-3 shows a clear antiplasticizing effect. For 1000 sec of creep time, the compliance corresponding to that of pure PVC is attained at 15 wt-% rubber; and for the shorter creep time, it is attained at still higher rubber content because the time dependence of the linear viscoelastic compliance increases with increasing rubber content.

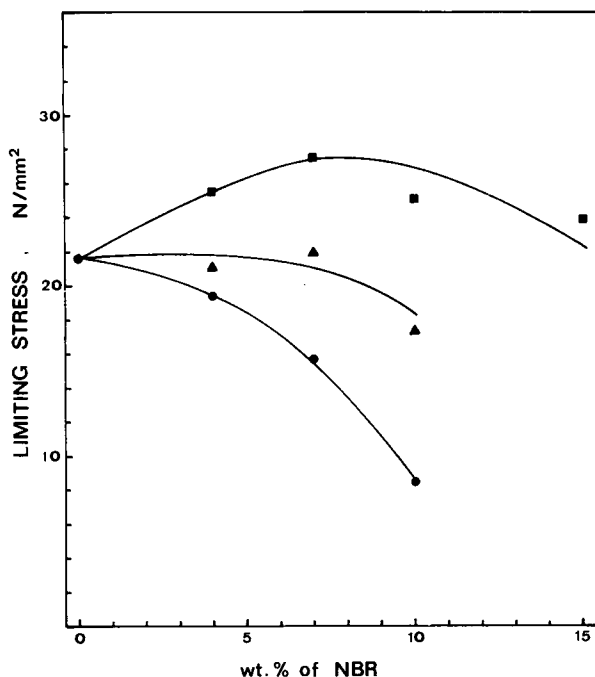


Fig. 3. Limiting stress vs. NBR content in the PVC/NBR blends for 10 sec creep time: (●) PVC/NBR-1; (▲) PVC/NBR-2; (■) PVC/NBR-3.

Figure 3 shows the limiting stress of linear viscoelastic behavior of the blends plotted versus NBR content. The general character of this figure is rather similar to the behavior of the compliance. However, the antiplasticizing effect is more clearly visible. The PVC/NBR-3 blend showed a maximum antiplasticization at about 7% NBR. For PVC/NBR-2 blends, there was some indication of a weak antiplasticizing effect in the composition range up to 7% of the NBR.

The antiplasticizing effect of NBR of PVC was also expected in gas transport results. The rates of permeation and diffusion of He, O₂, N₂, and CO₂ in PVC/NBR blends decreased, but activation energy for diffusion increased with increasing AN content in the NBR.⁸ This is due to reduced segmental mobility of the polymer chains because of increased interaction between PVC and NBR with increased AN content.

For a 10-sec creep time, the decrease in the linear viscoelastic creep compliance was about 14%. Under the same conditions, the increase in limiting stress as shown in Figure 3 is about 27%. Since the decrease in compliance is not proportional to the increase in limiting stress, we suspect that the mechanism behind the antiplasticization will also influence the transition to nonlinear viscoelasticity. For clarity, it must be mentioned that the limiting strain is, within the limit of the experimental uncertainty, independent of rubber content up to the concentrations shown in Figure 3. There is an exception, however, for the system PVC/NBR-1, which showed a decrease in strain limit from 0.007 for pure PVC and PVC with 4% rubber content down to 0.005 for 10% rubber content.

The molecular interpretation of the transition from approximately linear to marked nonlinear viscoelasticity was discussed by Bertilsson et al.²⁰ They found that the β -mechanism was involved in the linear-to-nonlinear transition.

Segmental motions can be stress activated at temperature far below the T_g , as shown for polycarbonate.²² According to Bertilsson et al.,²⁰ a coupling effect between the α - and β -transition mechanisms (providing conditions for the stress activated process) is responsible for the ostensible nonlinearity. Thus, it is possible to explain the occurrence of nonlinear viscoelastic responses without any irreversible deformation mechanisms being involved. All macroscopic deformations reported in this work were fully recoverable.

When the β -transition mechanism of PVC is restrained due to polar interaction with NBR, leading to secondary crosslinks, the coupling mechanism between the α - and β -mechanisms will be restrained in proportion to NBR content. A higher stress threshold for the appearance of nonlinear viscoelasticity will arise. At higher plasticizer or antiplasticizer contents, the possible sites for the secondary crosslinks will be saturated; and due to the large amount of flexible polymer substance added, the additive will act as a plasticizer. Thus, we get a maximum in modulus and linear stress limit for the plasticized blend if the system is compatible enough, i.e., the PVC/NBR-3 blend.

One may ask to what extent the crystallinity of the PVC will affect the transition from the linear to nonlinear viscoelasticity and to what extent a plasticizing additive will affect the crystallinity. Shtarkman et al.²³ have studied composition dependence of the crystallization on the plasticized PVC using small-angle x-ray scattering. It was found that small amounts of dioctyl phthalate (DOP) (10–15 wt-%) show no effect, but larger amounts could reduce the crystallinity slightly. Pezzin et al.²⁴ have reported that the β -transition of PVC plasticized by DOP was not affected by changes in crystallinity from 10% to 20%. This suggested that the rise in stress limit for the linear viscoelastic range is not attributed to an increase in crystallinity.

CONCLUSIONS

1. If NBR has a low AN content, the compatibility of the PVC/NBR blend will be lower and the stress on the PVC phase is comparatively high, leading to nonlinear viscoelastic behavior of the blend at low macroscopic stress levels and to a high deviation from linearity above the linear stress limit.

2. If the AN content in NBR is high (>20%), the compatibility of the PVC/NBR blend is increased. Small additions of NBR (<10%) will then act as antiplasticizer. In the composition range where the antiplasticizing effect has been demonstrated, the stress limit of linear viscoelasticity is increased and the deviation from linearity above the stress limit is relatively small.

3. The relation between the β -transition mechanism and the transition from the approximately linear to the marked nonlinear viscoelasticity agrees with the explanation of stress-activated nonlinear viscoelasticity proposed earlier.²⁰

4. The impact strength of a blend is inversely related to the blend compatibility.²⁵ The results show an unfortunate contradiction between the impact strength and the long-term load applicability of PVC blended with NBR.

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