FORMATION AND PROPERTIES OF SOME TWO-PHASE POLYMER SYSTEMS

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ABSTRACT

Polymers of different natures usually demix. The phases can interdisperse into domains only if their formation is thermodynamically favoured. This can be obtained by grafting or by synthesizing block polymers, but the effective structure depends on the technological process. Examples are given of interdisperse domains of grafted polymers obtained both from solutions and from heterogeneous phase polymerization. Quasi-spherical shapes are obtained by the first method.

The domain structure has very strong consequences on the properties. By quantitative stress analysis it is possible to demonstrate that a central domain, in a rigid matrix, when swollen, generates pressures which can easily break the matrix producing crazes. A range of water permeability is achieved in polyacrylic acid–polypropylene grafted films having different structures. The regularly distributed domain structure is the most permeable. If the matrix is rubberlike permeability is very small, in accord with theory.

In a stress field the tensile strength of a rigid matrix is lowered by the presence of included domains, but its impact strength is higher when the included domains are rubberlike.

The necessary conditions to get high impact structures are reviewed (difference in relaxation times, regular interdispersion of the phases, good adhesion, proper domain sizes). These structures can be obtained both starting by an elastomeric phase and successive grafting of rigid polymers and starting by a rigid phase and grafting of elastomeric polymers. Experimental examples are given.

Chemically different polymers separate very easily. Starting from a random mixture of two polymers A and B the tendency to separation is measured by the mixing free energy change ΔG_m with the opposite sign, which for amorphous polymers may be calculated according to the Huggins and Flory theory[1] (*Figure 1*).

This treatment leads to introduction of the dimensionless interaction coefficient

$$\chi_{B,A} \simeq (M_B/\rho_B RT)(\delta_B - \delta_A)^2$$

where M_B, ρ_B, δ_B respectively are molecular weight, density and solubility parameter of polymer B, considered as the solvent, δ_A is the solubility parameter of polymer A, R is the gas constant, T is the absolute temperature.

It may be demonstrated[2,3] that, with $\chi \geqslant 10$, the solubility of polymer A in B is reduced on equilibrium to less than one per cent.

The values of parameters δ of the different polymers may be either calculated according to Small[2] or found in the literature[4]. The lowest molecular
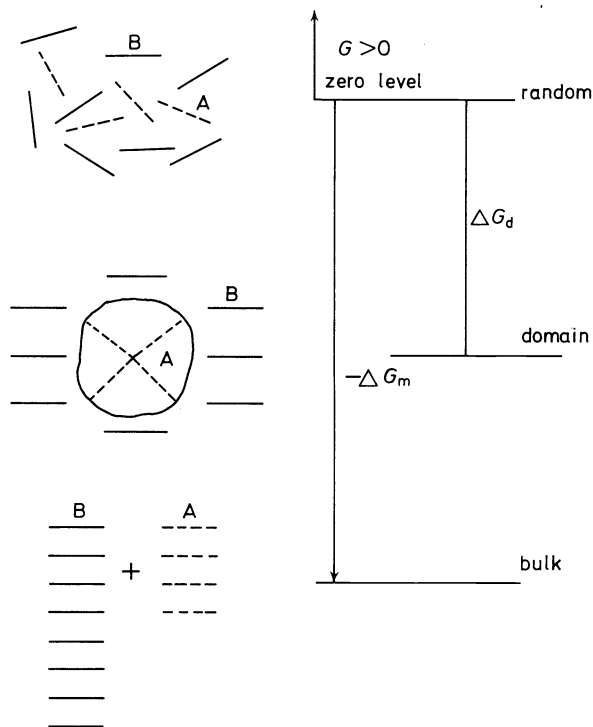

Figure 1. Formation of bulk or domain structures from a random mixture of two kinds of macromolecules: A and B

weights calculated in this way, which are required for demixing ($\chi = 10$), are usually of the order of a few thousands.

The formation of domains starting from the same reference state (random) is accompanied by a variation of the free energy ΔG_d, which differs from ΔG_m since it takes into account the constraints imposed at the junction points of molecules A and B, which must keep at the domain boundaries, as well as the surface free energy, which in an attempt to grow the domains in order to minimize itself gives rise to stresses and strains in the chains of the domain. As a matter of fact, the chains of A would tend to translate together with the domain border, but the cohesive forces do not allow the decrease in density at the centre of the domain. Meier[5] has demonstrated that—in the case he considered—formation of domains requires minimum molecular weights of A, from 2.5 to 5 times higher than those required for the simple demixing.

From what has been said above we can conclude that demixing into domains is not favoured if A and B chains are free, but is possible if they are joined. The above statements hold for both block and grafted polymers.

A description is given here of some experimental results we obtained by studying the structures of grafted polymers. Two methods have been used for structure formation: one starting from solution (homogeneous phase) and one building structures on preformed solids (heterogeneous phase).

STRUCTURES STARTING FROM SOLUTION

In this case the structures expected according to thermodynamics may be best approached, since the motion freedom of the macromolecules and of their segments is the highest possible. By grafting in orthodichlorobenzene at 120°C with benzoylperoxide as an initiator on polypropylene, we obtained for example solutions of grafted polyacrylic acid, grafted poly-β-hydroxy-ethylmethacrylate and grafted polyacrylamide[6, 7]. The solutions that contain both grafted polymer and homopolymer were shaped into films[7] (thickness 5–25 μm), which were stored in water. For investigations, films were treated with osmium tetroxide in water, conglobated in glycolmeth-acrylate, cut by the microtome and observed by transmission. In the case of films of polyacrylic acid (PAA) grafted on PP, the amounts of homopolymer are very low since water is an excellent solvent of the homopolymer. A structure with ellipsoidal domains has always been singled out[7] whatever is the percentage of PAA (from 20 to 60 per cent), the number density of which
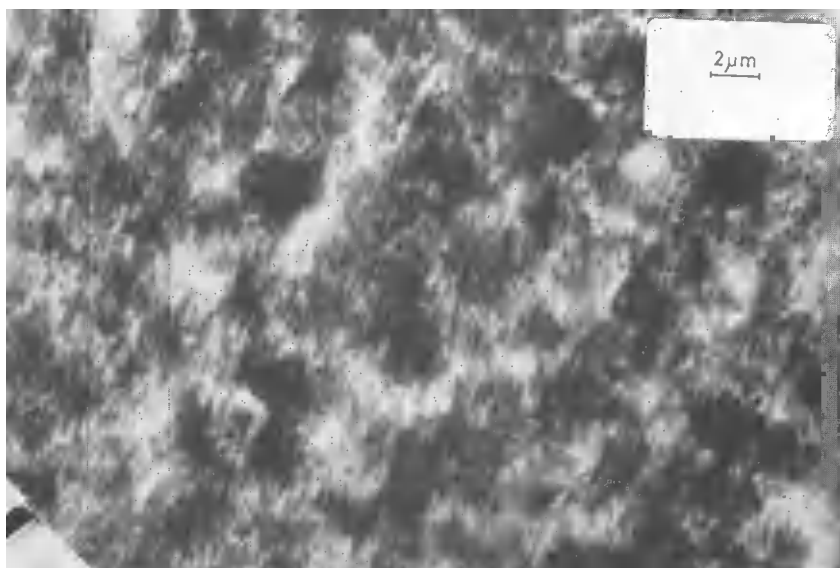

