

Structure-Property Relationships in Crosslinked Networks from *cis*-1,4-Polybutadiene and Methacrylic Acid. Swelling Behavior

F. DE CANDIA, A. TAGLIALATELA, and V. VITTORIA, *Laboratorio di Ricerche su Tecnologia dei Polimeri e Reologia—C.N.R., Napoli, Italy*

Synopsis

In the present paper, we report results obtained analyzing the swelling behavior of a composite system prepared from vulcanizing mixtures of *cis*-polybutadiene and methacrylic acid with different amounts of acid. Two solvents were used as swelling agents, decalin and the N,N-dimethylformamide. The structural data, given by low-angle x-ray diffusion spectra, were used to interpret the mechanical behavior described in terms of the Mooney-Rivlin equation and hysteresis loops. Structural and mechanical data give information about the swelling mechanism of the solvents and about the problem of the experimental deviations from the Gaussian theory of rubber elasticity.

INTRODUCTION

In previous papers,^{1,2} we have reported results obtained from studying the relations between the mechanical properties and the morphological structure of composite systems obtained on vulcanizing an elastomeric polymer in mixture with magnesium methacrylate.

These systems are characterized by the presence of rigid particles of poly(magnesium methacrylate) distributed and grafted in the elastomeric phase. The use of different swelling solvents can give rise to different structures and, therefore, to different mechanical behaviors. Relations between mechanical and structural data give some interesting information about the problem of the experimental deviations from the Gaussian theory of rubber elasticity.³

In a previous note,⁴ we have reported the preliminary results obtained on polybutadiene-methacrylic acid vulcanized mixtures. As described,⁴ in spite of the different chemical features of these systems in comparison with the salt-vulcanized mixtures, we obtain composite systems not too different in mechanical and structural properties. In fact, small-angle x-ray diffusion spectra indicate a phase separation with clustering of particles, probably poly(methacrylic acid). Moreover, the influence of swelling on the mechanical and physical properties provides insight to the effect of the solvent on the structure of the composites.

In the present paper, we report the effect of swelling treatment on the mechanical behavior taking into account the x-ray data. We have used decalin and N,N-dimethylformamide as swelling solvents, and the mechanical data were analyzed in terms of Mooney-Rivlin plots⁵ and hysteresis behavior.

EXPERIMENTAL

The experimental methods and conditions have been previously reported⁴ and can be summarized as follows. For the x-ray analysis, a Rigaku-Denki SA camera has been used. The conditions were: $\text{CuK}\alpha$ radiation; 40 kV, 20 mA; time constant, 4; scanning rate, $2^\circ/\text{min}$; angle range, $75^\circ-5^\circ$.

For the mechanical analysis, A Tensilon UTM-II of the Toyo Measuring

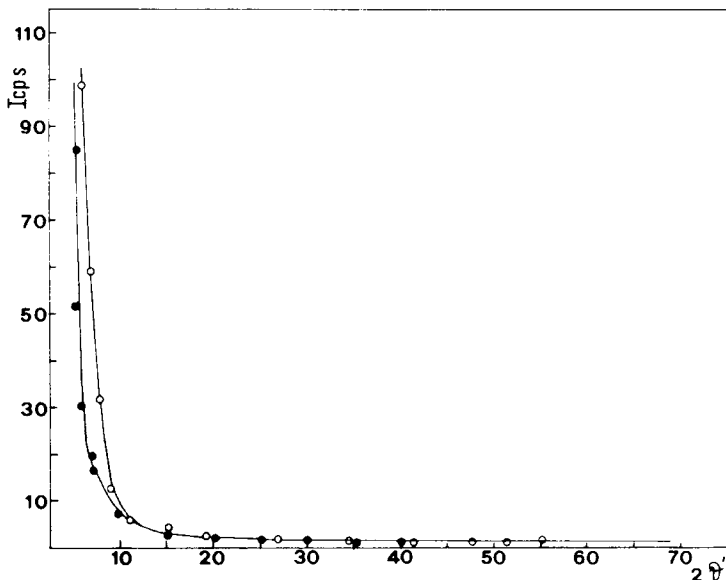


Fig. 1. Low-angle x-ray diffraction spectra. Sample PBMA10: (●) dry sample; (○) decalin-swollen sample, $V_s = 0.5$.

