Grafting of Methyl Methacrylate on EPR and EPDR: Impact Properties of Polyvinyl Chloride–Grafted Polymer Blends

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Synopsis

EPDM rubber can be brought into water suspension after swelling in *n*-heptane containing proper emulsifiers and in shear stress; particles reach dimensions as low as 150 Å. Methyl methacrylate in emulsion can be grafted easily with Bz_2O_2 on the rubber. Grafting yields depend particularly on the monomer/rubber ratio. The grafted polymer can be recovered by precipitating the emulsion with acetone, which eliminates the homopolymer. The grafting mechanism is discussed in terms of different initiators (AIBN and Bz_2O_2) and unsaturated (EPDM) and saturated rubber (EPR); AIBN and PMMA radicals were inactive in abstracting hydrogen atoms from rubber chains. Mechanical properties of the blends with PVC of the raw graft product are discussed on the basis of the grafted polymer composition and synthesis conditions. Very high impact strength can be reached at 15% rubber content in the blend for a grafted polymer obtained from a monomer/rubber ratio equal to 0.75.

INTRODUCTION

In a previous paper,[1] we dealt with the grafting by radical polymerization of methyl methacrylate (MMA) on polybutadiene in emulsion. Very good impact properties were obtained with blends of polyvinyl chloride (PVC) and grafted polymer; butadiene–methyl methacrylate copolymer is a good toughener for PVC too.

The present paper deals with the synthesis and properties of MMA grafted polymers on saturated ethylene–propylene rubber (EPR) and on ethylene–propylene-diene rubber (EPDM) containing double bonds which are not in the backbone chain.

These rubbers cannot be polymerized by a radical mechanism, therefore, they must be prepared in a reactor other than the one used for grafting. Since grafting was done by employing water-emulsified monomer, a new technology was developed to achieve rubber dispersions in water to obtain a very large interphase surface to favor grafting. This paper demonstrates the importance of the initiator type as well as the monomer/rubber ratio in determining grafting efficiency. The mechanical properties of the raw reaction product and its blends with PVC, which are functions of the grafted polymer concentration, are also illustrated. The results achieved are interesting from a practical point of view.

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EXPERIMENTAL

Materials

EPR CO 034: 30% by weight propylene, 70% by weight ethylene—Mooney viscosity MC (1 + 4) at 110°C = 40.

EPDM: EPCAR 585: ethylene, propylene, 5-ethylidene-2-norbornene terpolymer: 33% by weight propylene, 8.5% by weight ENB, 58.5% by weight ethylene—Mooney viscosity MC (1 + 4) at 100°C = 62.

BDH MMA purified from stabilizer (hydroquinone) by treatment with $NaHCO_3$–NaOH in-water solution, water washing, dehydration with $CaCl_2$, and final distillation at a pressure of 100 mm Hg.

PVC K60 M, average viscosimetric molecular weight 45,000, mass polymerized.

2,2-Azobisisobutyronitrile (AIBN-C) produced by Noury van der Lande.

Benzoyl peroxide (Bz_2O_2) produced by Carlo Erba, recrystallized from chloroform solution.

Elvanol 50-42 polyvinylalcohol–polyvinyl acetate copolymer by Dupont.

Dupanol: blend of alkyl sulphates mainly consisting of CH_3—$(CH_2)_{10}$—CH_2OSO_3Na.

Antioxidant 2246: 2,2-methylene-4-methyl-6-tert-butylphenol produced by American Cyanamid Co.

Lead tribasic sulphate (PVC stabilizer), a commercial product of Commer Co.