Figure 2. Cross section of polyacrylamide (PAAM) grafted (24.6%) on polypropylene (PP) after extraction of the homopolymer
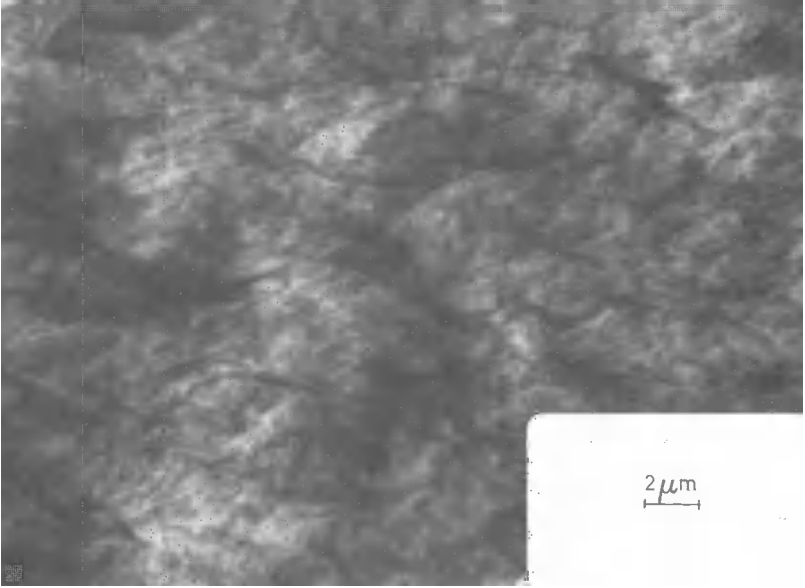
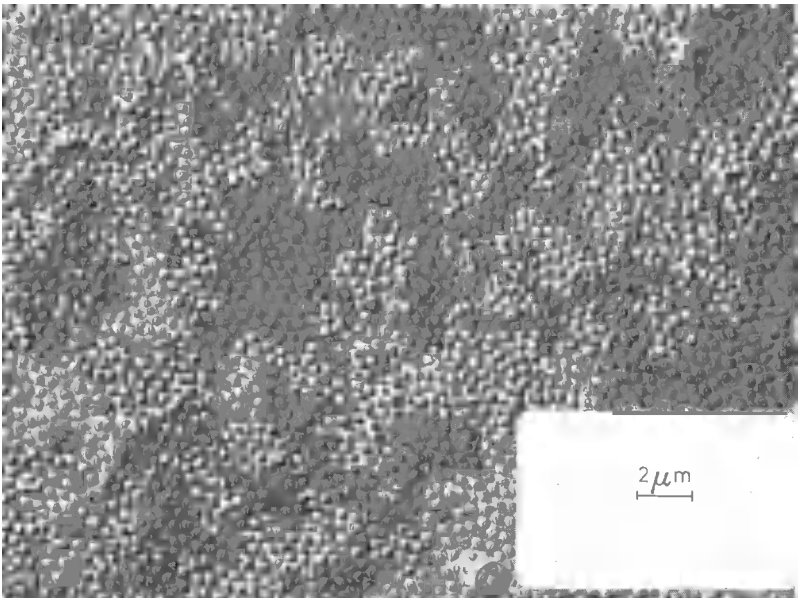Figure 3. Cross section of polyacrylamide grafted (24.6%) on PP in the presence of PAAM homopolymer (9%)

Figure 4. Surface replica of PAAM grafted (24.6%) on PP, see text

is higher when percentages are highest. Often, the average equivalent diameter was about 0.05 μm. The same type of structure has been detected by us in films of polyacrylamide (PAAM) grafted on PP (grafted PAAM 24.6 per cent) after homopolymer extraction with boiling water (*Figure 2*). Instead, before extraction the structure is partially fibrous (*Figure 3*) and this must be attributed to the presence of homopolymer ($\simeq 10$ per cent) which, beyond a certain limit, cannot be located in the ellipsoidal regions. An analogous fibrous structure has been found[7] in the case of poly-β-hydroxyethylmethacrylate (PGM) grafted on PP and containing 15 per cent of homopolymer. All surface replicas of all films described above have shown that the structures contain regularly arranged spherical domains (see e.g. *Figure 4* concerning PAAM). Since no homopolymer can exist on the surface (very accessible to water) it is proved that the structure of the amorphous polymers bound to polypropylene is that of spherical or ellipsoidal domains.

Similar structures have been found in films obtained from cyclohexanone solutions of PVC grafted with β-hydroxyethylmethacrylate at 60°C with chelate of bis(−)ephedrine of Cu(II). Structures with spherical domains have also been observed in films consisting of polyacrylic acid grafted on EPDM rubber, obtained by chain transfer with BZ_2O_2 in benzene solution[8].

The conclusion may be drawn that when starting from solutions, the preferential structure of grafted polymers in the solid state is that exhibiting regularly distributed domains of a spherical type shape, when the continuous phase (polymer B) is both crystalline and amorphous (vitreous or elastomeric).

STRUCTURES OBTAINED BY OPERATING IN THE HETEROGENEOUS PHASE

In this case we started from preformed solid polymers; other polymers were bound to them by grafting: in this case, structures may be hardly foreseen on the basis of thermodynamic considerations since the kinetic conditions were determining. As an example we show the section (*Figure 5*) of a bioriented film (thickness 20 μm) of PP peroxidized with air in the presence of surface agents[9] and subsequently grafted with acrylic acid according to a method described by us[10]. It contains grafted PAA (42.5 per cent). The polyacid has wedged itself into interlamellar regions which lie in the plane of orientation and which are more accessible to oxygen and to the monomer.