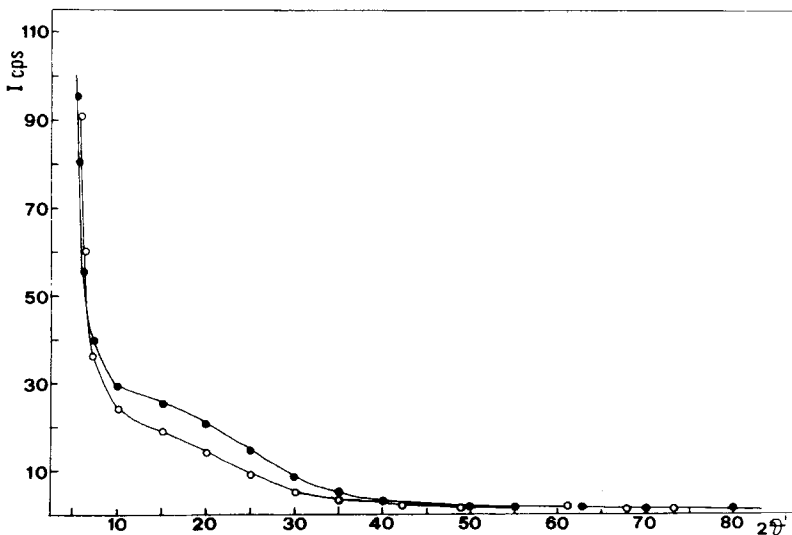


Fig. 2. Low-angle x-ray diffraction spectra. Sample PBMA20: (●) dry sample; (○) decalin-swollen sample, $V_s = 0.5$.

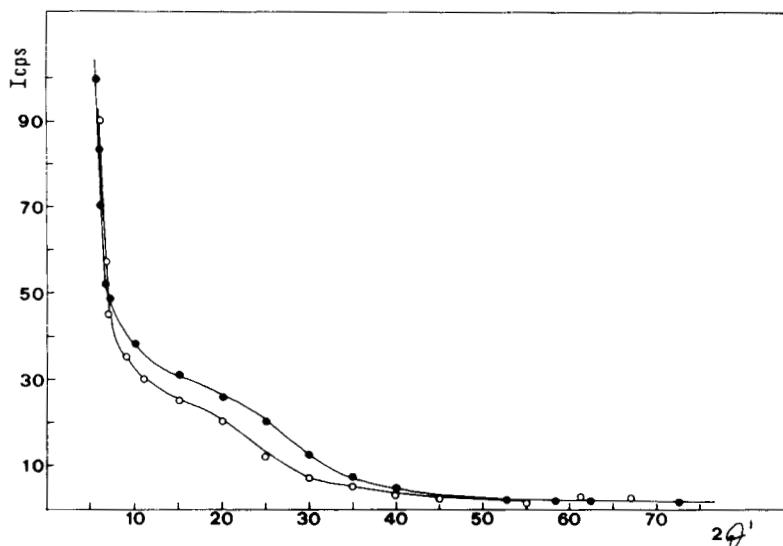


Fig. 3. Low-angle x-ray diffraction spectra. Sample PBMA30: (●) dry sample; (○) decalin-swollen sample, $V_s = 0.5$.

Instruments Co. Ltd has been used. The strain was increased step by step and the stress detected by 10-min intervals. Mechanical data were obtained in a room thermostated at 20°.

The samples used have been previously described⁴ and are indicated as PBMA0, PBMA10, PBMA20, PBMA30, and PBMA40, depending on the acid amount, that is, 0%, 10%, 20%, 30%, and 40%, respectively. Distillate acid, polymer, and peroxide were mixed under vacuum for 10 min at 50° with a rubber mill. The mixture was vulcanized at 145° for 45 min.

