

Structure-Property Relationships in Some Composite Systems. Deformation Mechanism

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Synopsis

In the present paper, we report the photoelastic behavior of composite elastomeric systems. The samples were obtained by vulcanizing mixtures of *cis*-polybutadiene and a polar monomer. The polar monomer used was methacrylic acid or magnesium methacrylate. The photoelastic analysis was carried out on samples with different monomer amount and in different swelling conditions. This kind of analysis gives informations about the deformation mechanism of these systems.

INTRODUCTION

In previous papers, we have reported the experimental data obtained studying composite systems where we have an elastomeric matrix and rigid particles randomly distributed in the matrix. The investigated systems were prepared by vulcanizing mixtures of the elastomer and a polar monomer such as methacrylic acid or magnesium methacrylate. We have described particularly the relationships between structural and physicommechanical properties, giving particular attention to the swelling mechanism and its effects.¹⁻⁴

The main result given by the structural data is the presence of two phases as a consequence of the different polarity between the elastomer and the other component. It is therefore possible to obtain a selective swelling of the two heteropolar phases, with a sensitive influence at a mechanical and structural level. The analysis and discussion of the data give some understanding of the phenomena of experimental deviation from the Gaussian theory of elasticity.⁵

On the basis of the previously obtained data, and considering the different swelling mechanisms, when solvents with different polarity are used, we have analyzed in the present paper the deformation mechanism in different swelling conditions. The analysis is carried out detecting the birefringence as a function of the true stress with increasing and decreasing strain.

EXPERIMENTAL

The birefringence measurements were carried out using an apparatus previously described³ and following the Senarmont method⁶ in order to calculate the birefringence value. The value of the stress was given by a transducer

TABLE I
 Sample Compositions

Sample ^a	Monomer	Amount monomer %
PBO		
PBMA10	methacrylic acid	10
PBMA20	methacrylic acid	20
PBMA40	methacrylic acid	40
PBMg10	magnesium methacrylate	10
PBMg20	magnesium methacrylate	20
PBMg30	magnesium methacrylate	30

^aFor all the samples dicumylperoxide DCP was used as initiator in the amount of 0.3%. The vulcanization conditions were 45 minutes at 145°C.

(Statham Instruments). Retardation angle and stress were detected at the same time, with 10-min intervals between different values of the strain. The sample length was increased and decreased going along a maximum value that was twice the initial undeformed length. The temperature was 25°C. The preparation technique of the samples has been described.¹⁻⁴

In the present paper, the elastomer used was *cis*-1,4-polybutadiene. The heteropolar monomers used were methacrylic acid and magnesium methacrylate. In Table I, we report the sample compositions.

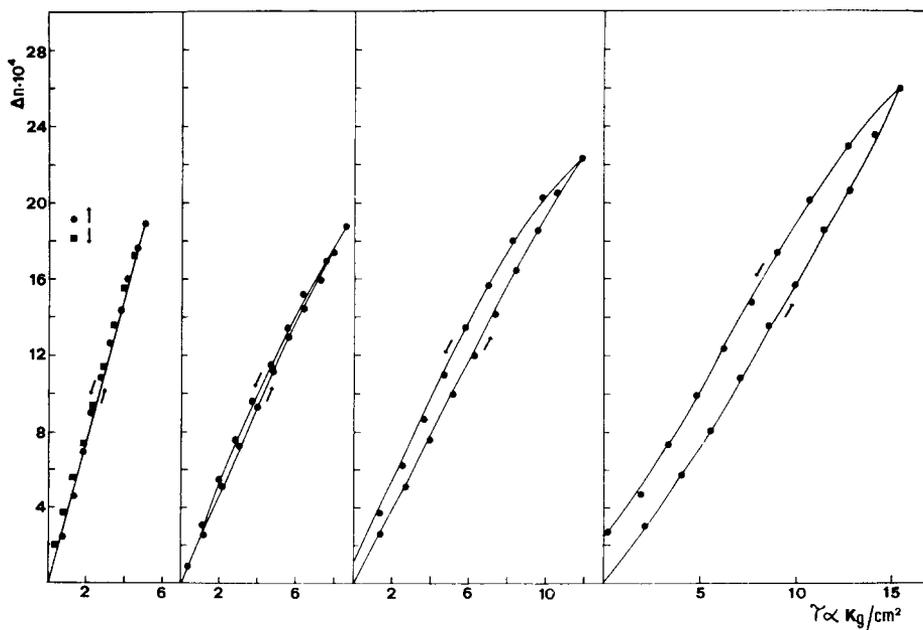


Fig. 1. Photoelastic hysteresis cycles obtained on PBMA dry samples. The birefringence is reported as a function of the true stress. Going from left to right, PBO, PBMA10, PBMA20, PBMA40.