A far more regular distribution of PAA domains is that obtained starting from a non-oriented PP film, peroxidized and grafted. Domains have an equivalent diameter of about 0.03 μm. In this case the absence of a preferential orientation of the crystals allows us to obtain a structure similar to that of the films obtained from solutions.

Interesting structures may be obtained starting from solid spherical particles. For example by grafting with (liquid) butadiene, stiff granules of peroxidized PP, with an average diameter of 20 μm, we obtained a grafted product (at 18 per cent rubber) that, after moulding, exhibits the structure of rubber particles (diameter 0.3 μm) dispersed in the PP matrix. Moulding obviously allows a re-arrangement and an agglomeration of elastomeric
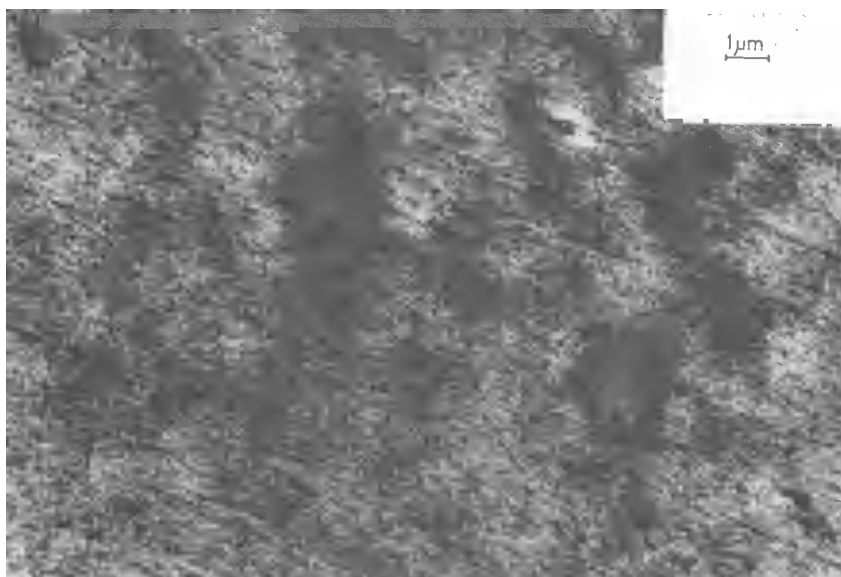
Figure 5. Section of polyacrylic acid (PAA) grafted on PP (42.5 %) (bioriented film)
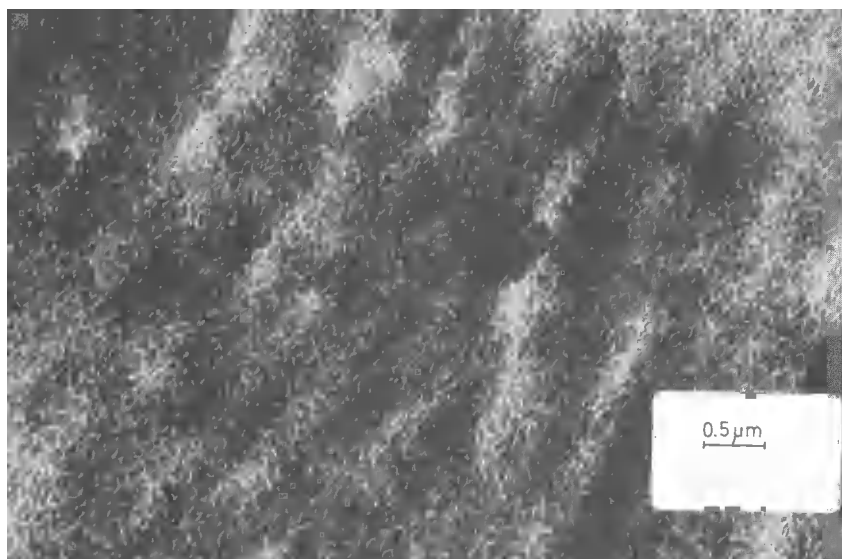

Figure 6. Section of a commercial MBS (Kane Ace B22)

regions. If the initially spherical particle is elastomeric and if a rigid polymer is grafted on it, the structure may have a polygonal honeycomb shape. This is due to the fact that the holes initially present among tangent spheres cannot persist after moulding, owing to the high cohesive forces among the rigid molecules. An interparticulate continuum of stiff material is formed and this causes deformation of the low-elastic-modulus material (the elastomer). *Figure 6* shows a sample of commercial MBS (Kane Ace B22), which, as revealed from analysis, consists of methylmethacrylate, butadiene, styrene, acrylonitrile, characterized by elemental analysis C = 84.3, H = 9.4, O = 6.1, N = 0.43 per cent. This material is a two-phase polymer system made by an elastomeric heart-shaped structure and by a stiff shell. Similar structures were obtained by us after grafting methylmethacrylate on polybutadiene spheres.

What has been stated above leads to the conclusion that the structure of the dispersed phase in the two-phase polymer systems extensively depends on the physical conditions of synthesis, although the spherical shape is the most frequent. Both obtaining and adjustment of the various structures is still highly empirical.

INTERNAL STRESSES AND POROSITY

The arrangement of the dispersed polymer, within a matrix of a different polymer, supplies the composite with particular properties.
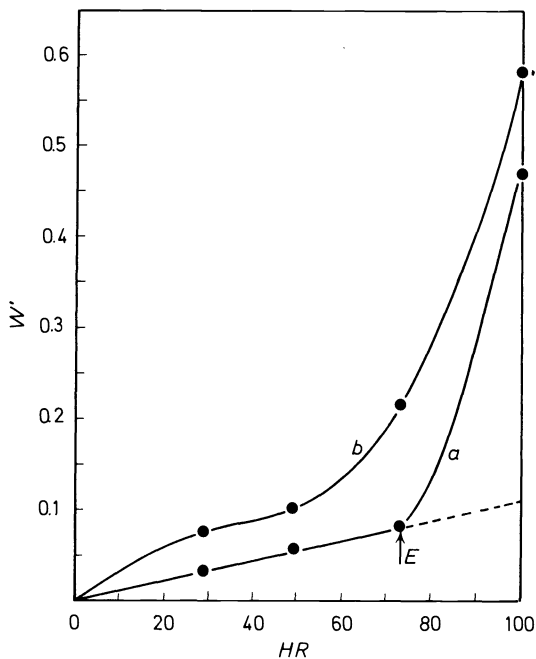

Figure 7. Water adsorption curve for a PAA grafted (52% by weight) on PP (*W'* indicates g H$_2$O/g grafted polymer); HR denotes relative humidity

For example, by selective swelling of one of the phases, internal stresses may arise in the system which determine its porosity.

