

Processing and Characterization of Blends of Fluoroelastomers with Semirigid Liquid Crystal Polymers

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SYNOPSIS

Fluoroelastomers (FEs) usually have working temperatures above 150°C and a great resistance to aggressive agents such as oils, fuels, aliphatic and aromatic solvents, steam, moderate acid, and basic environments. Liquid crystal polymers (LCPs) can be effective processing aids and reinforcing agents for elastomers. These characteristics are very attractive to lower melt viscosity and to stiffen and strengthen the final product through a simple blending. Among the LCPs, the semirigid LCPs seem the most appealing for blending with flexible thermoplastics (FTs) because their processing temperatures can be arranged to be in the same processing temperature range of FTs and because the presence of flexible segments can improve the compatibility with the flexible matrix. This is very important especially for FEs that are subjected not only to mechanical degradation, but also to thermal degradation. Blends of FEs with two types of semirigid LCPs show easy processability and enhanced mechanical and thermomechanical properties. These improvements were observed both for pure FEs and for filled vulcanized systems. The improvement of the mechanical properties is below that expected on the basis of the additive rule due to the incompatibility between the components; nevertheless, an impressive increase of the elastic modulus, up to 40 times, was noticed by adding 20% of LCP. In vulcanized systems, the tensile strength is also increased, whereas the elongation at break is slightly reduced. The working temperature is also drastically increased both in vulcanized and in unvulcanized systems. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The most important effects of blending flexible polymers with liquid crystalline polymers (LCPs) concern processability and mechanical properties.¹⁻⁴ Both improvements are very useful when the thermoplastic matrix is an elastomer. Many rubbers are difficult to process because of their inherently high viscosity and most need reinforcing agents and/or crosslinking to enhance their poor mechanical properties. Moreover, the processing of these materials is usually long and expensive.

Blending rubbers with LCPs can give rise to materials having easy processability and good mechanical properties in a single step. Nevertheless, only a

few patents and articles have been devoted to this subject and include fluoroelastomers (FEs),^{5,6} silicic rubbers,⁷ SEBS rubbers,⁸⁻¹⁰ vinylic rubbers usually used in tire manufacturing,¹¹ and EPDM rubbers.^{12,13}

A possible obstacle to the use of this technology can be attributed to different processing conditions and to the incompatibility between the elastomers and the LCPs. These latter, indeed, call for quite high processing temperatures, usually much higher than those adopted for rubbers. Moreover, the strongly different chemical nature of the two components gives rise in most cases to blends with poor mechanical properties. Both problems can be overcome, or at least reduced, by using semirigid LCPs.

LCPs, prepared by melt condensation of equimolar amounts of an aliphatic diacid, e.g., sebacic acid (S), and 4-4'-dihydroxybiphenyl (B) with different amounts of 4-hydroxybenzoic acid (H), and

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Table I Main Characteristics of the Materials

	Composition	Commercial Name	Density (g/cm ³)	Mooney Viscosity
V70	Vinylidene fluoride Hesafuoropropene Tetrafluoroethylene Chlorotrifluoroethylene	Viton B70	1.86	46
TN	Vinylidene fluoride 1 Hydropentafluoropropylene Tetrafluoroethylene	Tecnoflon	1.77	65–80

4-hydroxynaphthoic acid (N), were disclosed recently by Eniricerche.^{14–16} These LCPs have melting points in the 150–300°C range and rheological and mechanical properties depending on the length of the diacid and on the composition.^{16–18} It is then possible to design semiflexible LCP samples for each thermoplastic matrix to fit the range of processing conditions and the desired mechanical properties. Several blends with these LCPs have been already studied^{18–25} and have been found to have some advantages with respect to those of wholly aromatic LCPs, from the point of view of processing and phase compatibility.

Fluorine-containing rubbers, as do other fluorinated polymers, show a high thermal resistance (above 150°C) and are stable in the presence of oxygen, sulfur oxides, amines, and fluorhydric acid. Moreover, they are highly resistant in respect to oils and fuels, aliphatic and aromatic solvents, hydraulic fluids, polar solvents, and moderately acid and basic environments. With particular formulations, the resistance to acids, bases, steam, and water at high

temperature can be also enhanced. Due to these peculiar characteristics, FEs are widely used in the motor industry and as linings of security valves in oil wells where high thermal resistance in strongly aggressive environments is required.

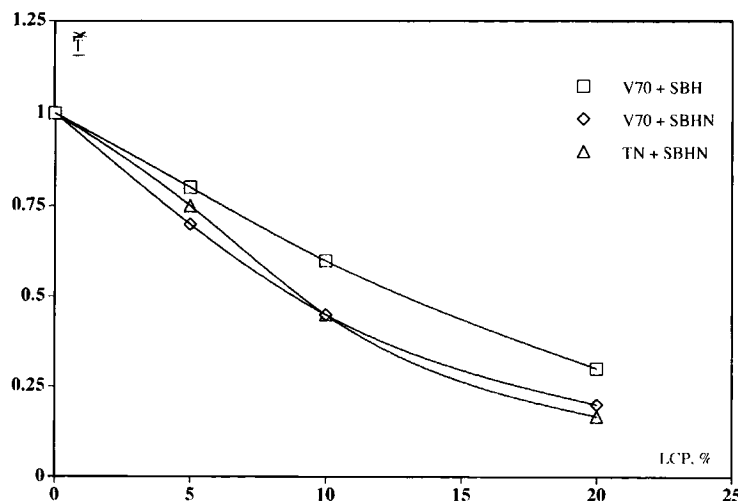
EXPERIMENTAL

Materials

The FE rubbers, Viton B70 (VB) and Tecnoflon TN80 (TN), used in this work are two different materials manufactured by DuPont and Montefluos, respectively. Their main characteristics are reported in Table I.

The LCPs are manufactured by Eniricerche (Italy) and are synthesized by melt condensation of sebacic acid (S), 4-4'-dihydroxybiphenyl (B) with different amounts of 4-hydroxybenzoic acid (H), and 4-hydroxynaphthoic acid (N).