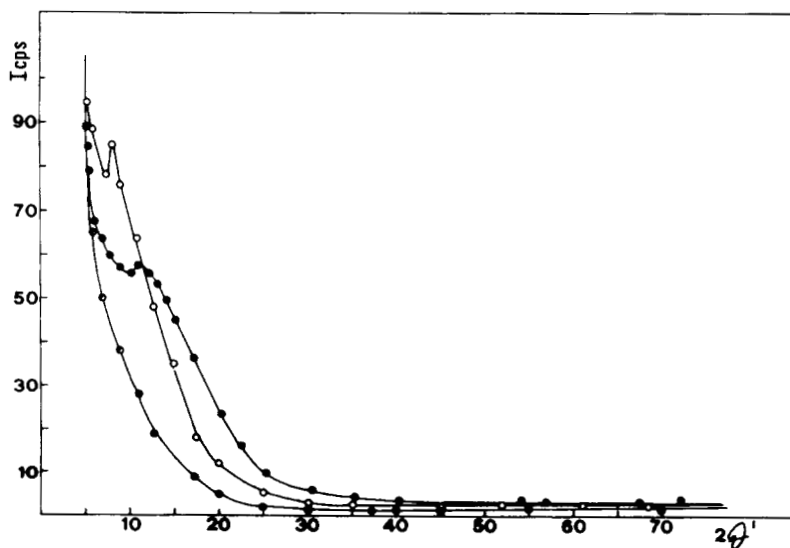


Fig. 4. Low-angle x-ray diffraction spectra. Sample PBMA40: (●) dry sample; (○) decalin-swollen sample, $V_s = 0.5$; (◐) N,N-dimethylformamide-swollen sample, $V_s = 0.5$.

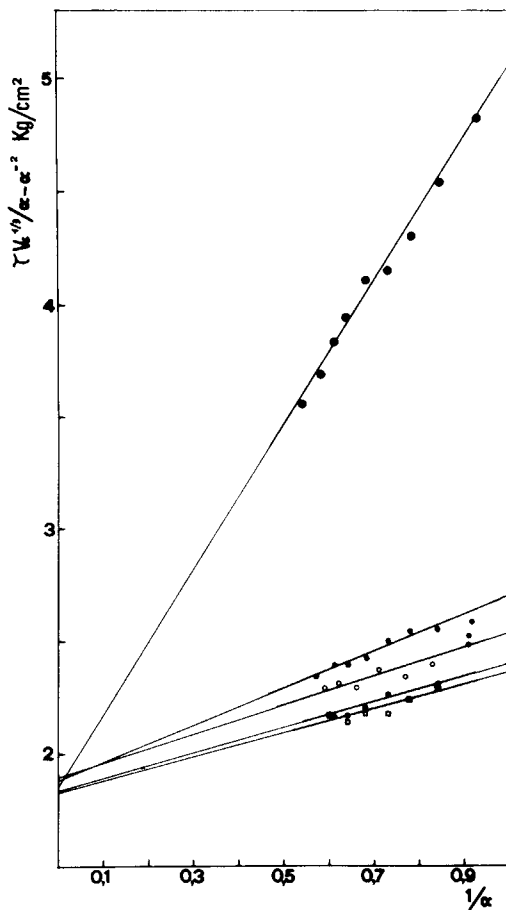


Fig. 5. Mooney-Rivlin plots obtained on decalin-swollen PBMA10 sample. From top to bottom: $V_s = 1$, $V_s = 0.492$, $V_s = 0.412$, $V_s = 0.360$, $V_s = 0.303$.

RESULTS

In Figures 1–4 we report the x-ray diffraction spectra obtained on swollen samples. For PBMA10, PBMA20, and PBMA30, only decalin was used as swelling solvent, while for PBMA40, decalin and N,N-dimethylformamide were used. In each case, the swelling degree was about $V_s = 0.5$, where V_s is the volume fraction of the dry network in the swollen sample. In Figures 5–8, the Mooney-Rivlin plots obtained on decalin-swollen samples are shown. Figures 9 and 10 refer to the Mooney-Rivlin data given by samples where the swelling solvent was N,N-dimethylformamide.

