Polymer Bulletin 4, 233–240 (1981)

Polymer Bulletin

Physico-mechanical Properties of *cis* and *trans* Polyisoprene Binary Networks

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SUMMARY

In the present paper we report the physico mechanical properties of elastomeric systems obtained vulcanizing mixtures of cis and trans polyisoprene.

The presence of the trans polymer strongly affects the physical behaviour that is typical of a biphasic system,where a plastic component is segregated in the elastomeric matrix.The experimental results are reported and discussed giving particular attention to the structural features and to the general problem of the physical behaviour of elastomeric systems.

INTRODUCTION

In previous papers(1-3) we reported the results obtained analyzing the physico-mechanical properties of elastomeric biphasic systems where a glassy phase is segregated in the elastomeric matrix.

The experimental data indicate that the elastic behaviour is ruled by the reduced conformational mobility of the elastomeric chains,connected to the presence of the rigid glassy particles.

In the present paper we have investigated the thermomechanical behaviour of binary networks obtained vulcanizing mixtures of polyisoprene cis and polyisoprene trans,at different content of the trans polymer.

For these systems a biphasic structure where one component is segregated in the other one can be expected.

The obtained results,that regard samples where the cis polymer is the dominant component,can be indeed explained assuming that the trans polymer

0170-0839/81/0004/0233/$01.60

is partially segregated as organized plastic phase in the rubbery cis polymer.

Therefore the main difference between these and the previously studied(1-3) systems is the thermodynamic state of the segregated phase.

In the trans polyisoprene,in fact,the glass transition temperature is at about -60°C (4),that is considerably below the temperature range experimentally investigated(10-60°C),and that is very similar to the glass transition of the rubbery matrix.

Moreover the trans polymer can crystallize in two different crystalline forms(5) with melting point at about 45°C and 60°C respectively,and therefore,in the temperature scale of our analysis,can be present as segregated structurally organized phase,susceptible of plastic deformation.

The aim of the present paper was to investigate the influence that the structurally organized phase plays on the physical behaviour of the vulcanized rubberlike matrix.

The obtained results show that the physical behaviour of the elastomeric cis polymer strongly depends on the trans content.

The observed effects are relevant when the trans content is high (20% polyisoprene trans),but still detectable at low trans content (5% polyisoprene-trans).

EXPERIMENTAL

Materials:

The used polyisoprene cis was the natural rubber, while the polyisoprene trans was a synthesis product made by the Polymer Corporation Ltd(Sarnia,Ontario, Canada),with M_v=350000 .

The networks were prepared mixing,in a rubber mill,the cis and the trans polyisoprene at 80°C for 30' and adding to the mixture the 0.3% of dicumylperoxide as vulcanization initiator.

The mixing temperature was sufficiently high to permit a blending of two liquid components,and sufficiently low to avoid the chemical degradation of the dicumylperoxide during blending.

The vulcanization was carried out at 140°C for 45 minutes.These conditions were normally used to vulcanize natural rubber samples(6),and the degradation phenomena are not relevant.

Four samples were prepared, containing respectively 0,5,10,20% in weight of polyisoprene trans, and their code is respectively S-0,S-5,S-10,S-20.

Analysis procedures:

The stress-strain and the stress temperature measurements were carried out using a dynamometer equipped with a thermostatted oil bath(± 0.2°C).

The stress-strain isotherms were obtained stretching the sample step by step and detecting the stress with five minutes intervals between two successive strain values.

The stress-temperature measurements were obtained stretching the sample to the desired strain value and waiting at constant strain for a stress value constant with the time (generally less than 30 min); after that, the temperature was increased at the rate of 1°C/min and the stress was detected as a function of the temperature. Not relevant plot shiftings in temperature scale can be observed as effect of large changes in the heating rate.

The mechanical hysteretic behaviour was analyzed using a dynamometer of the "Toyo Instruments", the "Tensilon UTM-II" equipped with an air thermostatting box (± 1°C).

The thermal analysis was carried out using the differential scanning calorimeter DSC IB of the Perkin-Elmer.

RESULTS

The isothermal stress-strain plots were detected in the temperature range 10÷60°C.

At each temperature two plots were detected; one plot refers to the first stress-strain run after the vulcanization cure, while the second plot refers to the second mechanical run after 30' of relaxation at zero load and at room temperature.

In fig.1 we report the stress-strain plots obtained at 20°C, and going up to λ =2 as maximum strain value. Data of fig.1 refer to the first mechanical run.

A stress-hardening phenomenon on increasing the trans polymer concentration is present; the observed hardening is particularly drastic changing the concentration from 10 to 20%.