The general formula is

**Figure 1** Torque as a function of the LCP content.

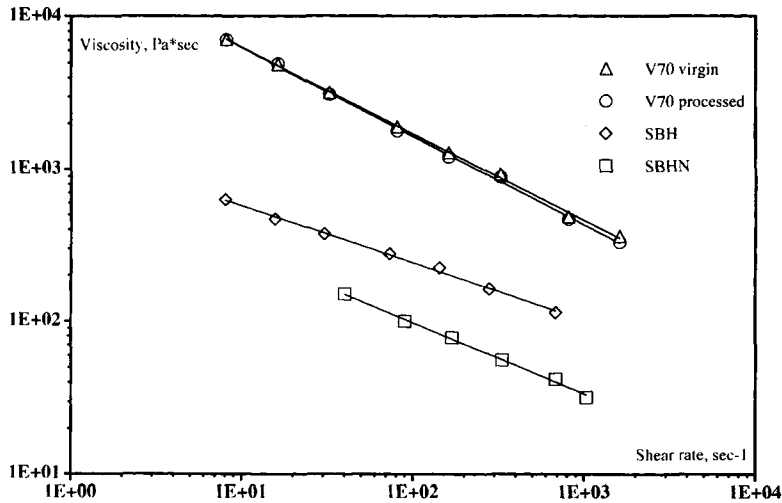
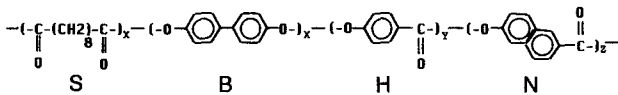


Figure 2 Flow curves of V70, virgin and after processing, and of the two LCP samples.



The two LCPs used here are designated as SBH 1 : 1 : 2 and SBHN 1 : 1 : 3 : 5 where the figures show the molar amounts of each component.

The main curing agents for FEs are bisphenols, peroxides, diamines, and high-energy radiation and they can be chosen depending on the final application of the elastomer. The curing agents used for vulcanization were

- Masterbatch elastomer/benzyltriphenylphosphonium chloride 67/33 wt/wt %.
- Masterbatch elastomer/bisphenol AF 50/50 wt/wt %.

- Maglite D (high-activity magnesium oxide).
- Calcium hydroxide.

In some blends, 30 phr of carbon black (CB) was also added.

Blends Preparation

The blends were prepared in a mixing chamber of 50 cm³ attached to a Plasticorder Brabender Model 651 at a mixing speed of 30 rpm and at a temperature of 200 and 220°C for blends with SBHN and SBH, respectively. Before processing, the pellets of the LCPs were dried for at least 24 h in a vacuum oven at 120°C. The dried pellets were then tumbled, in a predetermined weight ratio, together with the FEs.

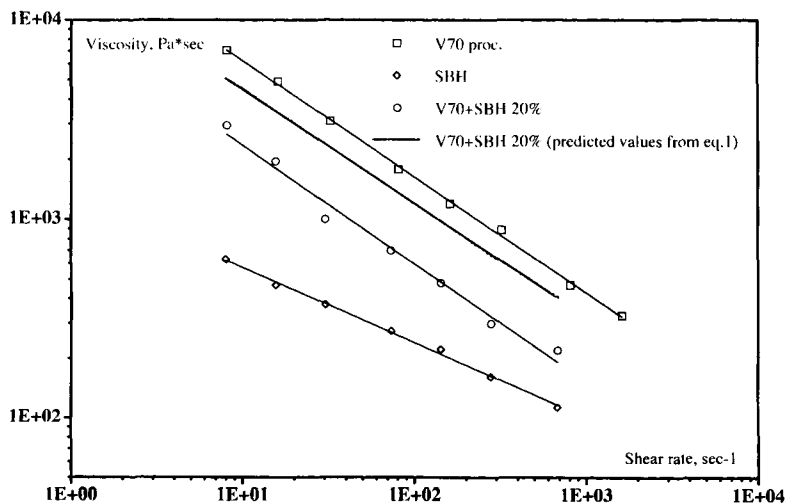


Figure 3 Flow curves of V70/SBH system and curve from eq. (1) for the blend with 20% of SBH.

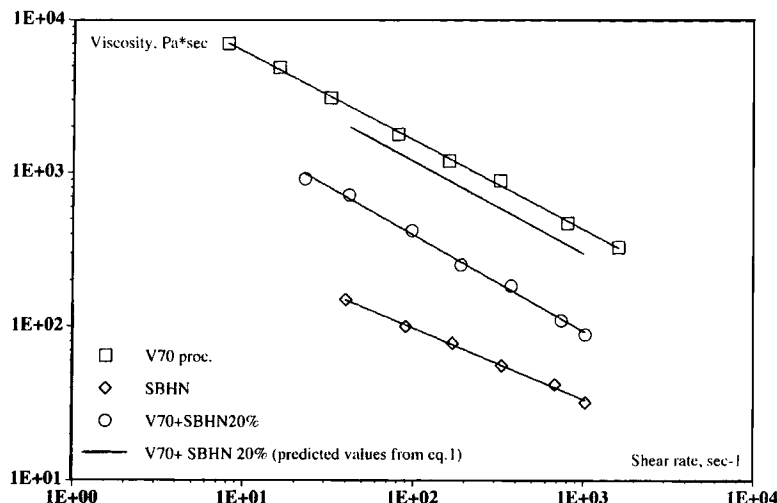


Figure 4 Flow curves of V70/SBHN system and curve from eq. (1) for the blend with 20% of SBHN.

One minute after the torque reached a steady constant value, the material was discharged. In some cases, the discharged blends showed a bad appearance and the two polymers were macroscopically separated. The two components showed large differences in both melt density (FEs about 1.8 g/cm³ and LCPs about 1.05 g/cm³) and viscosity. Both characteristics imply that the melt LCP can migrate toward the rotors, avoiding the mixing of the two phases. The torque goes to zero in these cases, the blending does not occur, and the discharged material shows the two components well separated. The use of proper rotors, a careful dry blending of the solid components, LCPs with high molecular weight, and the correct choice of the processing conditions remarkably reduces this undesired phenomenon. In particular, high temperatures, reducing the differences in density and viscosity, should improve the quality of the mixing. Unfortunately, the degradability of the FEs does not allow one to process them at high temperatures. Above 200°C, both VB and TN begins to produce hydrofluoric acid, a product of the degradation reactions, so that the maximum processing temperature chosen was 220°C. Under these conditions, the mixing was effective and the number of bad blends strongly reduced.