For the swollen samples, the stress is corrected by the factor $V_s^{1/3}$. Therefore, in the Mooney-Rivlin plots, the function $\tau V_s^{1/3} / \alpha - \alpha^{-2}$ is reported versus $1/\alpha$, where τ is the force on the unit of underformed cross-sectional area and α is the strain ratio.

In Table I, the nonequilibrium mechanical properties data are reported. Results were obtained detecting the hysteresis loops of the sample in different swelling conditions and calculating the total mechanical energy given to

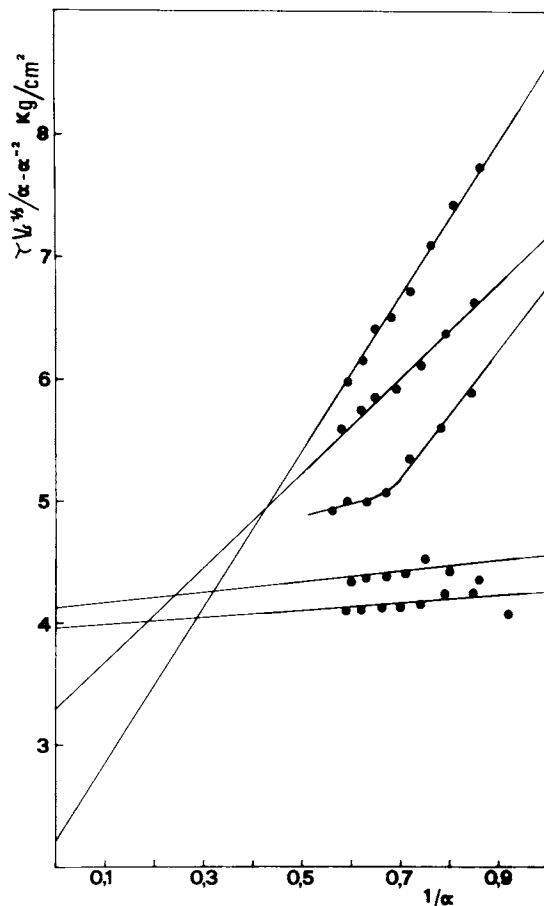


Fig. 6. Mooney-Rivlin plots obtained on decalin-swollen PBMA20 sample. From top to bottom: $V_s = 1$, $V_s = 0.869$, $V_s = 0.703$, $V_s = 0.517$, $V_s = 0.414$.

the system by deformation ΔF_{tot}) and the amount of this energy that is dissipated on decreasing the strain (ΔF_d); ΔF_{tot} and ΔF_d were calculated by graphical integration.

TABLE I
Nonequilibrium Mechanical Properties

Sample	Solvent	V_s	ΔF_{tot} cal/ cc $^{\circ}$ 10 2	$\Delta F_d/\Delta F_{tot}$
PBMA10	—	1	8.7	0.132
PBMA10	decalin	0.5	5.4	0.055
PBMA20	—	1	16.9	0.278
PBMA20	decalin	0.5	8.2	0.142
PBMA30	—	1	19.3	0.232
PBMA30	decalin	0.79	15.3	0.228
PBMA30	N,N-dimethylformamide	0.85	15.3	0.267
PBMA40	—	1	26.7	0.267
PBMA40	decalin	0.5	18.4	0.258
PBMA40	N,N-dimethylformamide	0.5	8.7	0.048