We quote the case of PAA grafted on PP. A film prepared from solution and containing grafted PAA (52 per cent), on contact with moist air with different moisture contents absorbs water at room temperature according to what is indicated in *Figure 7*, curve *b*. The same film, compacted by compression moulding absorbs less water (curve *a*). The difference must be attributed to capillary condensation in the pores present in the structure[11]. The presence of the pores is demonstrated also by the low selectivity in the inverse osmosis process of such types of films obtained by extraction[12]. Generation of microfractures may be explained on the basis of high pressures exerted on the PP matrix, when the PAA domains contain a substance (water) capable of swelling them.

In fact, let us consider a single spherical domain of a polymer A in the swollen state immersed in matrix B which cannot be swollen, but which is permeable and has indefinite dimensions. The state of stress in A, after the swelling has been hindered by the stiffness of B, is a state of uniform pressure characterized[13] by the stresses and strains shown in *Table 1*(a).

Table 1. Stress/strain relationships in a sphere

(a) Hydrostatically compressed from outside

$$\sigma_{rr} = \sigma_{\phi\phi} = \sigma_{\theta\theta} = -p \qquad e_{rr} = e_{\theta\theta} = e_{\phi\phi} = -p/(3\lambda + 2\mu)$$
$$\sigma_{r\theta} = \sigma_{r\phi} = \sigma_{\theta\phi} = 0 \qquad e_{r\theta} = e_{r\phi} = e_{\theta\phi} = 0$$
$$3e_{rr} = \Delta = -p/k$$

(b) Hollow sphere internally loaded at $R = R_0$ with pressure p, unloaded at $R = \infty$

$$\sigma_{rr} = -p(R_0/R)^3 \qquad e_{rr} = -(p/2\mu)(R_0/R)^3$$
$$\sigma_{\theta\theta} = \sigma_{\phi\phi} = \tfrac{1}{2}p(R_0/R)^3 \qquad e_{\theta\theta} = e_{\phi\phi} = (p/4\mu)(R_0/R)^3$$
$$\sigma_{r\theta} = \sigma_{r\phi} = \sigma_{\theta\phi} = 0 \qquad e_{\theta\phi} = e_{r\phi} = e_{r\theta} = 0$$
$$\Delta = 0$$

In the table, we adopted the Love's notation[13] for the indexes; K is the compressibility modulus, μ is the torsional modulus, λ the Lamais coefficient of swollen A and Δ is its cubic dilatation. $\Delta = \Delta V/V$, i.e. the ratio between the actual variation ΔV of the volume of A due to the elastic reaction of B, and the initial volume of domain A.

The stresses in material B can be likened to those present in a hollow sphere with infinite external radius and loaded internally by pressure p and unloaded externally: see *Table 1*(b). Now consider, *Figure 8*(a), the sphere of material A in the anhydrous state characterized by radius R_A surrounded by material B and limit observation to a radial vector L_A

$$L_A = R_A + a_0$$

Now let us superpose two effects:

(a) A swelling of the sphere up to R_0 without any variation of a_0 and without appearance of internal stresses.
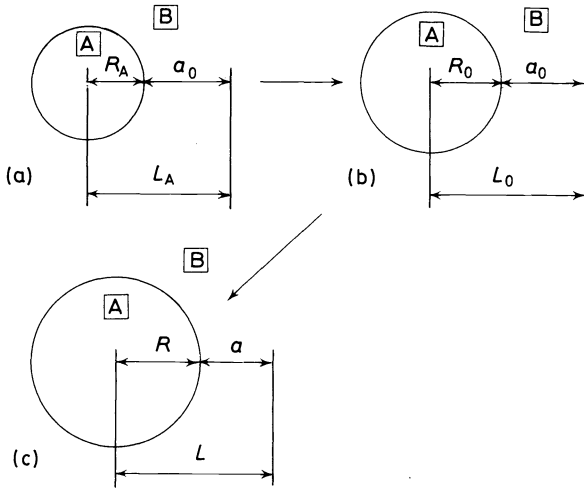
Figure 8. Domain A immersed in a B elastic matrix

(b) A contraction of the system so as to reach the actual state of stress and strain. The vector modulus now is

$$L = R + a$$

The elastic elongation

$$\Delta L = L - L_0 = R - R_0 + a - a_0$$

is related to the internal stresses and may be expressed as a function of the interfacial pressure p by using the expression of *Table 1*(a)

$$(R - R_0)/R_0 = -p/3K$$

and the expression deriving from *Table 1*(b)

$$a - a_0 = \int_{r = R_A}^{r = R_A + a_0} e_{rr}\, \mathrm{d}r = \frac{-p}{2\mu_B} \int_0^{a_0} \left(\frac{R_A}{R_A + a}\right)^3 \mathrm{d}a$$

$$= \frac{-pR_A}{4\mu_B}\left[1 - \frac{1}{(1 + a_0/R_A)^2}\right]$$

The relation between R_0 (unloaded swollen sphere) and R_A (anhydrous sphere) may be easily expressed by admitting the additivity of the volumes: we have

$$R_A^3 (1 + t) = R_0^3$$

where $t = \Delta V_A/V_A$ indicates the relative variation of the volume having radius R_A. If Δw is the weight increase of the weight unit of the composite, ρ the density of the adsorbed substance and v_2 the volume of the adsorbing

polymer in the weight unit of the composite, we have

$$t = \Delta w/\rho v_2$$

From this we obtain

$$R_0 = kR_A \text{ where } k = (1 + t)^{\frac{1}{3}}$$

and so

$$L - L_A = kR_A \left[1 - \frac{p}{3K} - \frac{p}{4\mu_B k} \left(1 - \frac{1}{(1 + a_0/R_A)^2} \right) - R_A \right] \quad (1)$$