Vulcanization

The procedure to prepare the blend to cure consists of adding to the elastomer (or to the elastomer with LCP) the two masterbatches (2 and 3.6 phr, respectively); after 2 min of mixing (50°C and 20 rpm), 30 phr of carbon black (if requested) is added, and after

4 min, 3.4 phr of Maglite D and 6.9 phr of calcium hydroxide are added.

One minute after the torque reached a steady constant value, the material was discharged, introduced into a mold, and pressed for about 10 min (177°C, 150 MPa). The sheet obtained was then placed in an oven and kept for 24 h at 230°C for postcuring treatment.

Rheological Properties

Flow curves of the pure polymers and blends were determined using a capillary viscometer Rheoscope 1000 (CEAST, Italy) at 220°C with a capillary of 1 mm of diameter and length-to-diameter (L/D) ratio of 40. Due to the high L/D ratio, Bagley corrections were not applied, while Rabinowisch corrections were applied throughout.

Mechanical Properties

The Young's modulus (E), the tensile stress (TS), and the elongation at break (EB) of all the investigated materials were measured using an INSTRON mechanical testing machine (Model 1122). The samples were prepared by compression molding in a Carver laboratory press at 220°C. All the values were averages of at least seven measurements.

Dynamic Mechanical Properties

The dynamic mechanical properties of the materials were obtained using a viscoelastometer Rheovibron Model DDV II on samples similar to those used for

mechanical properties (thickness 0.5 mm, width 5 mm, length 15 mm) at a frequency of 110 Hz and at a heating rate of about 1°C/min.

Some specimens were also analyzed with a Rheometrics instrument Model RSA2 on compression-molded samples (48 × 5 × 2 mm). The specimens were subjected to a flexural deformation of less than 1% at a heating rate of 2°C/min.

Morphology

The morphology was studied by scanning electron microscopy (SEM) using a Philips instrument Model 501. The samples were fractured in liquid nitrogen and then coated with gold using an SPI sputter coater.

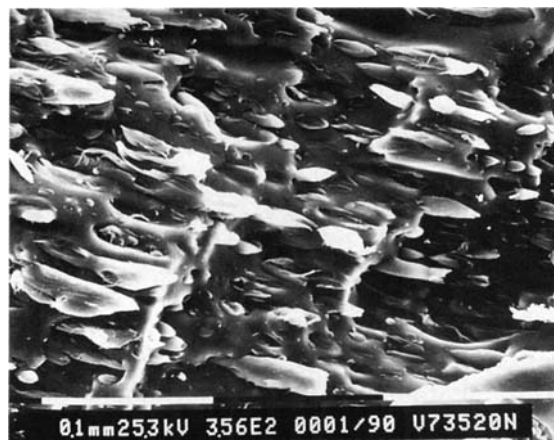


Figure 6 SEM microphotograph of a blend of V70 with 20% SBHN.

RESULTS AND DISCUSSION

Processing

The torque during mixing can be considered as a good parameter for evaluating the processability of polymeric systems. A decrease of the energy necessary for processing generally indicates better processability. In Figure 1, the dimensionless torque, T , at the end of mixing (when a constant value is reached) is reported as a function of the LCP content for all the investigated blends. The dimensionless torque is the ratio between the value of the blends and that of the pure elastomer matrices. The reduction of the torque is very impressive upon addition of small amounts, 5%, of the two LCPs. By increasing the LCP content, a dramatic decrease of

the torque is observed, so that with 20% of LCP, the torque is 15–30% of the value for the pure elastomer depending on the nature of the matrix and the dispersed phase.

SBHN seems slightly more effective than is SBH as a processing aid, inducing a larger reduction of torque and, consequently, a better processability. This can be attributed to the lower viscosity of SBHN with respect to SBH.¹⁸ As for the two investigated matrices, only very small effects are observed in the processability.

Rheological Properties

As already said, thermal degradation can play an important role on the final properties of FEs. In

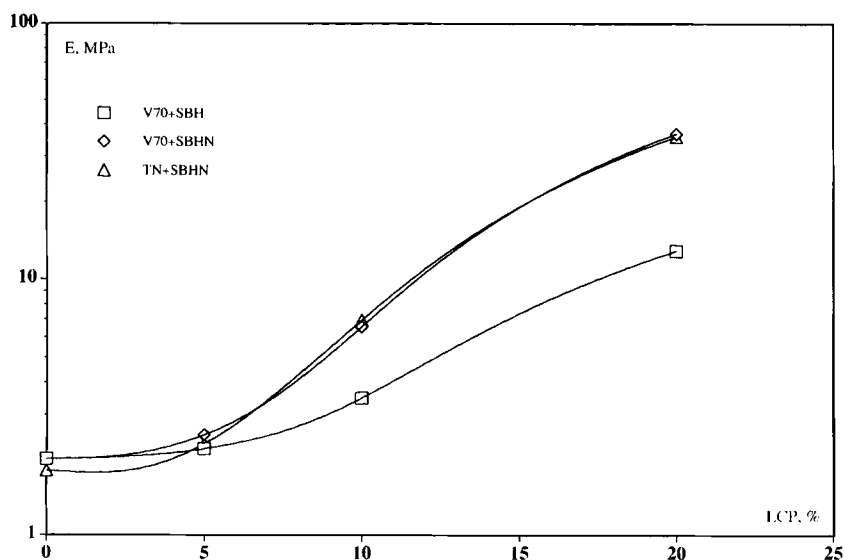


Figure 5 Modulus as a function of the LCP content.