Preparation of Rubber Suspension

The best way to graft monomers on a preformed polymer is to operate in solution, especially when the polymer is soluble in the monomer. Industrially, however, the heterogeneous graft polymerization by emulsion is often made trying to attain an interphase surface as large as possible. Starting with a bulk polymer, stable emulsions are barely obtainable because of the difficulties involved in the attainment of very small latex particles. A rubber-in-water suspension was produced characterized by a very large interphase surface stable under stirring and most efficient for the grafting reaction, as seen from the grafted polymer morphology examination (Fig. 1). In a patent application,[2] an EPR latex was described that was obtained by dispersing in water rubber previously swollen in toluene, under strong mechanical stirring and shearing stress and in the presence of a proper surfactant. Toluene was then removed by steam-stripping under vacuum. Swelling agent removal prior to grafting is not necessary. The swelling agent must, however, be adequately selected so as not to reduce grafting efficiency and may be recovered on completion of the reaction. For example, EPDM (20 g) cut in small pieces having a volume of ~0.1 ml each, was kept at room temperature for 24 hr in contact with 100 g of benzene until a homogeneous paste was obtained. The paste was then subjected to shear in a rotary high speed cutter (Ultra Turrax of Pabish Co.), with simultaneous stepwise addition of small portions of an emulsion consisting of 500-ml water and 3-g Elvanol 50-42, thus obtaining a sufficiently stable suspension. Toluene, carbon tetrachloride, cumene, and *n*-heptane were also used as swelling agents. However, with the exception of *n*-heptane, all other swelling agents appeared

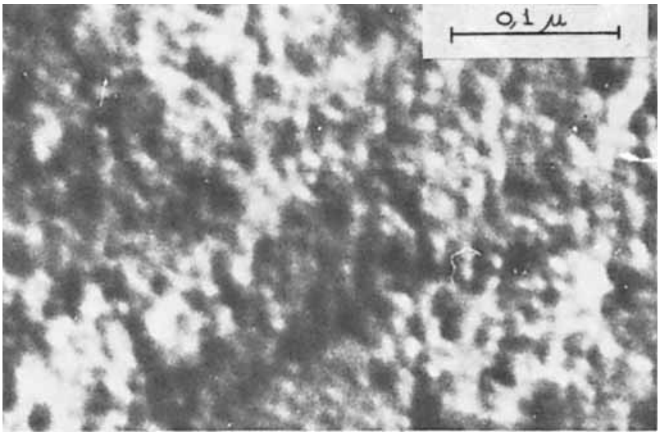

Fig. 1. Morphology of EPDM grafted with MMA (M/R = 1.32; I/R = 0.032). Composition: EPDM = 56%; g-PMMA = 44%.

to be unfit for the grafting reaction since they can generate stable radicals, which act as inhibitors in the grafting reactions.

Grafting Reaction and Products Separation

After obtaining a water–n-heptane swollen rubber suspension, MMA monomer containing dissolved initiator (AIBN or Bz_2O_2) was gradually added under stirring. Later the system was introduced into an oscillating vessel or into a vessel provided with a rotary stirrer and allowed to react for 24 hr at 60–65°C. On completion of the reaction, a significant improvement was noticed with regard to the stability of the latex. The raw reaction product was recovered by precipitation with acetone.

The following synthesis has been ascertained through a number of experiments. EPDM (25 g) was swollen with 150-ml n-C_7H_{16} and dispersed in 500-ml water containing 3-g Elvanol 50-42. During stirring (Ultra Turrax) 20-ml MMA containing 0.8-g dissolved benzoyl peroxide was added to the suspension. The reaction was conducted for 24 hr at 65°C in the oscillatory vessel. The reaction product was precipitated with acetone and, thereafter, washed by acetone, filtered, and vacuum dried. The weight of the raw product thus recovered was 41 g. Acetone is a solvent for PMMA homopolymer. Raw products were used as such for the mechanical tests.

A quantitative evaluation of the grafted PMMA present in the acetone precipitated raw product was made by completing the PMMA extraction with methyl ethyl ketone (MEK). The raw grafted product was kept in contact with MEK at room temperature in a closed flask for 48 hr. After filtering on a fritted filter, acetone and ethanol washing, and drying at 50°C for 10 hr at reduced pressure, the residue (which is the grafted polymer) was weighed. The method allows an exact evaluation of the grafted PMMA and is based on PMMA homopolymer being soluble in acetone and in MEK. Experimental results are illustrated (Table I).