Here R_A is known from microscope measurements on anhydrous samples and by the imposition of a value of t depending (*Figure 7*, curve *a*) on the partial pressure of the adsorbed substance, it is possible to measure $L - L_A$ and to calculate the corresponding interfacial pressure p, once K and μ_B are known. The highest value of p that may be reached without damaging the composite is its yield value p_y. This may be calculated by the von Mises criterion[15], admitting that the highest energy that may be accumulated in a simple tensile test $(\sigma_y^2/2E)$ at yield is equal to that occurring in the actual conditions. On the basis of the expressions of *Table 1*(b) for the main stresses, shear being absent, the maximum energy is

$$(3/4E) p_y^2 (1 + v)$$

As σ_y of PP equals 300 kg/cm², we have $p_y = 210$ kg/cm². For the value of t for which in the compact composite the formation of fractures starts (point *E* of *Figure 7*) it is possible to calculate with equation 1 the corresponding strain $(L - L_A)/L_A$. For example for the sample of *Figure 7* containing 40 per cent by volume of PAA, this strain is five per cent ($t = 0.222$;
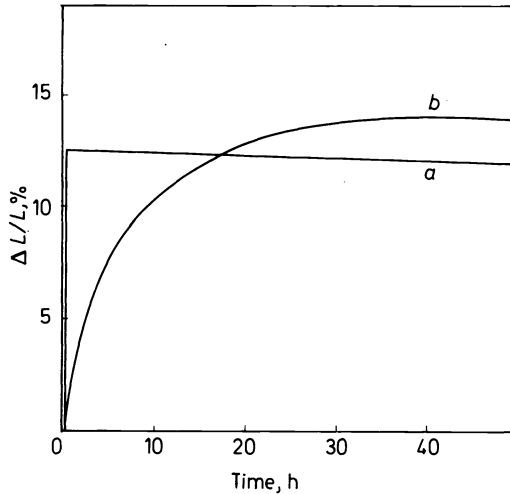

Figure 9. (a) Percentage elongation of a film of PAA grafted (32%) on PP against time. (b) The same for a film of PAA grafted (14%) on EPDM

$R_A = 0.025\,\mu m$; $L_A = R_A/\sqrt[3]{0.40}$; $K = 100000\,kg/cm^2$; $\mu_B = 10500\,kg/cm^2$; $a_0 = L_A - R_A = 0.37\,R_A$).

Elongations of real films obtained by extraction, immersed in water are far higher. For example, in films containing 23 per cent by volume of PAA (*Figure 9*) they already are twelve per cent. This demonstrates that the yield strength of PP is exceeded. Therefore it becomes possible to obtain a permanent set of microfractures, which decreases the average elastic modulus and makes the system more deformable. Such microfractures are open only when internal stresses are present, i.e. when PAA is swollen. This is demonstrated by the fact that surface area measurements carried out by the gas adsorption method (e.g. with nitrogen) and by the mercury penetration method do not give appreciable values, being carried out in the absence of water, while water adsorption curves give sure indications of the existence of porosity (*Figure 7*).

If the material that surrounds the sphere has a lower modulus μ_B, formula 1 suggests lower interfacial pressures, while t, R_A and elongation remain the same. *Figure 9*, curve b shows that an EPDM grafted with PAA (content of PAA = 14 per cent) obtained from solution, crosslinked with S_2Cl_2 and containing domains with a radius that is practically equal to that mentioned above ($R_A = 0.025\,\mu m$), exhibits an evident elongation during hydration, but microfractures of the matrix are not probable due to the low elastic modulus. In agreement with this point of view, water permeability of non-hydrophilic grafted elastomeric materials is low (see *Table 2*) in comparison with microfractured materials. Two-phase films with a stiff matrix, chemically identical, but whose structure differs from the spherical domains, generally present a lower permeability to water. For example, bioriented PP, grafted with PAA having lamellar structure (*Figure 5*) is slightly permeable (*Table 2*): this is connected with the existence of large areas of stiff material

Table 2. Liquid water permeability of grafted films having different structures. Test method as in reference 12

Matrix	Grafted polymer polyacrylic acid, %	Structure of domains	Permeability mg H_2O/h cm mmHg
Polypropylene (extraction)	57	spherical	independent of thickness
Polypropylene (not oriented)	81	spherical	18×10^{-5}
Polypropylene (bioriented)	81	lamellar	1.9×10^{-5}
EPDM rubber (3.5 ENB)	14	spherical	1.7×10^{-5}

which are not subjected to stress concentrations capable of causing regularly disposed microfractures.

STRUCTURE AND MECHANICAL PROPERTIES

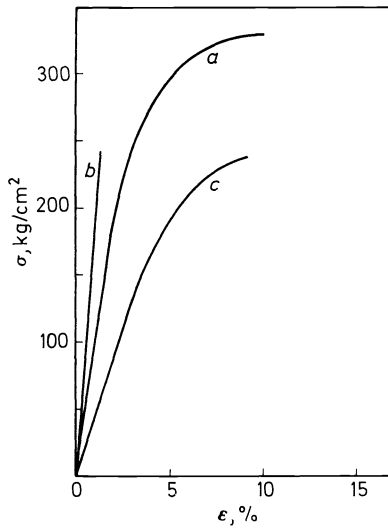The presence of heterogeneity in a system subjected to external forces

Figure 10. Tensile stress/strain curve: (a) polypropylene; (b) PAA grafted (41 %) on PP in dry conditions; (c) the same as in (b) but in the presence of water

causes local variations of stresses with regard to those which would exist, were the system homogeneous. Stress and strain distributions around a spherical inclusion present in a continuum subjected to a simple tensile force have been found by Goodier[16]. If θ is the angle between the direction considered and the stretching direction, it may be demonstrated that, with the inclusion of a lower modulus than the matrix, a stress $\sigma_{\theta\theta}$ exists in the
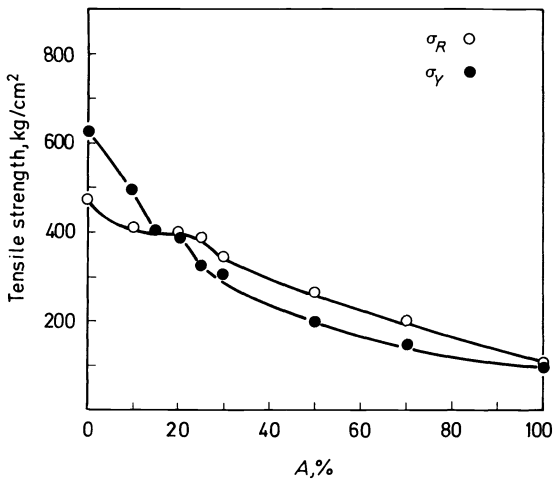

Figure 11. Yield σ_y and tensile strength σ_R of PVC and Kane Ace B22 against percentage of the latter

matrix, which is highest on the equatorial plane ($\theta = 90°$) exactly at the borderline of the sphere and which does not depend on the other angular coordinate ϕ. This stress is higher than the average stress σ applied, falls off rapidly with the distance r from the centre of the sphere and as soon as θ departs from 90°, but is dangerous for material stability.

Such remarks justify the experimental behaviour of tensile curves of the many grafted materials obtained by us. *Figure 10* shows for example the tensile curve of a PP film obtained from a solvent (curve *a*), and a film of PP grafted with 41 per cent PAA (with spherical domains) dry (curve *b*) and wet (curve *c*).