Table II Comparison Between Experimental Data and Theoretical Data from Eq. (1) for 20% LCP Blends

Sample	E (MPa) Experimental	E (MPa) Theoretical Values (LCP Oriented)	E (MPa) Theoretical Values (LCP Unoriented)
TN + SBHN 20%	36	18,002	256.4
V70 + SBHN 20%	37	18,002	256.4
V70 + SBH 20%	13	6902	127.4

Figure 2, the flow curves at 220°C of the LCPs and of virgin and processed V70 are reported. At this temperature, the processing does not induce any degradation phenomenon as suggested by the two flow curves which are practically superimposed, suggesting that no structural changes occurred. The flow curve of the other fluoroelastomer, not reported here, shows the same behavior. The viscosities of the two LCP samples are drastically lower than that of the matrices.

The blends of V70 with 20% of LCPs (Figs. 3 and 4 for V70/SBH and SBHN, respectively) are between those of the two components and it is evident that there is a dramatic drop of viscosity of the FEs by adding small amounts of LCPs. The blend with SBHN shows lower viscosity due to the lower viscosity of this LCP sample. The intermediate values of the viscosity of the blends are in line with a phenomenological model already proposed,^{26,27} which suggests that the viscosity of the LCP-based blends is intermediate between those of the components if the viscosity of the matrix is higher while a minimum in the viscosity–composition curves is observed when the viscosity of the dispersed LCP phase is higher.

As is well known, for miscible blends, a property “ P ” can be determined by a linear combination of the properties of the pure components according to the following equation:

$$P = P_1v_1 + P_2v_2 \quad (1)$$

where P_1 and P_2 are the properties, and v_1 and v_2 , the volume fractions of the pure components. In our case, all the blends show viscosities intermediate between those of the pure components, but it is worth noticing that the values are below the theoretical curves obtained from eq. (1) and plotted in the same figures, confirming that the two components are strongly incompatible. The lower viscosity of the blends explains the drastic reduction of the torque previously observed.

Mechanical Properties

Unvulcanized Blends

The values of the elastic modulus (E) as a function of the concentration of LCP are reported in Figure

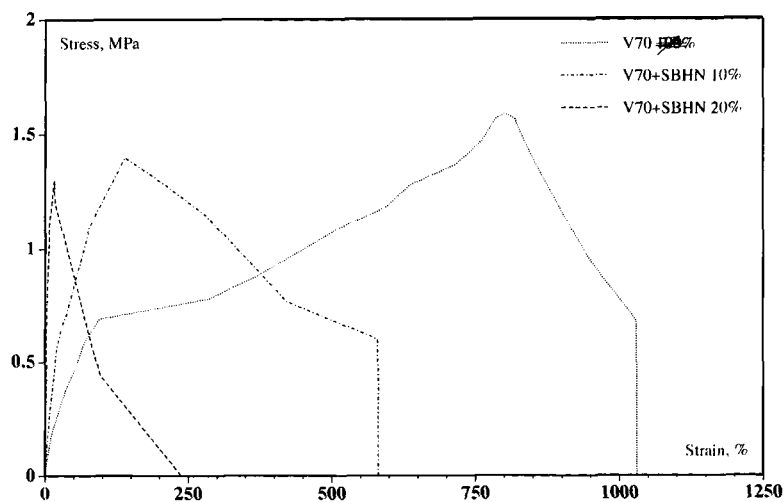


Figure 7 Stress–strain curves of V70 and of the blends with SBHN.

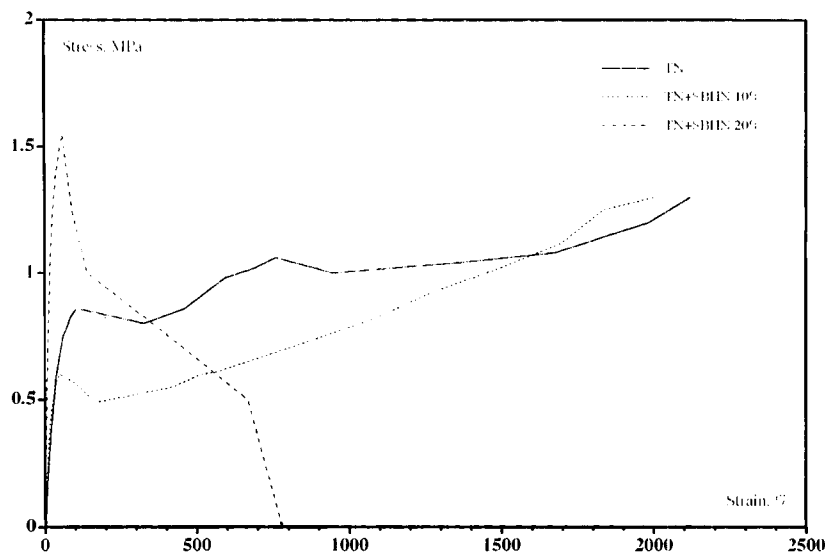


Figure 8 Stress-strain curves of TN and of the blends with SBHN.

5. A very noticeable rise of the modulus both for V70 and for TN mixed with SBHN is observed. With 20% of this LCP, the modulus is about 20 times the values of the pure matrix, but also with SBH, a significant increase of the modulus (about seven times the modulus of the pure elastomer for the blend with 20% of SBH) is observed. In Figure 6, an SEM micrograph of a blend of V70 with 20% of SBHN is shown. The dispersed LCP particles are in the form of short fibrils, but it is notable that very little adhesion between the two phases is evident. For this reason, despite this morphology, values well below the theoretical predictions evaluated through eq. (1) are observed. In Table II, the theoretical values of the modulus for the blends with 20% of LCP are re-

ported. The values of the modulus of the LCPs strongly increase with orientation and the values relative to both unoriented polymers (0.42 GPa for SBH²⁸ and 0.85 for SBHN²⁹) and those obtained for long oriented fibrils (about 23 GPa for SBH and 60 GPa for SBHN)¹⁶⁻¹⁸ were used in the calculations. The experimental values of the modulus are below those calculated using the isotropic values of the modulus of the two LCP samples. This behavior has to be attributed to the limited adhesion between the two phases, confirming the incompatibility also in the solid state.