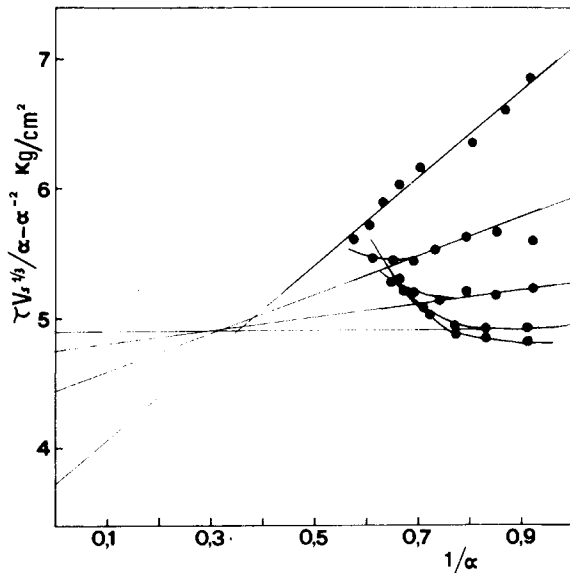


Fig. 7. Mooney-Rivlin plots obtained on decalin-swollen PBMA30 sample. From top to bottom: $V_s = 1$, $V_s = 0.793$, $V_s = 0.651$, $V_s = 0.532$, $V_s = 0.469$.

DISCUSSION

The main feature of the investigated materials is to give rise to phase separation with clustering of the particles, rigid if compared to the elastomeric phase. The chemical nature of the particles can be easily suggested, considering that the radical vulcanization reaction and the thermal treatment produce polymerization of the methacrylic acid. The poly(methacrylic acid) is characterized by the presence of one carboxylic group per monomeric unit and therefore, as a consequence of the high polarity, is not soluble in the *cis*-polybutadiene. It is the difference in polarity of the components that induces phase separation and formation of a composite system. The swelling behavior can be reconciled in terms of biphasic structure.

In fact, we can consider the x-ray data of Figures 1-4. For PBMA10, 20, and 30, only with decalin was it possible to obtain a sufficiently high swelling degree ($V_s = 0.5$). The diffusion spectra (Figs. 1-3) indicate that no structural change takes place; only a difference in the diffused intensity is observable between the dry and the swollen samples. The difference may be ascribed to the different thickness of the dry and swollen samples. Two solvents were used with PBMA40: decalin and *N,N*-dimethylformamide. The effect of decalin has a more intense maximum at a lower value of the angle, but the diffusion spectrum clearly indicates that the clustering is still present. On the other hand, the strong decrease in the intensity observed for the *N,N*-dimethylformamide-swollen sample seems to suggest a strong decrease in the phase dishomogeneity.

These results can be interpreted by assuming that decalin can swell only the unpolar elastomeric phase without any structural change and increasing in such a way the main distance between particles of poly(methacrylic acid).

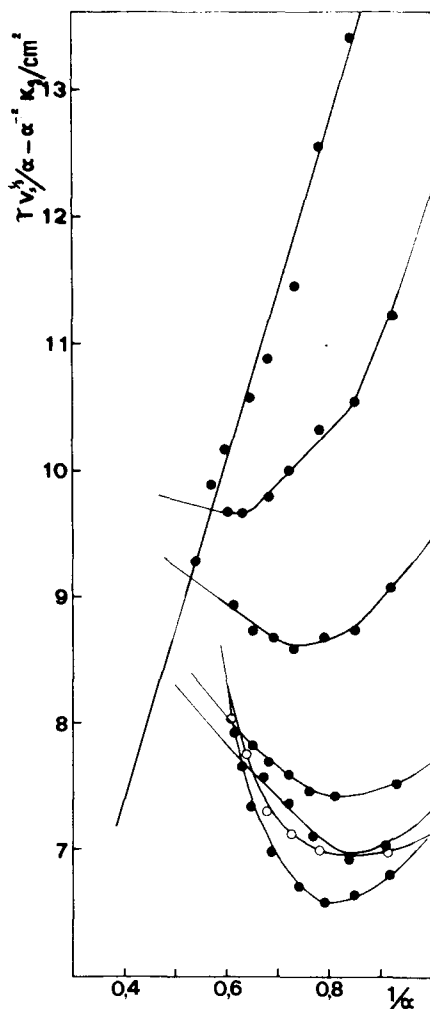


Fig. 8. Mooney-Rivlin plots obtained on decalin-swollen PBMA40 sample. From top to bottom: $V_s = 1$, $V_s = 0.784$, $V_s = 0.643$, $V_s = 0.458$, $V_s = 0.369$, $V_s = 0.358$, $V_s = 0.326$.