TABLE I

Percentage of Monomer Converted into Grafted Polymer and Composition of Raw Grafted Products in the Case of Saturated and Unsaturated Ethylene–Propylene Rubbers as a Function of Initiator Type[a]

Rubber	EPR		EPDM		
Initiator	Bz_2O_2	AIBN	AIBN	Bz_2O_2	Bz_2O_2
Monomer/rubber ratio (g/g)	0.75	0.75	0.75	0.75	1.9
Grafting yield (%)[b]	21.7	$\simeq 0$	44.3	93	37.5
PMMA (%) in the raw grafted acetone precipitated polymer (90–98% whereof grafted)	14.3	$\simeq 0$	26	43	45

[a] Reaction conditions: Reaction temperature 65°C; reaction time 24 hr; initiator/rubber weight ratio 0.032; elvanol/rubber weight ratio 0.12; *n*-heptane/EPDM weight ratio 6; *n*-heptane/EPR weight ratio 12; water/rubber weight ratio 500/25.

[b] As grafted monomer/initial monomer ratio.

Morphology

The morphological analysis was made by an electron microscope (ITACHI); ultrathin sections of the bulk molded EPDM grafted polymers and their blends were prepared. A low temperature ultramicrotome had to be used and the temperature of the sample and of the knife were arranged as a function of the sample properties; usually, the temperature of the sample should be maintained around the glass transition temperature of the polymer and the temperature of the knife has to be 20–40°C higher. In this case, the samples were cooled with liquid nitrogen to approximately −90°C and the knife to −60°C.

The staining was obtained by exposing the sections to the vapor of aqueous OsO_4 solutions at room temperature for several hours. Consequently, in the electron micrographs the EPDM phase appears dark and the PMMA and PVC appear bright. Figures 1 and 2 show the morphologies of the grafted copolymer obtained with M/R = 1.32 and I/R = 0.032 having the composition (EPDM 56%; PMMA 44%) and a blend of 30 pph of the graft with 70 pph of PVC.

Figure 1 shows spherical domains of different size and shape, because of the grafting of PMMA on EPDM rubber in suspension. The average dimensions of the spheres are 150 Å. It is not possible to define the position of the rubber inside the domains; it can be argued that the PMMA is on the outside.

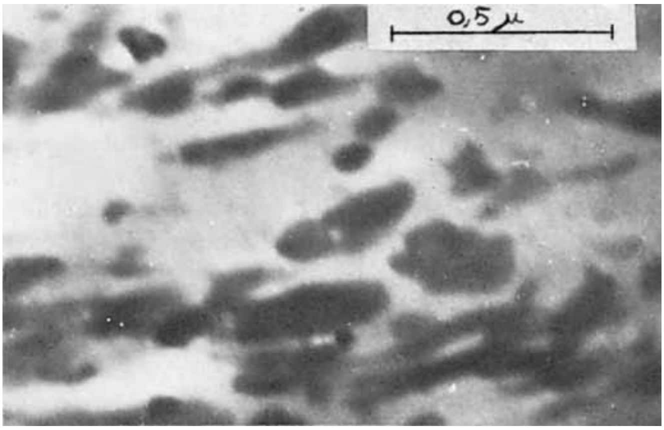

Fig. 2. Morphology of a blend of PVC (70 pph) and grafted EPDM of Figure 1 (30 pph).

Figure 2 shows the random distribution of the grafted copolymer in the PVC matrix and grafted particle agglomerations.