It was very difficult to evaluate the ultimate properties for some materials. In Figures 7 and 8, typical stress-strain curves for some samples of the

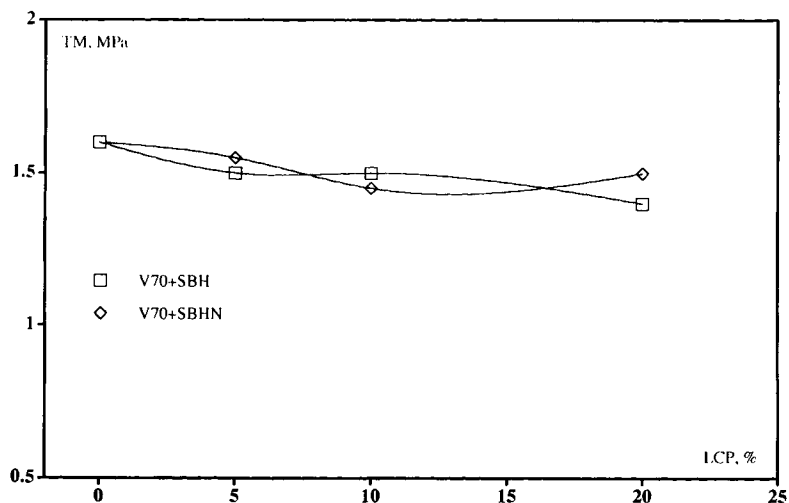


Figure 9 Maximum stress of as a function of the LCP content for the V70/LCP systems.

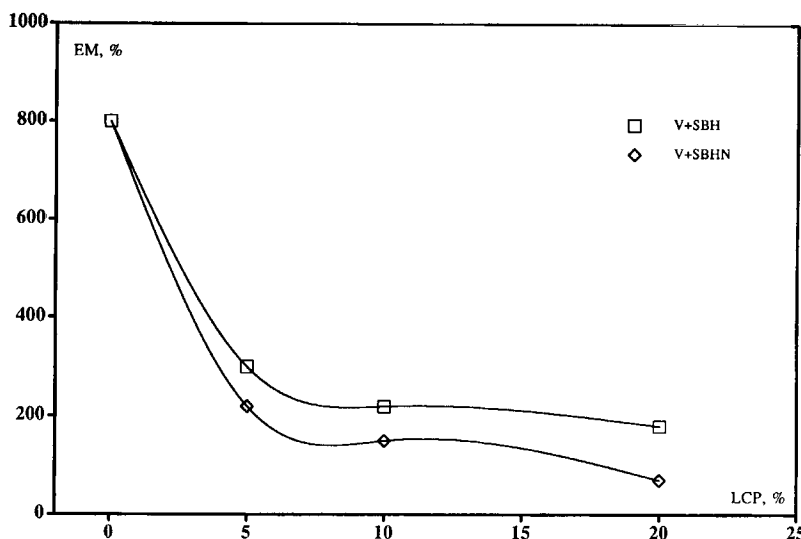


Figure 10 Elongation at the maximum stress as a function of the LCP content for the V70/LCP systems.

V70 and TN systems, respectively, are reported. For the V70 system (Fig. 7), a sharp rupture is not observed but a progressive breaking of the sample with a progressive reduction of the stress to zero is. It is, then, very difficult to determine the ultimate properties, and for this reason, the maximum stress (TM) observed in the stress-strain curve and the elongation at the maximum stress (EM) were evaluated for comparing the ultimate properties of the samples of this system instead of the tensile stress and of the elongation at break. This procedure was followed for the V70 system but not for TN and some of its blends, because, within the maximum strain allowed by our apparatus, the maximum in the stress-strain curve is not yet reached (see Fig. 8).

While the TM for the V70 system is unaffected by adding the LCP (Fig. 9), there is a dramatic effect on the EM even at low concentrations of LCP (Fig. 10). The stretchability of the elastomer is, indeed, strongly reduced by adding even small amounts of LCPs. In particular, a very strong decrease is observed at a higher content of SBHN: from 800% of the pure matrix to 70% of the blend containing 20%

Table III Mechanical Properties of TN-based Blends

SBHN (%)	TM (MPa)	EM (%)
0	> 1.3	> 2000
5	> 1.4	> 2000
10	> 1.4	> 2000
20	1.4	70

of this LCP sample. For TN (Table III), the EM is larger than 2000% for the pure elastomer while is about 70% for the blend with 20% of SBHN.

The maximum stress is almost not affected by the different structure of the two LCPs, while blends containing SBH show values of the strain higher than the values of the blends containing SBHN. A better adherence between the flexible matrix and the less rigid LCP sample, already noticed for other blends,²⁰⁻²⁴ can explain this behavior. Moreover, the rigidity of SBHN would lead to stiffer blends with higher TM and lower EM with respect to SBH-containing blends.

Table IV Mechanical Properties of Vulcanized and Unvulcanized Blends

Samples	<i>E</i> (MPa)	TS (MPa)	EB (%)
V70	3.4	6.7	200
V70 + CB	33	12.8	120
V70 + CB + SBHN20%	140	20.4	50
TN	2.8	8.2	200
TN + CB	24	12.3	70
TN + CB + SBHN20%	95	16.8	50
V70 + SBHN20% unvulcanized	37	—	—
TN + SBHN20% unvulcanized	36	—	—