This picture is supported by the data of PBMA40, where the maximum that could be related to a regular distance between particles is shifted toward lower angles, indicating an increase of the distance. The *N,N*-dimethylformamide, on the contrary, being a polar solvent, can swell the rigid particles and dissolve them, the structure is destroyed, and the diffused intensity goes strongly down. This picture is similar to that previously given for the salt vulcanizates.^{1,2}

The interpretation given for the structural data is supported by the mechanical behavior. In Figures 5–8, the effect of decalin on the stress-strain behavior is shown. For PBMA10, for which the spectrum does not indicate a phase separation, the behavior is similar to a conventional elastomeric network; the first term of the Mooney-Rivlin equation, $2C_1$, is constant with the swelling, while the second term, $2C_2$, decreases on increasing the swelling degree; $2C_1$ and $2C_2$ are, respectively, the intercept and the slope of the graphs in Figures 5–10.

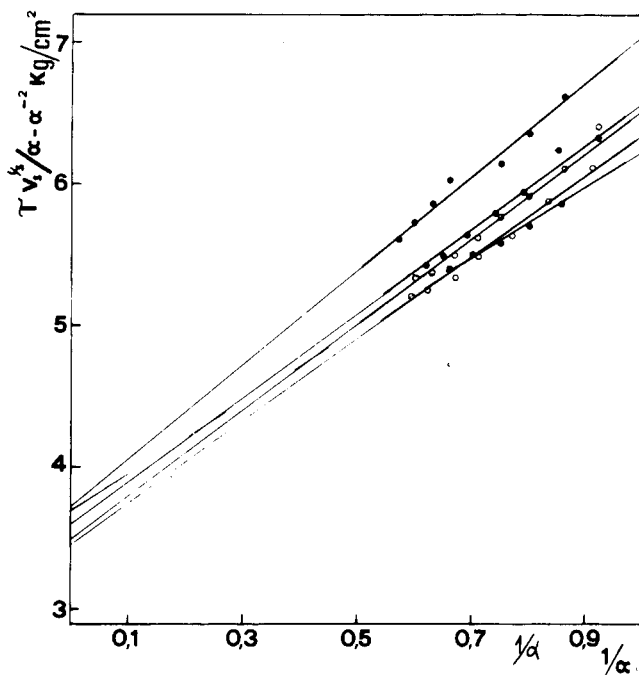


Fig. 9. Mooney-Rivlin plots obtained on N,N-dimethylformamide-swollen PBMA30 sample. From top to bottom: $V_s = 1$, $V_s = 0.869$, $V_s = 0.850$, $V_s = 0.825$, $V_s = 0.757$.

For PBMA20, we observe an increase in $2C_1$, while for the swollen PBMA30 and PBMA40, the Mooney-Rivlin equation is not verified; $2C_1$, when measurable, increases with swelling and $2C_2$ has a value that depends on the strain and is changing from positive to negative values.

The increase in the $2C_1$ term and the upturn with change in the sign for the $2C_2$ term, as reported for the salt vulcanizates,^{1,2} can be explained taking into account the selective swelling of the elastomeric region by decalin. In fact, the polybutadienic macromolecules are linked by grafting to the polymethacrylic particles or partially enclosed in them. The fraction of each macromolecule free to extend and to contract is not high at high concentration of methacrylic acid, and the segments with conformational freedom are short. Therefore, when the selective swelling increases the main distance between particles, the short segments with elastomeric behavior are easily stretched up to non-Gaussian values of length. It is the non-Gaussian behavior of the short chains that explains the increase in C_1 and upturn in the C_2 term, as previously pointed out^{1,2} and as reported by other authors.⁶

It is also interesting to consider the effect of the acid amount on the C_2 value for the dry samples. Calculating $2C_2$ for the four samples, we obtain PBMA10 $2C_2 = 3.40$ kg/cm², PBMA20 $2C_2 = 6.40$ kg/cm², PBMA30 $2C_2 = 3.60$ kg/cm², PBMA40 $2C_2 = 13.40$ kg/cm², that is, a nonregular but clear increase in C_2 with acid amount and therefore with clustering of the particles.