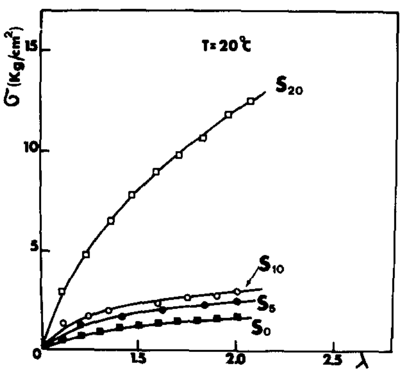

Figure 1: Stress strain plots obtained at 20^{o} C on the four analyzed samples. The code explanation is in the text.

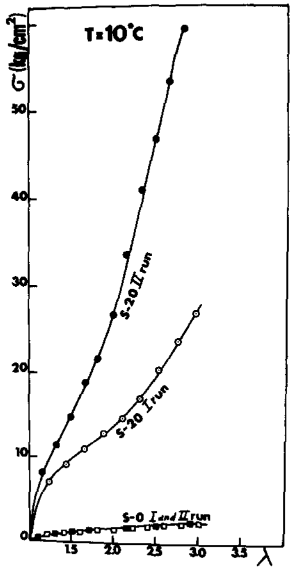

Figure 2: Stress-hardening as observed on sample S-20 at 10^{o}C compared with S-0.

A second hardening phenomenon of different kind is connected with the mechanical history of the sample;indeed the second stretching run is characterized by higher stress value.

In fig.2 we report the results obtained on sample S-20 at 10°C,where this effect is maximum,and on sample S-0 where it is completely absent.

The temperature dependence of the first and second hardening phenomena,as obtained from the isothermal stress-strain plots shows that,as pointed out,the phenomena are not only related to the sample composition,but also to the temperature.

The first and second hardening effects are more relevant indeed on increasing the trans polymer content and decreasing the temperature.

A direct picture of the temperature effects on the physical behaviour can be given by the direct thermomechanical analysis.

In fig.3 the stress-temperature data,obtained as described in the experimental section,are reported.The strain value was 1.5 .

Fig.3 shows that the tensile stress depends on the sample composition and on the temperature value.

The temperature dependence is characterized by a relevant drop in a relatively sharp range around 50^{o}C.

Moreover on samples S-5,S-10,S-20,the hysteretic behaviour was analyzed;the dissipated mechanical energy Δ w was calculated by graphical integration of the isothermal hysteresis loops and was reported

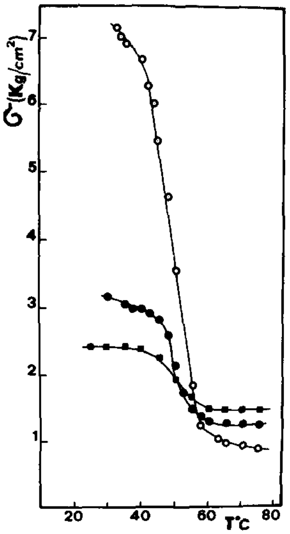

Figure 3: Stress-temperature plots obtained as described in the experimental section. o Sample S-20 ● Sample S-10 ■ Sample S-5

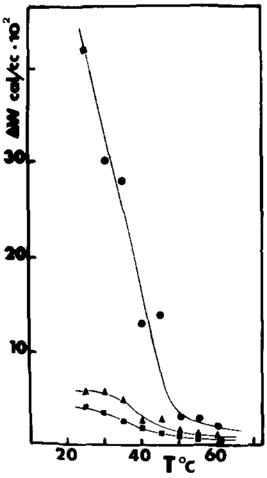

Figure 4: The dissipated mechanical work, calculated using the hysteresis loops, reported as a function of temperature ● Sample S-20 ▲ Sample S-10 ■ Sample S-5

as a function of the temperature in the range 25÷60°C. Results are shown in fig.4.

The calorimetric analysis shows that in sample S-20 an intense endotherm centered at about 44°C is present;the enthalpic content of the transition is increased by a stretching.The obtained data refer to a stretching up to λ =3 at 10°C.

Sample S-10 gives a signal much less intense and does not give any evidence of effects due to the stretching,while Sample S-5 does not give any detectable calorimetric signal.

DISCUSSION

The study of the influence that an organized phase plays on the rubbery matrix is a first aspect of this paper;the second is more generally related to the problem of polymer blending.

As matter of fact,following the specific nomenclature and literature(7),we have to consider,on the basis of the preparation method,the analyzed samples as vulcanized polymer blends,or,even if more improperly,as interpenetrating polymer networks.

The obtained results indicate that the structural model is a biphasic blend where a plastic structurally organized phase is segregated in a rubberlike matrix.

The hardening phenomenon connected with the trans polymer content,as shown in fig.1,can be indeed explained assuming that the trans polymer can crystallize as segregated phase and can play therefore a filling effect on the rubberlike matrix.

The crystallization of the trans polyisoprene in cis/trans polyisoprene blends has been recently observed in a structural study(8),and the quantitative analysis indicates,in our composition range,a crystallinity smaller than 10%.

We can expect that the vulcanization process further on reduces this value,and therefore the analyzed samples should be characterized by few per cent in crystallinity.Nevertheless this concentration is enough to produce the hardening effects.