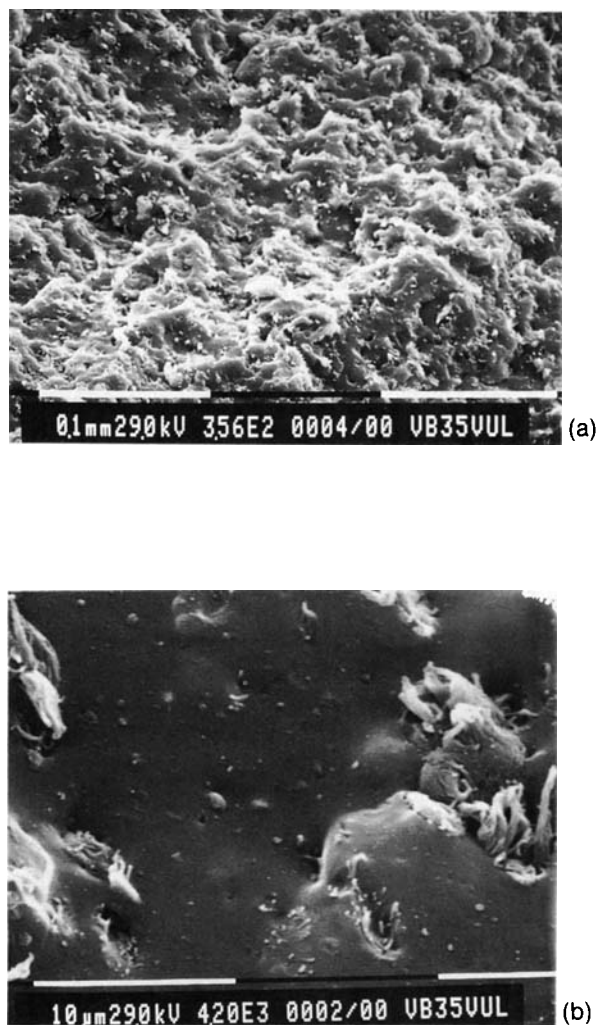


Figure 11 SEM micrographs of the same sample, V70/SBHN + CB vulcanized blend, at two different magnifications.

Vulcanized Blends

The results for CB-filled and unfilled vulcanized FEs and for CB-filled and unfilled 20% SBHN containing

blends are shown in Table IV. The results relative to the unvulcanized blend with 20% of SBHN are also reported in the same table.

Both for V70 and for TN, adding the LCP causes a strong increase of the modulus. In this case, the increase is, almost surprisingly, more than 40 times for V70- and more than 45 times for TN-based blends. The morphology of the blends can explain the remarkable rise of the modulus. In Figures 11(a) and (b), two SEM micrographs referring to the same sample, the V70/SBHN + CB vulcanized blend, at two different magnifications are shown. Particles of CB embedded and well dispersed into the matrix and a bundle of short fibrils fairly adherent to the matrix are observed. Moreover, the adhesion of the LCP particles appears to be enhanced with respect to the unvulcanized material. The morphology of incompatible blends is determined by their interfacial tension and by the applied stress, but the different specific volume determined by curing can also affect the morphology. The vulcanized materials undergo variations of volume greater than do the unvulcanized ones, giving rise to smaller voids between the matrix and LCP and therefore to better adhesion. The components remain, however, strongly incompatible as the values of modulus observed are well below the theoretical predictions (Table V). It is worth noticing that the modulus of the unvulcanized blends (36 and 37 GPa for the two systems) is higher with respect to the pure vulcanized rubber.

For the vulcanized materials, it has been possible to evaluate the properties at break because in all the tests a sharp breaking point could be observed. While for unvulcanized blends the maximum tension appeared unaffected by adding the LCP, for vulcanized rubbers, a significant increase is observed. Moreover, in vulcanized samples, the break occurred when a maximum value of tension was reached, so that the maximum stress, TM, and the tensile stress, TS, are the same.

Table V Experimental Values and Theoretical Predictions of the Modulus for Vulcanized Blends

Material	E (MPa) Experimental	E (MPa) Theoretical, Oriented	E (MPa) Theoretical, Unoriented
V70	3.4	—	—
V70 + CB	33	—	—
V70 + CB + SBHN20%	140	18,023	278
TN	2.8	—	—
TN + CB	24	—	—
TN + CB + SBHN20%	95	18,017	272

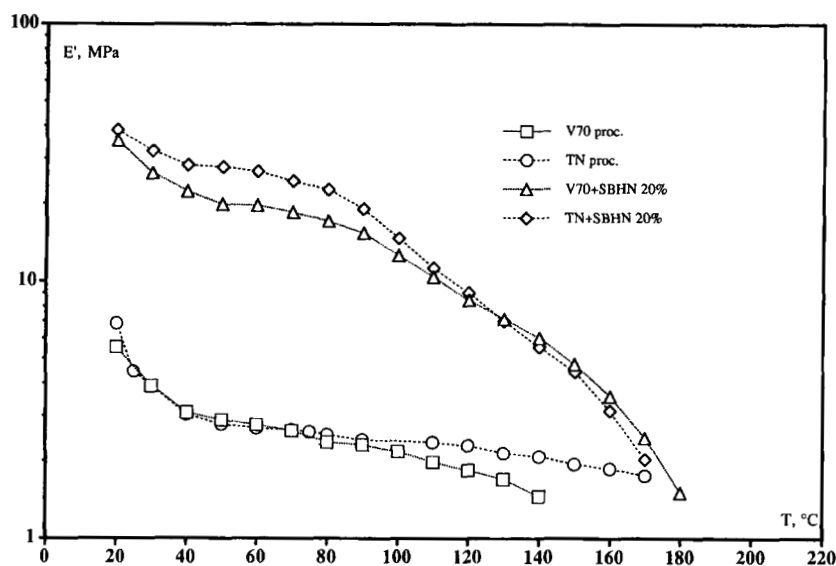


Figure 12 Storage modulus as a function of the temperature for V70, TN, and their blends with 20% of SBHN.

The best properties are obviously shown by the CB-filled blends. For the system TN + SBHN + CB, TS is twofold with respect to pure vulcanized rubber. For the system VB + SBHN + CB, TS is threefold with respect to the pure vulcanized VB, and also in this case, even if the best values are again performed by the CB-containing blend, the system VB + SBHN presents values of TS much higher than those of the pure matrix.

The elongations at break (EB) decrease both for VB- and for TN-based blends, but differently from the unvulcanized ones, the decrease is less dramatic, being about fourfold for both rubbers. The higher

values of TS and the contained decrease of EB are due to the better adhesion between the LCP and the rubber just discussed for the modulus.