Considering C_2 as deviation term from the ideal elastic behavior, for which $C_2 = 0$, we observe that C_2 can be broadly related to the degree of structuration in the sample, in other words, to the degree of intermolecular interaction. This suggestion has been previously pointed out in our papers^{1,2,7,8,9} and by

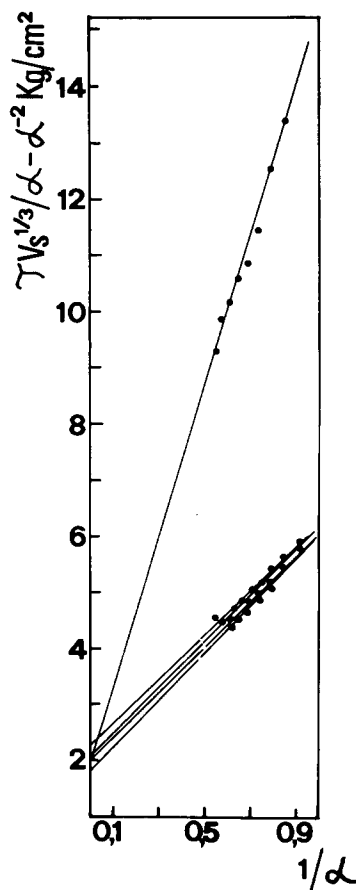


Fig. 10. Mooney-Rivlin plots obtained on N,N-dimethylformamide-swollen PBMA40 sample. From top to bottom: $V_s = 1$, $V_s = 0.600$, $V_s = 0.537$, $V_s = 0.511$, $V_s = 0.477$.

other authors.¹⁰ Giving now our attention to the results of Figures 9 and 10, we can observe a swelling behavior similar to the conventional vulcanizates. C_1 is constant and C_2 decreases when the solvent amount increases. This result supports the model suggested for the swelling mechanism N,N-dimethylformamide. The solvent dissolves the polymethacrylic particles, the total conformational freedom of the elastomeric chains is restored, and the non-Gaussian effect on C_1 and C_2 , observed for the decalin-swollen samples, disappears. It is important to consider with some attention the behavior of the C_1 term of Figures 9 and 10. In fact, C_1 is identified with the Gaussian ideal modulus^{3,11} when independent from the swelling degree, as in our case; but it is very difficult to give a molecular significance to C_1 in systems such as PBMA30 and PBMA40 that are composites and present, therefore, in the material a dishomogeneity in the modulus value. This result in general calls for great caution on interpreting at the molecular level the Mooney-Rivlin data. As previously suggested,^{7,12} only in highly swollen systems with ideal behavior or in systems with $C_2 = 0$ in the dry state^{8,13,14} is it possible to identify C_1 with the Gaussian modulus and use C_1 to calculate the molecular weight of the network chains.

To conclude, we want to consider the data of Table I. The term $\Delta F_d/\Delta F_{\text{tot}}$ is a measure of the degree of irreversibility of the deformation process, irreversibility that, of course, is related to the presence of rigid clusters and to the possibility of their orientation and deformation under stress. The data agree well with the structural and the other mechanical results. Particularly for the samples at high acid content, decalin has no significant effect on the viscoelastic behavior because it does not change the structure, while the N,N-dimethylformamide, when in sufficient amount (PBMA40), with destruction of clustering, produces a strong decrease in the dissipated energy. In another paper, the viscoelastic and photoelastic behavior will be reported in order to give a picture of the effect of the clustering on the deformation mechanism.

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