RESULTS

In Figure 1, we report the photoelastic data regarding the samples PBO, PBMA10, PBMA20, and PBMA40 in the dry state. The birefringence Δn is

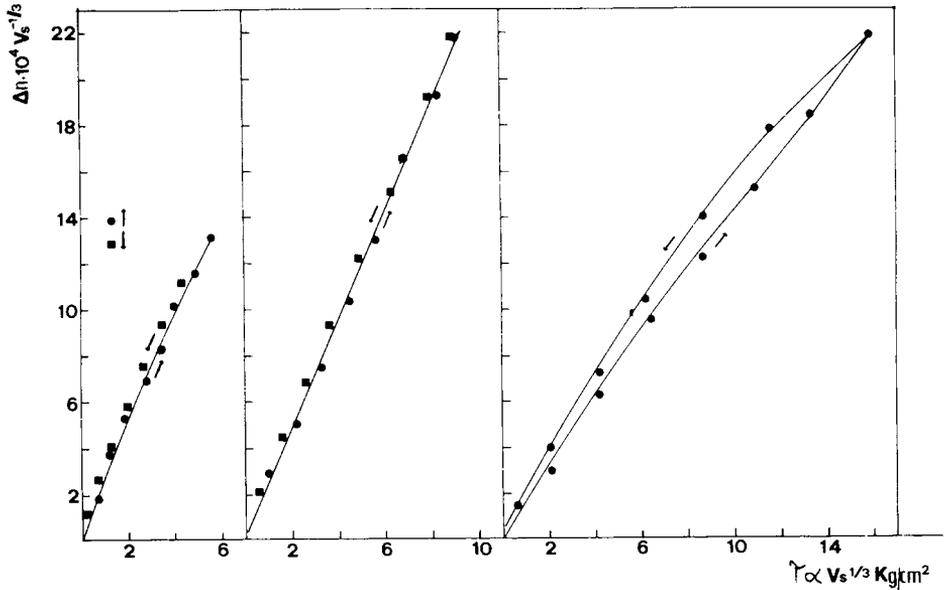


Fig. 2. Photoelastic hysteresis cycles obtained on PBMA *n*-hexadecane-swollen samples. The birefringence and the true stress are corrected respectively by factors $V_s^{-1/3}$ and $V_s^{1/3}$. Going from left to right, PBMA10 $V_s = 0.479$, PBMA20 $V_s = 0.477$, PBMA40 $V_s = 0.569$.

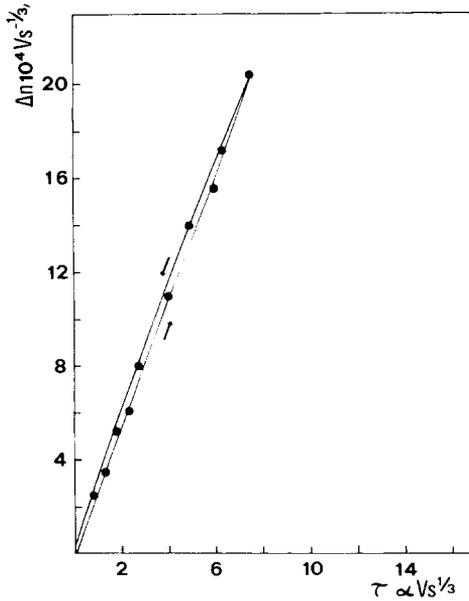


Fig. 3. Photoelastic hysteresis cycle obtained on PBMA40 *N,N*-dimethylformamide-swollen sample, $V_s = 0.600$.

TABLE II
Photoelastic Coefficients in Different Swelling Conditions

Sample	Swelling solvent	V_s	P.C., (kg/cm^2) ⁻¹ $\times 10^4$
PBMO	—	1	3.80
PBMA10	—	1	2.35
PBMA10	<i>n</i> -hexadecane	0.479	2.34
PBMA20	—	1	1.89
PBMA20	<i>n</i> -hexadecane	0.477	2.33
PBMA40	—	1	1.68
PBMA40	<i>n</i> -hexadecane	0.569	1.36
PBMA40	N,N-dimethylformamide	0.600	2.72
PBMg10	—	1	2.57
PBMg10	<i>n</i> -hexadecane	0.55	2.25
PBMg10	N,N-dimethylformamide	0.58	8.97
PBMg20	—	1	1.68
PBMg20	<i>n</i> -hexadecane	0.60	2.40
PBMg20	N,N-dimethylformamide	0.57	7.32
PBMg30	—	1	1.42
PBMg30	<i>n</i> -hexadecane	0.55	4.11
PBMg30	N,N-dimethylformamide	0.58	6.45

reported versus the true stress $\tau\alpha$, where τ is the force on the unit of undeformed cross-sectional area and α is the strain ratio. The arrows indicate the increasing and decreasing strain.