Thermomechanical Properties

Unvulcanized Materials

The values of the dynamic moduli for the virgin and for the processed rubbers are almost the same, confirming that the processing does not induce any significant degradation of the matrix. The results of the blends were compared with those of the pro-

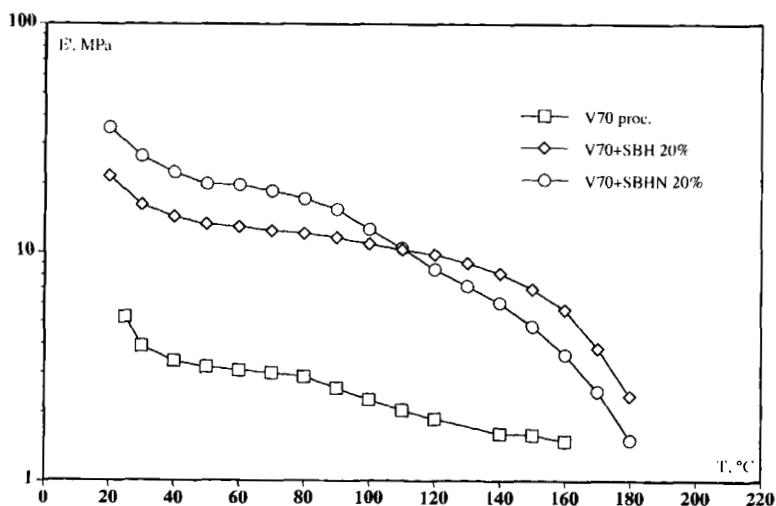


Figure 13 Storage modulus as a function of the temperature for V70 and its blends with 20% of SBHN and SBH.

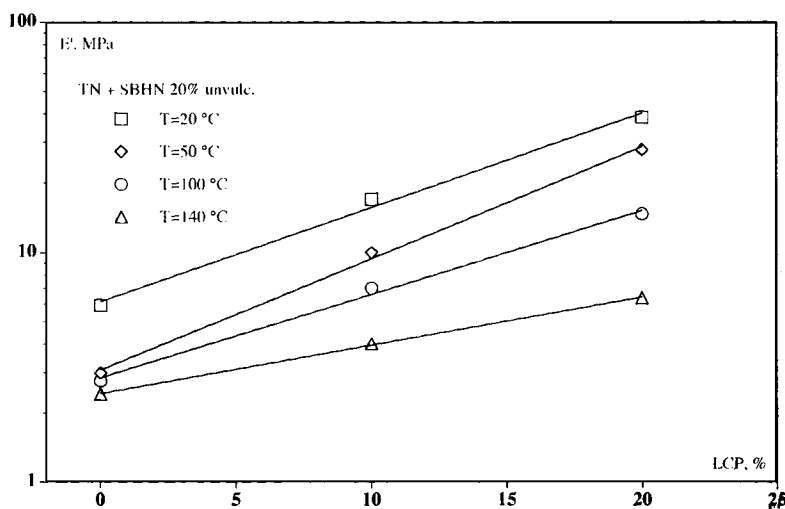


Figure 14 Storage modulus of TN/SBHN blends as a function of the LCP content at different temperatures.

cessed material. In Figures 12 and 13, the storage modulus, E' , of the two elastomers and of the blends with 20% of SBHN are reported.

E' shows a remarkable increase by adding SBHN, and this leads to a large increase of the working temperature. The influence of these elastomeric matrices is almost negligible. Also, SBH allows one to obtain higher values of E' even if slightly less than those of SBHN (Fig. 13). At higher temperatures, however, the storage modulus of the blend with SBHN decreases more rapidly, while for the blend with SBH, a plateau is observed in the same temperature range. Above 100°C, the storage modulus of the blend with 20% of SBH is higher than that of the blend with 20% of SBHN. This phenom-

enon is again strictly connected with the structure of the two LCPs. SBHN is less crystalline than is SBH due to the large naphthoic group in the backbone and, for this reason, shows a worse behavior at high temperatures.

To study the influence of the amount of the LCP level in the blends, values of E' at various temperatures were plotted as a function of the content of LCP in Figures 14–16. TN with 20% of SBHN shows at 100°C a value of modulus higher than that of the pure matrix at 20°C (Fig. 14); similar results are obtained when the matrix is V70 (Fig. 15) and the results are even better by adding SBH (Fig. 16). The blend with 20% of SBH shows at 140°C the same modulus of the matrix at 20°C. This latter, better,

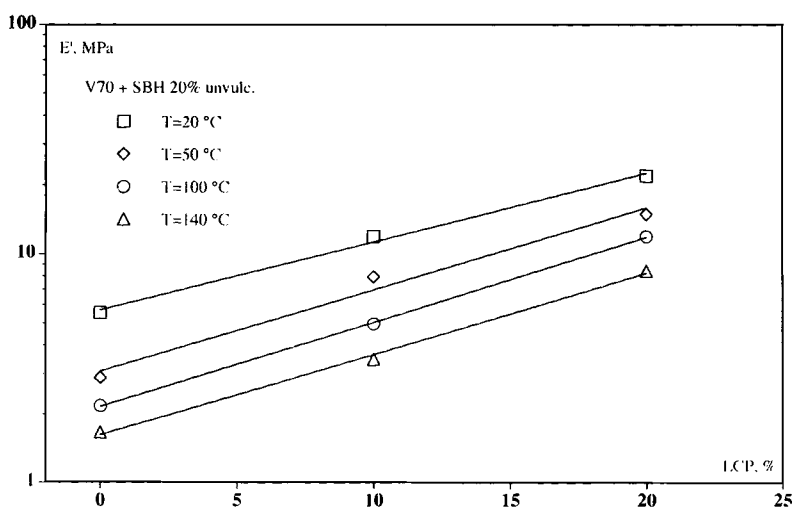


Figure 15 Storage modulus of V70/SBHN blends as a function of the LCP content at different temperatures.