A similar reduction in the strength is also observed when included domains are not chemically bound to the matrix. For example *Figure 11* shows the behaviour of tensile yield σ_y and tensile strength σ_R of mixtures of a PVC (K 60) with commercial MBS (Kane Ace B22), the particles of which, as revealed by investigations under a microscope, are well dispersed.

IMPACT STRENGTH

Stiff materials considered as Maxwell elements at room temperature exhibit very high relaxation times and therefore the severe stresses applied in the impact test persist dangerously in the material without any practical relaxation. The stiff material must be mixed with another material exhibiting a relaxation time lower than the testing time (10^{-4} s), that is with an elastomer the percentage of which should not be too high, not to exceedingly reduce
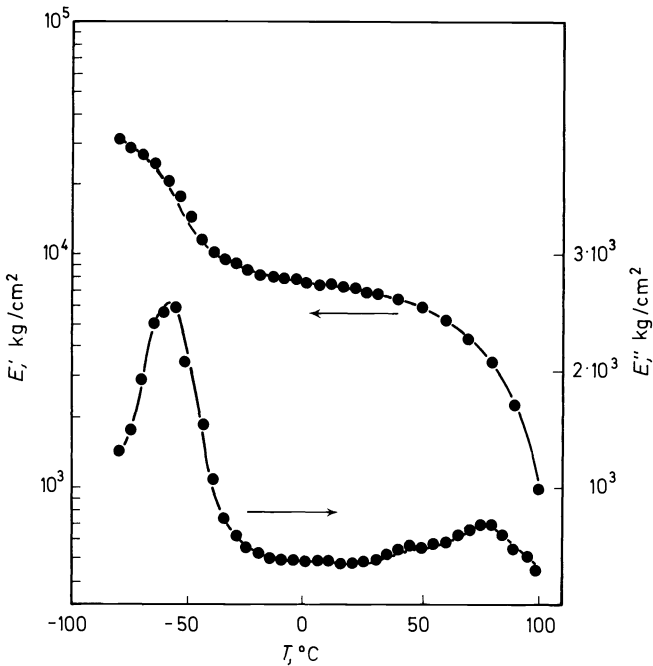

Figure 12. Elastic moduli E' and E'' of Kane Ace B22 against temperature T

the overall elastic modulus of the system. We found always—studying the behaviour with temperature of the complex elastic modulus of high-impact grafted polymers prepared by us (PVC and EPR; PP and BR) and of a commercial MBS grafted polymer (Kane Ace B22) (*Figure 12*)—that the two relaxation processes are clearly visible; as to impact, the matrix behaves as a stiff material.

The earliest theory of rupture was proposed by Merz[17]; it assumes that rubber absorbs energy by simple elongation. However, it may be calculated[18]

$$\frac{\Delta}{\sigma} = \frac{1-2\nu_B}{E_B} - \frac{(1+3\cos 2\theta)}{4E_B}\left(\frac{a}{r}\right)^3 \frac{5(1-2\nu_B)(E_B-E_A)}{(7-5\nu_B)+(8-10\nu_B)E_A}$$
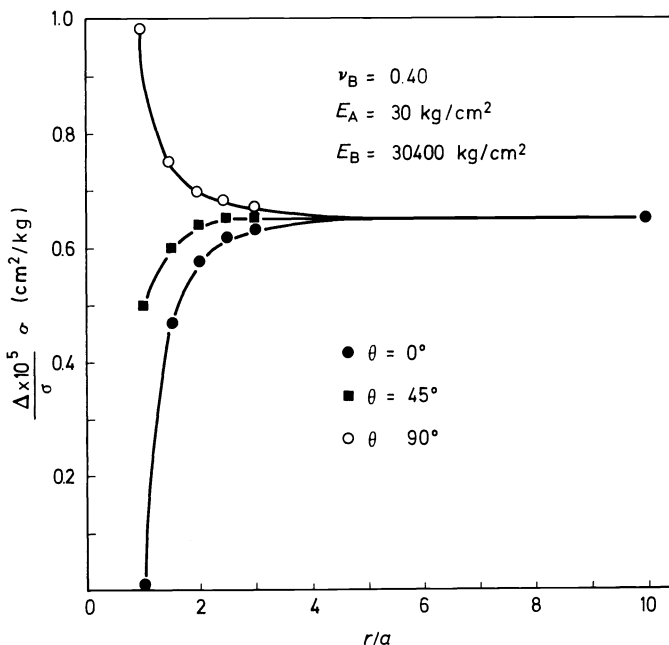

Figure 13. Dilatation for unit stress (Δ/σ) for different angles and distances around an included particle

that only ten per cent of rupture energy may be attributed to such deformation. Furthermore it has been later ascertained that crazes are formed in the matrix, which are low-density and high-orientation regions, perpendicular to the direction of fracture. For the formation of crazes[19], very high energies are required (about 5×10^8 erg/g). Therefore, the formation of crazes justifies the high impact strength.

A second interesting theory, though not quite satisfactory, is that proposed by Newman and Strella[18, 20]; around a particle immersed in a matrix subjected to an uniaxial stress, a state of hydrostatic tension and a dilatation Δ exist. *Figure 13* represents Δ according to Goodier[16], as a function of the

ratio between distance r and radius a of the particle for different angles θ, having assumed a rubberlike inclusion in a rigid matrix. Dilatation causes an increase in free volume in the matrix: hence it facilitates plastic flow and microbrownian motions, inducing tenacity. However, the calculated increases in volume are not such as to generate the free volume that the matrix possesses above its T_g. For example, as to high-impact PS subjected to tensile stress, the highest increase in volume ($r = a$, $\theta = 90°$) is $0.99 \times 10^{-5}\,\sigma$ ($G_2 = 10\,\text{kg/cm}^2$, $G_1 = 10000$, $v_1 = 0.3$ at 23°C). For $\sigma_R = 300\,\text{kg/cm}^2$ and $\alpha = 25 \times 10^{-5}\,\text{K}^{-1}$ (cubic dilatation coefficient) by equalling the mechanical dilatation at rupture to the thermal one, the value of $\Delta T = 12°C$ is obtained. It is useless to remark that T_g is well above 35°C. Furthermore empty spherical holes, according to this theory, should be more efficient than included rubber spheres, since they cause higher dilatations. This is contrary to reality[21].

A satisfactory theory has not yet been put forward. We add here some original remarks on the importance of the grouping of dispersed domains, which has not yet been adequately considered.