In Figure 2, results obtained on *n*-hexadecane-swollen samples are reported, while in Figure 3, the photoelastic behavior of the N,N-dimethylformamide-swollen PBMA40 sample is shown. For the samples with a smaller amount of acid, using N,N-dimethylformamide it was not possible to obtain a swelling degree sufficiently high to give rise to appreciable effects. The birefringence Δn and the true stress $\tau\alpha$, measured on the swollen samples, were corrected with the factor $V^{-1/3}$ and $V_s^{1/3}$, respectively, where V_s is

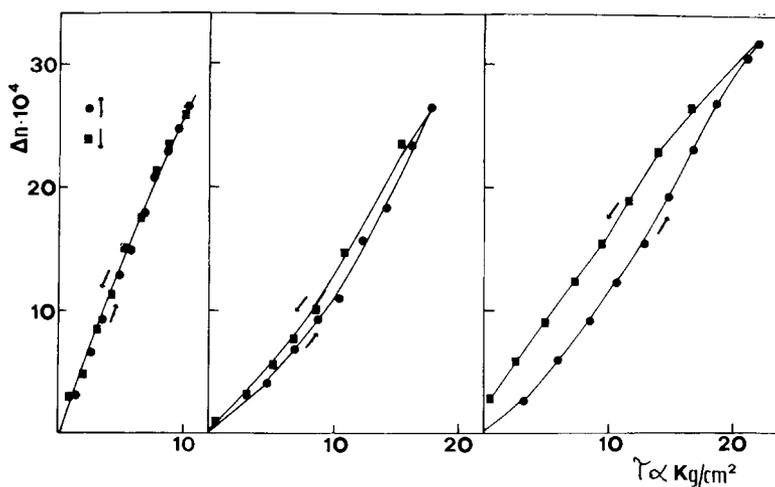


Fig. 4. Photoelastic hysteresis cycles obtained on PBMg dry samples. Going from left to right, PBMg10, PBMg20, PBMg30.