The sharp discontinuity observed in the tensile stress going from sample S-10 to sample S-20 could be explained considering that the filling effect is not only connected to the filler concentration but also to the particles dimension and shape(9).

Therefore a change in morphology on increasing the trans polymer content can have a discontinuity effect on the properties.

The second hardening is connected to the presence of filling particles too,as effect of a plastical deformation of the crystalline regions.

As matter of fact the first mechanical run can produce a partial orientation of the plastic component in the stretching direction,giving rise in such a way to the stress hardening observed in the second run.

The first and second hardening effects based on this picture,well agree with the thermal behaviour, as shown in fig.3 where the three samples show a sharp stress decrease,drastic in the sample S-20,in the temperature range 40°-60°C that is the temperature range where the two melting transitions of the trans polyisoprene occur(5).

This explains that the effects related to the phase separation are reduced or disappear when the melting transition gives rise to a completely amorphous system.

The hysteretic data,on the other hand,confirm this picture,as matter of fact the plastic dissipative component of the mechanical force is reduced by melting of the plastic phase,and Δ w decreases as observable in fig.4.

In our opinion above the melting temperature,the system is still biphasic,with two amorphous components.Really considering the blending temperature,a good miscibility of the two components in the amorphous state should have as a consequence a homogeneous vulcanization mixture.

The vulcanization process reduces pratically to zero the possibility of large scale molecular diffusion,and therefore itis difficult to immagine how the trans polymer homogeneously distributed in the sample could crystallize,particularly in the concentration range investigated.

Therefore we suggest a low miscibility of the two components even above the melting temperatures of the trans polyisoprene.

This conclusion seems to be in little disagreement with other authors(10) that,on the basis of a dynamic mechanical analysis,suggest complete miscibility in the amorphous phase.However,to conclude on this problem a more direct analysis is required.

On the basis of the obtained results,an other aspect that we believe important can be pointed out, and it is related to the general problem of the physical behavior of a rubberlike network(11-12).

In particular seems to us noteworthy that a very little amount of organized phase can produce relevant effects on the rubbery matrix.In fact,even if the calorimetric analysis does not show evidence of melting transitions,as in sample S-5,the behaviour is significantly different from a conventional vulcanized elastomer. Particularly relevant in this sense are the thermomechanical data of fig.3-4 where a negative stress-temperature coefficient is evident;this effect is relevant in sample S-20 but still present in samples S-10,S-5,while it is well known that this coefficient has to be positive in the elastomeric systems where the retractive force is mainly entropic(13).

Similar effects were observed on ethylene-propylene copolymers(14-16),and it seems reasonable to point out that this paper gives an other experimental evidence of a direct relationship between order phenomena, hysteresis behaviour and deviations from the rubberlike behaviour, as predicted by the gaussian theory (17).

REFERENCES

1. F.de Candia, A.Taglialatela, V.Vittoria
J.Appl.Polym.Sci. 20 ,831, (1976)
2. F.de Candia, A.Taglialatela, V.Vittoria
J.Appl.Polym.Sci.20, 1449, (1976)
3. F.de Candia, A.Taglialatela, V.Vittoria
Rheol.Acta 16 , 95, (1977)
4. J.Brandrup, E.H.Immergut
Polymer Handbook II ed.J.Wiley
5. E.G.Lovering, D.C.Wooden
J.Polym.Sci. A2, 7, 1639, (1969)
6. L.Mullins
J.Appl.Polym.Sci. 2, 257, (1959)
7. L.H.Sperling
J.Polym.Sci.Macrom.Reviews 12, 141, (1977)
8. A.J.Carter, C.K.L. Davies, A.G.Thomas
MacroFlorence 1980.IUPAC Preprints vol.3,250.
9. J.C.Halpin, J.L.Kardos
J.Appl.Phys. 43, 2235, (1972)
10. A.J.Carter, C.K.L. Davies, A.G.Thomas
First Joint Italian-Polish Seminar on Multicomponent Systems.Capri, ITALY.Oct.1979
Preprints pag.51
11. K.Dušek, W.Prins
Adv.Polym.Sci.6, 1, (1969)
12. R.F.Boyer
J.Macromol.Sci.Phys. B12, 253 (1976)
13. J.E.Mark
Rubb.Chem.Techn. 46, 593, (1973)
14. F.de Candia, V.Vittoria
J.Appl.Polym.Sci. 17, 3243, (1973)
15. F.de Candia, R.Russo; V.Vittoria
J.Phys.Chem. 80,2961, (1976)
16. F.de Candia, R.Russo, V.Vittoria
J.Macromol.Sci.Phys. B18(2), 251, (1980)
17. L.R.J.Treolar
The Physics of Rubber Elasticity
Clarendon Press, Oxford 1975.

Received December 11, 1980
Revised and accepted February 2, 1981