After applying a sufficient stress, the 'crazes' nucleate[22] at the points where internal energy is not minimum, i.e. at the interphase surface, and propagate into the matrix. It is quite probable that in a real system adhesion is not perfect at all points of the sphere. Hence nucleation of the craze outside the plane, foreseen as the most probable according to Goodier[16] which is equatorial in respect of the stress axis, cannot be excluded. Furthermore, particles are seldom really spherical and even the thermal history may exert some influence. Rupture of oriented materials in crazes causes a microfracture. The rate of propagation of a fracture, of length $2c$, is governed by the transfer of the elastic energy W_d accumulated in the system to the fracture region that requires energy both in order to generate new surfaces (W_s) and to move with a certain rate (W_v). By applying the principle of energy conservation

$$\frac{\partial}{\partial c}(W_d + W_s + W_v) = 0 \qquad (2)$$

the Griffith formula is found[23] when fracture moves slowly and the Mott, Roberts and Wells formula is found[24] if the rate is not negligible. The rate with which a fracture moves is in the latter case

$$c = 0.38(E/\rho)^{\frac{1}{2}}(1 - C_0/C)^{\frac{1}{2}}$$

in a material of modulus E and density ρ; $2c_0$ is the Griffith length.

The term $(E/\rho)^{\frac{1}{2}}$ is the rate of elastic longitudinal waves in the material. It is of an order of thousands m/s in the matrix and of tens m/s in the elastomer. Equation 2 can be applied not only to cracks, but also to crazes. Notwithstanding the different expression, $\dot{c}$ for a craze is expected to be of the same order of magnitude as the rate of crack propagation. When by passing through the matrix the craze meets an elastomeric domain having a size almost identical with that of the craze, it undergoes a violent deceleration. It has been experimentally observed[25] that, under such conditions, craze branching may take place. In this case the Yoffe theory too[26] foresees

the possibility of fracture branching. Every branching doubles the area involved in the fracture. It is thus possible to demonstrate[21] that the fracture area and therefore the fracture energy is an exponential function on basis two of the number of times in which the craze and the particles meet.

IMPORTANCE OF PARTICLE SIZE AND DISTRIBUTION

The size of a craze is characteristic of the stiff material: in some cases this has been experimentally ascertained[27]. For example in S/AN it is 0.5–0.7 μm, whereas in PS it is between 0.9 and 2.8 μm. In fact each polymer is characterized by its own interfacial tension that comes into play when empty spaces are generated, and by its own tensile strength and elastic modulus, which participate in the expression of the elastic energy that is transformed during crazing into fracture work. If we accept the branching theory, we see that the condition required for fracture branching is that a craze meets a particle of rubber; therefore the minimum dimension of a particle must be that of the matrix craze in which it is situated. For example, as to the S/AN copolymer, experience shows[28,29] that the minimum diameter is 0.1–1 μm whereas for PS it is higher (2 μm). In order to limit the average free distance among the particles it would be better to keep the diameter either equal to or slightly above this limit. As a matter of fact if we suppose that the space is divided into cubic primitive cells with edge D, we have $ND^3 = V$ where N is the number of spheres in the volume V. For $\frac{1}{6}N\pi d^3 = C_A V$ we obtain

$$D = d(\pi/6C_A)^{\frac{1}{3}}$$

The room available to fracture lines is therefore the larger the longer the edge D, diameter d, and the lower C_A: this may justify the increase in impact strength only after addition of a given amount of elastomer. The probability that a fracture line meets the particles is proportional to section Nd^2 and therefore to the ratio C_A/d. Even from this point of view it is convenient to keep d at low values. An apparent discrepancy is found, in the literature[30], where it is quoted that resilience of ABS increases on increasing the diameter of the particles: however, the examined diameters were below the dimensions of the craze of S/AN.

The elastomer domains tend to aggregate spontaneously because the interphase surface and consequently the free energy are reduced. However, the situation is quite different depending on whether the elastomer is as such and hence insoluble in the matrix, or whether it is covered by a layer consisting of a polymer identical with that constituting the matrix (e.g. in the case of grafted polymers) or similar to it (in the case, e.g. of some high-impact substances, such as Kane Ace B22). In the former case, elastomer A has no affinity for matrix B and the equilibrium constant of the aggregation transformation of z units A is high,

$$z\text{A} + \text{B} \rightarrow \text{A}_z + \text{B};$$
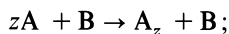
hence formation of aggregates is easy. In the other cases, formation of aggregates is not favoured since domain A behaves like matrix B. For example, choosing the coordination number 12 (and $z = 13$) we calculated
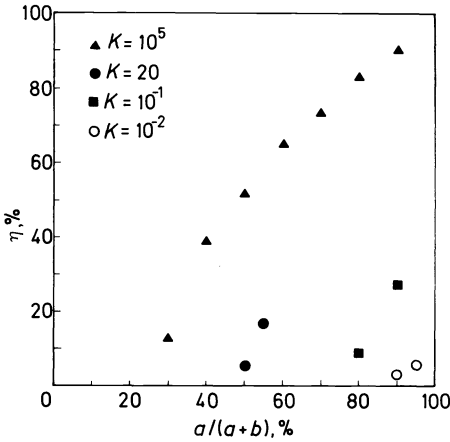
Figure 14. Aggregates yield (η) as a function of the percentage of A, for different aggregation constants

(*Figure 14*), the ratio η (yield) between the number x of aggregates A_z and the highest number that may be obtained stoichiometrically, starting from an initial number a of A units dispersed in a number b of B units as a function of the percentage $a/(a+b)$ of A in the system for different equilibrium constants $\overline{K}$. It is observed that the yield η in aggregates is the higher the higher $\overline{K}$ and the higher the initial percentage of the elastomer.
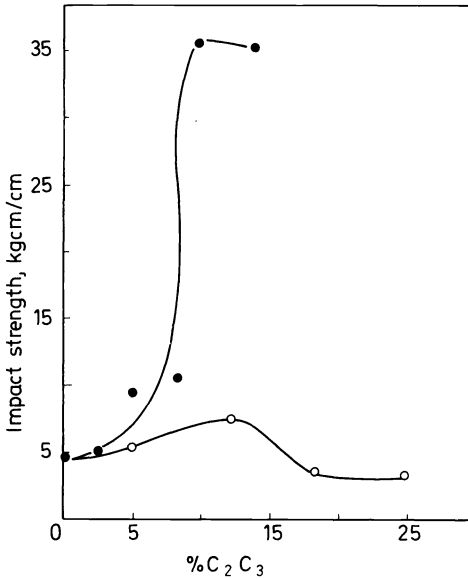

Figure 15. Impact strength of a mixture of PVC and PVC grafted on EPR ● in comparison with a physical mixture of EPR and PVC ○ against the percentage of EPR

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Agglomeration of z particles of A causes (as may be easily calculated) an increase in the distance among the A domain barycentres and therefore a decrease in impact strength.