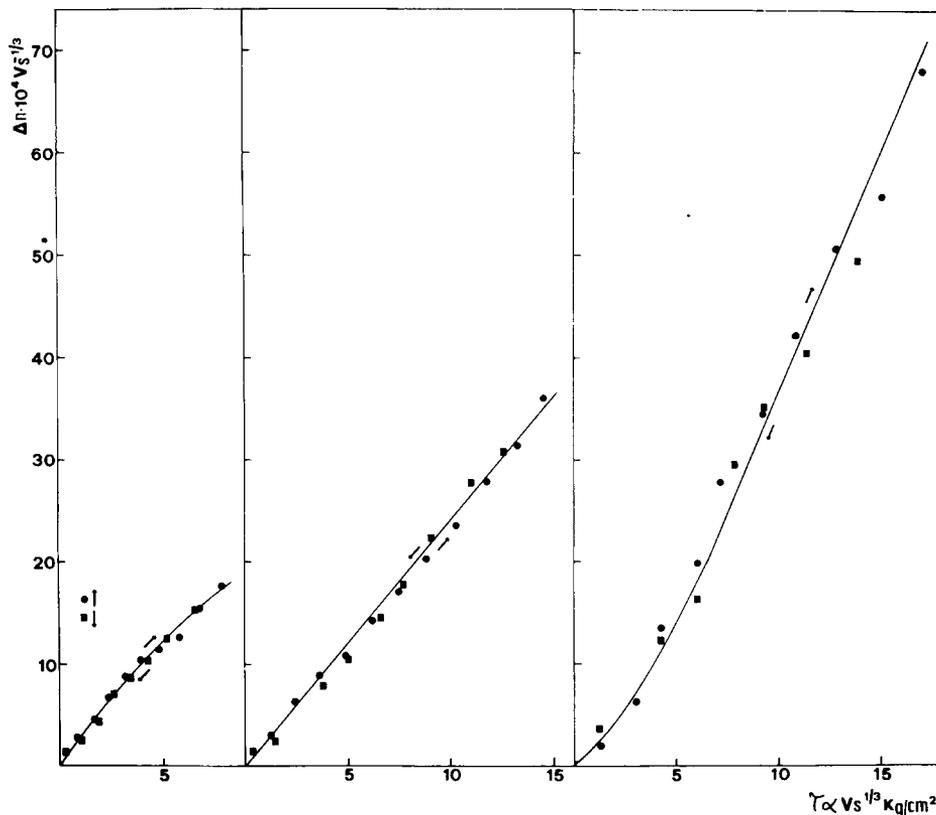


Fig. 5. Photoelastic hysteresis cycles obtained on PBMg *n*-hexadecane-swollen samples. Going from left to right, PBMg10, $V_s = 0.55$; PBMg20, $V_s = 0.60$; PBMg30, $V_s = 0.55$.

volume fraction of the dry network in the swollen sample. The reasons of these corrections are reported in the literature.⁵

In the same way, in Figure 4 photoelastic data regarding the samples PBMg10, PBMg20, and PBMg30 in the dry state are given. In Figure 5, results obtained on *n*-hexadecane-swollen samples are reported; and in Figure 6, the effect of the *N,N*-dimethylformamide as swelling solvent is shown. The salt vulcanizates before swelling with *N,N*-dimethylformamide were treated with dichloroacetic acid as previously described and then dried.

In Table II, the photoelastic coefficients (P.C.'s) obtained in different swelling conditions are given. The P.C. values were calculated using the slope of $\Delta n V_s^{-1/3}$ -versus- $\tau \alpha V_s^{1/3}$ plots with increasing strain.

DISCUSSION

In order to understand the present results regarding the photoelastic behavior and the deformation mechanism of the investigated composite systems, it is important to consider briefly the role that different solvents can play on the material morphology.¹⁻⁴ The swelling behavior is ruled by the difference in polarity between the two phases present in the material. In fact, using a nonpolar hydrocarbon solvent such as *n*-hexadecane, only the elastomeric phase will be swollen. On the other hand, use of a polar solvent

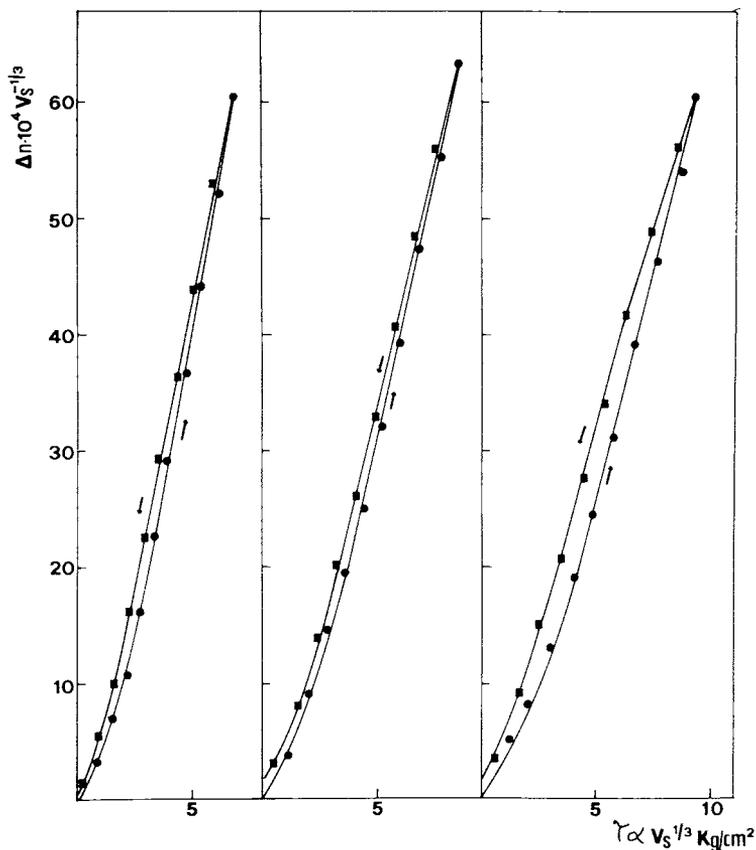


Fig. 6. Photoelastic hysteresis cycles obtained on PBMg N,N-dimethylformamide-swollen samples. Going from left to right, PBMg10, $V_s = 0.58$; PBMg20, $V_s = 0.57$; PBMg30, $V_s = 0.58$.

such as N,N-dimethylformamide will have as an effect the destruction of the clustering with the dissolution of the heterophase particles. These results have been previously reported.¹⁻⁴ Another aspect important to point out before discussing the data reported in the present paper is the significance of the photoelastic measurements when carried out while increasing and decreasing the strain in a cyclic way.