Mechanical Tests

Raw grafted polymers obtained by acetone precipitation, after drying, were subjected to calendering followed by molding either alone or in blend with PVC. Stabilizers (5 pph) were added, namely, antioxidant 2246 in the case of raw grafted products alone, and lead tribasic sulphate alone in the case of PVC blends. The calendering temperatures required to obtain a homogeneous sheet are a function of blend composition and range between 170 and 210°C. Molding temperatures were kept ~10° higher than calendering temperatures, other molding conditions are as follows: pressure 100 kg/cm^2, time 3–5 min. Sheets with thickness varying from 1 to 6 mm were thus obtained, in conformity with mechanical test requirements for A.S.T.M. standards. Tensile strength, tensile yield strength, and related elongations, notched Izod impact strength, deformation work at break, calculated by integration of curve σ, ϵ and Rockwell hardness L are shown (Table II and Figs. 4 and 5).

DISCUSSION

Grafting Reactions

Two types of rubber have been considered: one saturated (EPR) and another one (EPDM) containing pendant double bonds to study the influence of double bonds on grafting efficiency. There are initiators efficient in abstracting hydrogen atoms from the polymer chain to be grafted[3] and initiators that are not efficient[4] in this respect. Bz_2O_2 is an example of the former, and AIBN is an example of the latter. The two mentioned rubber types are quite sensitive to these two types of initiators.

The results (Table I) provide important qualitative suggestions concerning the grafting reaction mechanism. Grafting occurs by generation of active centers on the preformed polymer chain, either by transfer to the chain from the homopolymer macroradical or directly by the initiator action. The initiator may operate according to two different processes, i.e., either by addition to a double bond of the preformed polymer or by extraction of an active hydrogen atom from the chain.

Neither initiator AIBN nor MMA macroradicals are able, under our conditions, to abstract hydrogen from the saturated rubber chain during MMA polymerization, since the grafting yield on EPR is practically nil. The poor reactivity of MMA macroradical in this regard had already been ascertained in connection with polybutadiene grafting.[1] MMA macroradical reactivity is, therefore, negligible when compared to hydrogen extraction from both saturated and unsaturated rubbers. AIBN on the other hand[4] is not capable of abstracting hydrogen atoms from the main chain; the Bz_2O_2 is conversely capable of performing hydrogen abstraction, as demonstrated by grafting conducted on EPR in the presence of Bz_2O_2. Since the homopolymer macroradical is not efficient in abstracting hydrogen atoms, the generation of grafting active centers on the main chain is due solely to Bz_2O_2 transfer reaction.

TABLE II
Mechanical Properties of PVC Raw Grafted Product Blends as a Function of Composition[a]

Raw grafted polymer percent weight in the blend	0	10	20	30	40	50	100	Remarks[b]
Yield stress (kg/cm^2)	600	460	400	360	290	No yield	No yield	ASTM D 638
Tensile strength (kg/cm^2)	557	420	395	345	285	210	14.3	ASTM D 638
Yield strain (%)	8	8	8	7	6	No yield	No yield	ASTM D 638
Ultimate strain (%)	140	110	130	125	70	11	103	ASTM D 638
Deformation work at break (kg cm/cm^3)	725	430	460	420	200	20	9.5	ASTM D 638
Rockwell hardness (L)	104	95	90	88	85	78	—	ASTM D 785

[a] The raw grafted product was obtained with an M/R ratio equal to 0.75 and with a monomer grafting yield of 93%. Raw grafted product composition: EPDM 57%; PMMA 43%.

[b] Elongation rate 5 mm/min.

Let us now consider the results of grafting on unsaturated EPDM. Taking into account AIBNs and PMMA macroradical's inability to abstract hydrogen atoms from the ethylene-propylene copolymer chain, the data (Table I) shows that AIBN must inter-react with EPDM double bonds since, unlike the case of saturated rubber, grafting yields are appreciable. A comparison between the two initiators suggests that Bz_2O_2 is more efficient in ensuring considerable yields since it may be active with both the active center generating mechanism (i.e., hydrogen abstraction) and addition to the rubber double bonds.

Table I and Figure 3 also demonstrate that, other conditions being equal, grafting efficiency depends largely on the initial monomer/rubber (M/R) ratio.[5] Results indicate that while monomer is almost entirely grafted in the case of lower M/R ratios, it is more readily transformed into homopolymer than in a grafted product in the case of higher M/R ratios.