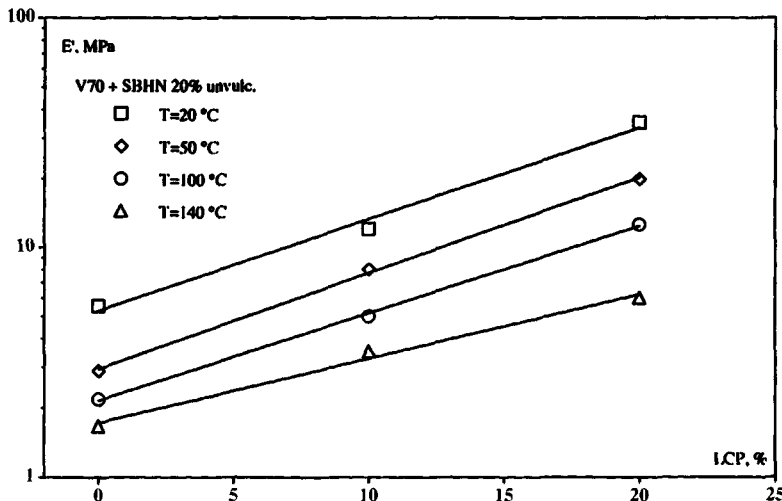


Figure 16 Storage modulus of V70/SBH blends as a function of the LCP content at different temperatures.

result is attributed to the higher crystalline degree of the SBH sample. These results highlight the remarkable improvement of the thermomechanical properties of the elastomers by adding the LCPs which allow one to use these rubbers at relatively high temperatures.

Vulcanized Materials

The thermal resistance of many polymers is usually enhanced by adding inorganic fillers to them, whereas the vulcanization has the same effect on the elastomers. The curves of the storage modulus vs. the temperature relative to the vulcanized

blends with and without 20% of SBHN are reported in Figures 17 and 18. Both for VB (Fig. 17) and for TN (Fig. 18), the increase of the modulus in the systems containing the LCP, as already said, is remarkable. Again, the best behavior is displayed by the CB-containing blends, but, also, the unfilled ones show values of the modulus higher than those of the pure matrix of about a decade. The more interesting feature is, of course, the behavior with temperature of the vulcanized filled materials and, in particular, of the blend with 20 of SBHN. The modulus-temperature curves of the blends show a significant decrease, but at temperatures of about 250°C, they show the same modulus of the vulcan-

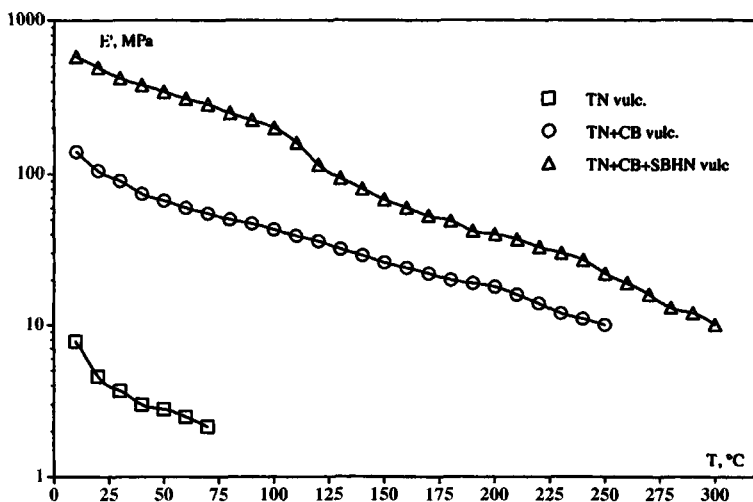


Figure 17 Storage modulus of vulcanized and vulcanized and filled TN/SBHN blends as a function of the LCP content at different temperatures.

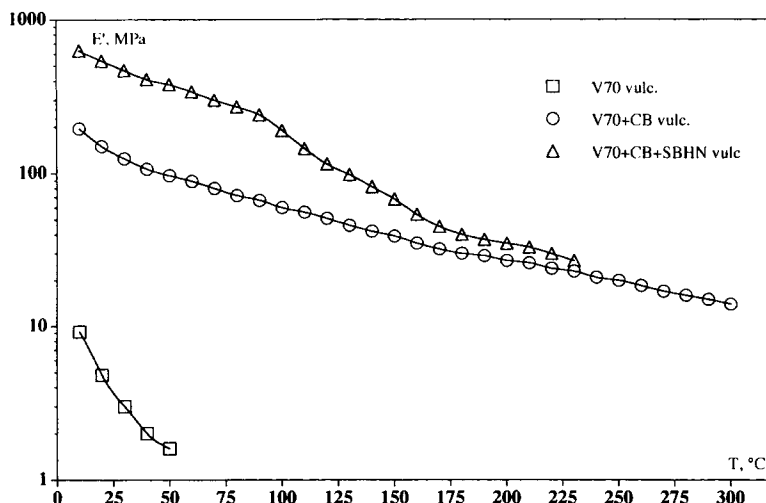


Figure 18 Storage modulus of vulcanized and vulcanized and filled V70/SBHN blends as a function of the LCP content at different temperatures.

ized elastomers at room temperatures. The dramatic enhancement of the working temperature and of the window for applications of the elastomers is clearly evident.

CONCLUSIONS

The efficiency of the two LCPs as processing aids is evident. The torque during mixing is much lower than that observed for the pure matrix also at low LCP contents and this effect is much more prominent at higher concentrations.

The improvement of the mechanical properties is remarkable both for unvulcanized and vulcanized systems, although the values are below those expected on the basis of an additive rule due to the incompatibility between the components. The modulus of the system VB/SBHN is about 20 times that of the pure elastomer for unvulcanized CB-filled blends and about 40 times for vulcanized CB-filled blends. Also, the tensile strength increases even if only in vulcanized systems. The elongation at break decreases significantly in all the systems for unvulcanized material, while in the vulcanized ones, the reduction is less marked.

There is also an upgrade of thermomechanical properties. The working temperature increases more than 100°C for the vulcanized blends containing CB and 20% of SBHN, but an improvement of thermal resistance is observed also for unvulcanized blends. A slight effect of crystallinity of the two LCPs was also noticed: The higher the crystallinity, the higher the thermal resistance.

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