Every phenomenon induced by the strain, such as chain aggregation or orientation and, in this case, particle deformation, when it takes place irreversibly in the time scale of the experiment produces a reduction of the entropy difference between the deformed and the undeformed state. Therefore, on decreasing the strain, we detect hysteresis loop of the force that, in elastomeric systems, is governed mainly by an entropic mechanism.

On the other hand, the same kind of irreversible phenomena, induced by the strain, have a positive effect on the birefringence that is governed by the different polarizabilities in the different directions. As a consequence of this kind of mechanism, therefore, with the birefringence as a function of the true stress, increasing and decreasing the strain, any orientation or aggregation phenomena will be observable as a relative reinforcement of the function Δn with respect to the function $\tau\alpha$. Of course, other relaxation phenomena take

place when a sample is deformed, phenomena such as chain and entanglement slipping, or other topological changes. These last relaxation phenomena have a negative effect both on the force and on the birefringence.

On the basis of this picture, we can now consider the present results. Data of Figures 1 and 4 clearly indicate that on increasing the monomer amount, we have an increasing effect on the photoelastic behavior.

Excluding the PBO and the PBMg10 samples, for which a completely reversible behavior is observable, the trend of the plots suggests the presence of irreversible phenomena such as chain aggregation or orientation, or particle deformation. The use of swelling solvents gives experimental evidence to understand which of these phenomena really takes place. Figures 2 and 5 show the photoelastic behavior of *n*-hexadecane-swollen samples.

Reversible deformation is restored for PBMA10, PBMA20, PBMg20, and PBMg30, while in PBMA40, we can still observe an irreversible behavior, even if reduced with respect to the dry sample. On the other hand, using *N,N*-dimethylformamide as swelling agent, the deformation reversibility for the PBMA40 sample is practically complete, while for the salt vulcanizates a residual irreversibility, even if reduced, can be observed.

These results seem to exclude the view that the macrodeformation of the specimen is accompanied by an irreversible microdeformation of the particles, even if the birefringence effects related to the shape of the particles are not relevant as compared to the effects related to the macromolecule conformation. The explanation for the photoelastic behavior must be imputed mainly to an irreversible chain orientation. In fact, *n*-hexadecane swells only the polybutadiene phase, does not break the links between elastomer and particles, and does not change in a significant way the magnitude of the elastic retractive force. Therefore, the factors responsible for an eventual particle deformation are not removed.

Our view is that the irreversibility is related to the reduced free volume due to the presence of rigid particles and to the reduced conformational mobility of the elastomeric chains, as previously suggested.¹⁻⁴ The deformation, moreover, can be accompanied by a change in the distribution of the particles, which in the deformed sample are distributed along the deformation axis.

n-Hexadecane decreases the internal viscosity of the elastomeric phase and removes partially or completely the suggested causes of irreversibility. In particular, the return of the chains to the initial undeformed conformational state and the return of the particles from an oriented to a random distribution, for the reduced viscosity of the medium, can take place more rapidly. This is supported by the observation that in the swollen samples, no residual deformation after the strain cycle is detected while this is not true for the dry samples.

On the other hand, the influence of the *N,N*-dimethylformamide on the photoelastic behavior is related to the different swelling mechanism.¹⁻⁴ In fact, considering the data of Table II, we can observe that, while *n*-hexadecane has an insignificant influence on the P.C. value, the *N,N*-dimethylformamide produces a strong P.C. increase. This result gives some suggestion in the interpretation of the decrease in the P.C. value on increasing the monomer amount, reported in Table II for the dry samples. The deformation mechanism investigated in this paper indicates that the macrodeformation of

the specimen is practically due to the elastomeric phase. The volume fraction of the elastomer decreases with the monomer amount, and, therefore, even if chains with a smaller freedom are stretched, the effect on the birefringence is not relevant³ while, on the other hand, the filling effect of the rigid phase is very strong.³ The integral result is, therefore, a decrease on the P.C. value. It is clear that the effect of N,N-dimethylformamide in destroying the clustering changes the structural situation and produces an increase in the P.C. value.

Particularly interesting is the result observed on the N,N-dimethylformamide-swollen salt vulcanizates, for which the P.C. value is very high. We believe this result is related to the contribution to the Δn of very polar units which, as a consequence of the declustering, can contribute to the optical anisotropy induced by the deformation.

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