This behavior is largely due to the difficulties connected with the diffusion of radicals, activating the grafting to the elastomeric particles. Diffusion is slower when reaction time is equal. The PMMA peripheral layer, is thicker due to the greater polymerization rate of the higher local monomer concentration, as a consequence of the higher M/R ratio. The foregoing agrees with Rosen's[6] observations.

The relationship between grafting efficiency and rubber chemical structure indicates that unsaturated rubber is always more easily grafted (Table I). Homopolymer formation may be reduced to very small quantities by selecting a low M/R ratio and operating with Bz_2O_2.

Considering industrial scale operations, the *n*-heptane used to swell the rubber can be recovered easily after the grafting reaction by steam stripping.

Mechanical Test Results

Figure 4 shows the results of Izod impact strength as a function of the raw grafted product content in a blend of PVC and of the raw grafted product obtained by grafting MMA on EPDM, with different M/R ratios using Bz_2O_2 as initiator (I). The composition of raw grafted product obtained with M/R = 0.75 and I/R = 0.031 was: EPDM 57%; PMMA 43%. The composition of raw grafted product obtained with M/R = 1.32 and I/R = 0.032 was: EPDM 56%; PMMA 44%.

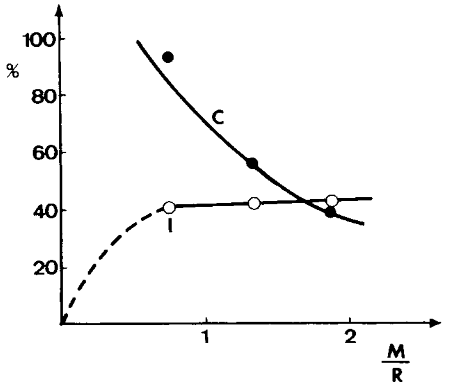

Fig. 3. Weight percentage of monomer grafted to EPDM (C) and weight percentage of grafted PMMA in the raw grafted product (I) against M/R by weight ratio.

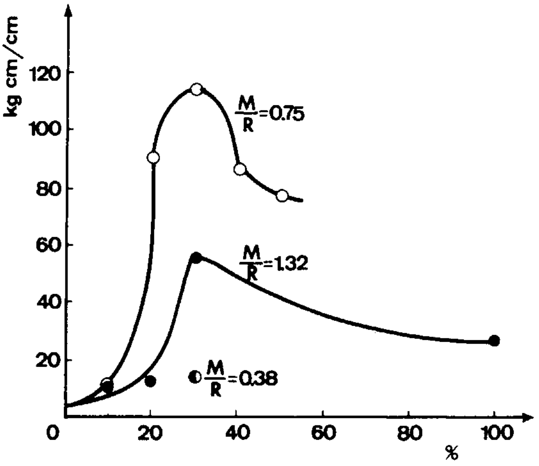

Fig. 4. Izod impact strength for PVC-raw grafted EPDM against raw grafted EPDM weight percentage at different monomer/rubber ratios (for other equal reaction conditions, see text).

Because of similarity in composition, curves (Fig. 4) would show a similar trend if the abscissa were referred to the rubber content. This does not apply to the raw grafted product obtained with M/R = 0.38 and I/R = 0.03 having the following composition: EPDM 83%; PMMA 17%. The raw grafted products are very poor in PMMA homopolymer, because the acetone that was used as precipitant is a solvent for PMMA. In all the raw grafted products, PMMA was linked by grafting from 93–98%.

A maximum peak (Fig. 4) is reached with raw grafted product content in the region of 30%. Peak intensity is a function of the initial M/R ratio. The best impact strength values are obtained in the presence of an M/R ratio equal to 0.75. With a very low M/R ratio (see M/R = 0.38), impact strength is lower as a result of an insufficient amount of grafted PMMA (curve I, Fig. 3). This is confirmed by the low impact strength values for EPDM grafting by AIBN instead of Bz_2O_2 as initiator, the former yields lower grafted PMMA percentages (Table I).