It is to be expected that—the composition being the same—the physical mixtures of an elastomeric copolymer ($\bar{K}$ value high) exhibit a much lower toughness than that of a grafted polymer (low $\bar{K}$). This has been widely proved by our experimental results. *Figure 15* shows the impact strength of grafted PVC on EPR (10 per cent EPR) in mixtures with PVC, compared to the physical mixtures. The same occurs for grafted PS on C_2C_3 (cf. ref. 31).

ADJUSTMENT OF ACTUAL DIAMETER OF DOMAINS

Not only, the size of the single elastomer particle (micelle), but also its tendency to aggregate have a considerable importance. The simplest and best known method to control the micellar size is the polymerization of the elastomer in emulsion.

According to Smith and Ewart[32] it is possible to adjust the number and size of the particles, depending on the type of surface agent used, on its amount and temperature of polymerization for a given monomer and initiator. The size decreases on increasing the two latter parameters[32].

The controlled growth of the particle diameter may be obtained through the insemination technique[33].

Micelles with a convenient size may be obtained even by suspension under stirring of preformed rubbers in monomers used to modify them, which swell them[34] or dissolve them[35]. All the controlling methods are essentially empirical.

The real dimensions of the elastomeric domains may be higher than those of the micelles, due to the grouping. To reduce grouping it is necessary to modify the A domain surface by graft or block polymerization, to approach
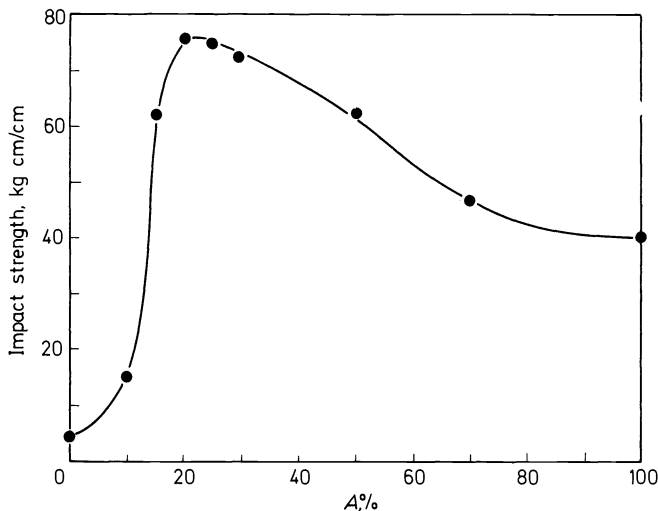

Figure 16. Impact strength of PVC and Kane Ace B22 compound against the percentage of the latter

as close as possible the values of the solubility parameter δ of the A polymer to that of the matrix. Furthermore, this causes an increase in adhesion. Adhesion is strictly required in order to allow the passage of crazes from the matrix to the elastomer and to get a good impact strength.

An interesting application of the above principles is the control of impact strength by dispersion of two-phase grafted polymers, in convenient stiff matrices. Such systems exhibit for a certain composition, a maximum of resilience (see, e.g. *Figure 15* and ref. 34). In particular we studied the mixtures of a PVC (K 60) with a commercial MBS (Kane Ace B22) (*Figure 16*). *Figure 6* shows its structure with polyhedral micelles with an equivalent diameter of 0.07 µm, each consisting of a central elastomeric region rich in double bonds (and therefore darker after treatment with osmium) and of a stiff peripheral region. By mixing Kane Ace with PVC for weight concentrations of 10 and 50 per cent, regular dispersions of the single micelles are obtained; instead, particles appear partially aggregated when they are present at 20 per cent (*Figure 17*). The excellent dispersibility (case of 10 and
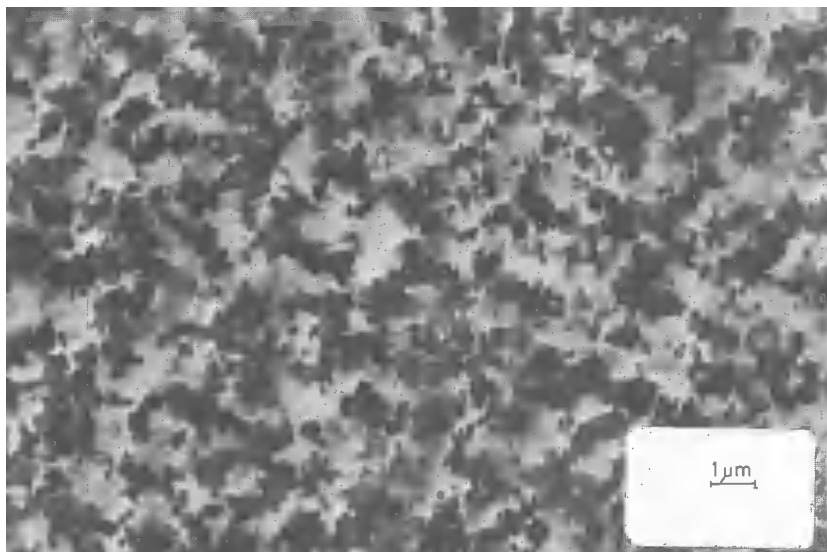

Figure 17. Cross section of a PVC and Kane Ace B22 compound (20 % of the latter)

50 per cent) suggests that the value of parameter δ of PVC is quite close to that of the copolymers constituting the peripheral layer, whereas the imperfect dispersion at 20 per cent, corresponding to high values of resilience (*Figure 16*) and at a crossing of functions σ_R and σ_y (*Figure 11*) is not cleared even if it might be ascribed to kinetic reasons. The decrease in impact strength for additive concentrations higher than 30 per cent is related to the fact that fracture processes in the elastomeric phase become even more important in respect of those occurring in the rigid phase. Fracture of the

elastomeric phase in a two-phase composite absorbs less energy than the same mass of the crazing stiff matrix. The specific fracture work (area of the $\sigma-y$ diagrams against the composition) is in agreement with this point of view; if the elastic energy accumulated in the system at tensile yield strength, is lower (for high percentages of rubber) also the fracture energy must be lower, due to the conservation energy principle.

ACKNOWLEDGEMENTS

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