M/R and Bz_2O_2/R ratios being equal, much lower impact strength (Table III) is obtained when operating in the presence of EPR, as compared with that attainable with EPDM; this occurs since grafted PMMA is present in much lower percentages in the former case (Table I).

Results demonstrate that impact strength depends not only on grafted PMMA amount per rubber weight unit, but is also a function of grafting conditions. Whenever operating with low M/R ratios (e.g., 0.38), the monomer is almost

TABLE III

Izod Impact (ASTM D 256) Strength (kg cm/cm) of Blends of PVC and MMA Raw Grafted Polymers Based on EPR and EPDM, Containing 30% by Weight Raw Grafted Product[a]

Initiator	AIBN	Bz_2O_2
EPR (kg cm/cm)	2.3	4.3
EPDM (kg cm/cm)	3	110

[a] The raw grafted products were obtained by polymerization at 65°C for 24 hr using an M/R ratio = 0.75 and an I/R ratio = 0.032.

entirely transformed into grafted polymer, but the PMMA percentage in the system is low and impact strength is also low. The higher the M/R ratio, the lower the percent monomer in the grafted product, but this has no relevance in our case, due to the fact that homopolymer was largely extracted by acetone. The raw grafted product has a composition that does not change significantly beyond M/R = 0.75 (Fig. 3, curve I). Impact strength values, however, differ considerably in blends with PVC from M/R = 0.75 to 1.32, presumably due to the difference in interphase zone structure with a practically equal raw grafted product composition. The chains grafted on elastomeric domains obtained with high M/R ratios are comparatively scarce in number and longer than with lower M/R ratios. The PMMA surface layer covering the rubber particle, subject to quicker growing with a high M/R ratio, may act as a barrier against the diffusion of monomer that, as the reaction goes on, may no longer reach the rubber. So the number of grafts should be lower. The phenomenon had been observed by Rosen,[6] to explain a lower grafting efficiency in heterogeneous systems. There would, therefore, be an optimum M/R ratio ensuring (in blends) in interaction between PVC and grafted rubber peripheral layers, to allow adequate adhesion along with a disturbance of the PVC molecules conformation. PMMAs solubility parameter is 9.3 $(\mathrm{cal/cm^3})^{1/2}$, which is very close to that of PVC that is 9.5 $(\mathrm{cal/cm^3})^{1/2}$ and is therefore sufficiently compatable. Fracture due to impact is still not thoroughly understood; not only adhesion, but also the matrix fracture mechanism (by yielding or crazing) as well as the morphology of rubber particles dispersed in the matrix[7] are of great relevance. The low impact strength values (4 kg cm/cm) for blends between PMMA homopolymer and the same grafted raw product (M/R ratio 0.75; I/R = 0.031), which had nevertheless given optimum results with PVC (Fig. 4), confirm that grafted product composition and morphology being the same, good adhesion between rubber and matrix is not a sufficient criterion to guarantee good mechanical results.

Figure 5 shows curves σ, ϵ for tensile tests of PVC K 60 homopolymer, of grafted MMA–EPDM polymer with M/R = 0.75 and I/R = 0.031 having the composition indicated in the initial part of this paragraph, and some blends. While the grafted raw product (Table II) does not exhibit yielding, PVC and all blends do yield at elongation ϵ_s, which are of the same order of magnitude in all cases. Conversely, the tensile yield strength decreases as the grafted product percentage increases in the blend. Tensile strength also decreases regularly as the grafted product percentage in the blend increases. The foregoing agrees with the concept that dispersed particles act as stress concentrators.

The tensile stress-strain curves relating to blends of PVC and PMMA grafted EPDM with an initial M/R ratio = 1.32 do not differ significantly in mechanical properties, with the exception of the impact strength. This must be related to the different fracture mechanisms under low speed tests (tensile strength) and under high speed tests (impact strength).

PMMA grafted on EPDM is a two-phase system; grafted product dispersed in PVC is a three-phase system. When a heterophase system is cooled from molding temperature, it is subject to internal stresses due to differing expansion coefficients of phases, if there is adhesion. Beck[8] has calculated the triple tensile state in the case of a two-phase material with spherical inclusions; with regard to the matrix, stresses are maximum on the interface with rubber. When the material is subjected to tensile strength, internal stresses take place in addition

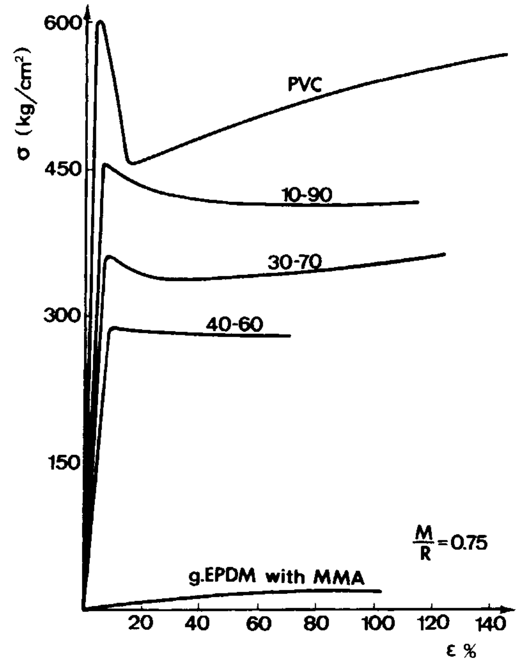

Fig. 5. Tensile stress-strain curves for PVC, raw grafted EPDM, and their blends: first number in blends indicates the weight percentage of raw grafted EPDM (for g-EPDM composition, see text).

to thermal stresses. On the basis of Goodier's[9] equations, Strella[10] concluded that the dilatation Δ in the matrix is a function of the load and of the distance from the center of the inclusion and of angle θ between the tensile applied load direction and the direction defined by the considered point and the rubber particle center. Dilatation Δ_2 due to thermal stresses is nil; therefore, the overall matrix dilatation coincides with the Δ calculated by Strella. At equal load Δ is maximum for $\theta = 90°$ on the inclusion surface. Shrinkage induced stresses of thermal origin are useful for the matrix ductile behavior since they reduce the maximum tensile stress due to the load application. Dilatation increases the free volume, the macromolecules mobility and ductility of the matrix. Grafted PMMA layer around the rubber particles probably increases the local free volume in the interphase region. Hence, the presence of inclusions can make the matrix yielding easier. Yielding and fracture happen at lower stress values. The results obtained for mechanical properties (σ_R, σ_S, deformation work) conform to the afore-said observations (Fig. 5 and Table III). Impact strength does not exhibit a downward trend against increasing rubber percentage, but shows a peak. The impact strength increase can be explained only from a qualitative point of view. The stresses generated within the matrix upon impact (in $\sim 10^{-4}$ sec) fail to have enough time available for relaxation, several yielding centers therefore originate, proportional to the number of included particles, where surface stresses are higher. Absorbed mechanical work thus increases concomitantly with the number of particles, at least until particles are so near that there is a significant superposition of the stress field around the particles.

CONCLUSIONS

Synthesis and properties of PMMA–EPDM grafted polymers, give a practical new contribution to high impact PVC technology. A new method has been developed to increase the rubber to be grafted at the aqueous emulsion interphase surface. The selection of adequate initiators proved to be an important factor in improving grafting yields. EPDM showed improved reactivity in respect to EPR. The high impact properties of PVC-raw grafted product blends is a result of a function of the amount of PMMA grafted per rubber weight unit as well as the grafting conditions. The impact strength of blends attains peak values with rubber percentage in the order of 15%; tensile yield stress, tensile strength, and break work of blends decrease with increasing grafted product percentage, in conformity with theory.[1,10]

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