PVC Mixtures with Processing Aids

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PVC Mixtures with Processing Aids
Part I. Mechanical Properties and Morphology

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The mechanical properties (dynamical, tensile) and morphology by electron microscopy have been studied on PVC mixtures with processing aids of different compatibility with PVC (copolymers of methylmethacrylate, polystyrene, polyvinylacetate) in the temperature range of 20–150°C. It has been found and interpreted that the mechanical properties of PVC in the temperature range of 100–120°C are favourably influenced by addition of a processing aid, which is compatible with PVC, has a sufficiently high molecular weight and its glass temperature is about 20°C higher than that of PVC.

I. INTRODUCTION

The modification of properties of hard PVC by adding another polymer is a rather well known method currently used in practice. The number of polymers and copolymers applied as modifiers is quite large and may be divided into two basic groups.

The first one involves rubber-like polymers and copolymers, which are added to PVC to improve its mechanical properties, particularly its toughness. The structure of the materials prepared in this way and the mechanism of the action of the modifiers have been for years the object of intensive investigations by numerous authors.

The other group involves polymers which are used for the modification of PVC under the general denomination—processing aids. While the mechanical properties of hard PVC are only insignificantly changed at room temperature by the addition of a modifier, the processing operations (milling, calendering,

extrusion, blow moulding and the like) in PVC melt are significantly facilitated.

Moreover, by the modification of hard PVC by means of processing aids of the polymethylmethacrylate type, its extensibility and, to some extent, even its strength at increased temperatures (100–120°C) is substantially increased.

Literature data about the use and properties of acrylic processing aids are rather sporadic and any satisfactory mechanism of the action of these modifiers[1-4] has not yet been suggested so far.

It is the object and purpose of this paper to suggest—on the grounds of studying the tensile properties of various processing aids in mixtures with PVC—the molecular mechanism of their action in the deformation process. It has been our aim to ascertain the qualitative relations between different important structural parameters of the modifier and the deformation behaviour of the investigated material.

II. EXPERIMENTAL PART

1. Materials applied

There have been used three different processing aids of the polymethylmethacrylate type such as Paraloid K 120 N, Degalan V 26 and Umakryl 70/30. In order to obtain a complete picture of the dependence there polyvinylacetate has been used as a polymer incompatible with PVC and with a glass temperature substantially differing from that of PVC. In addition to this, there polystyrene has been used that is a polymer also incompatible with PVC, however, with a glass temperature near to that of the modifier of the polymethylmethacrylate type.

The basic characteristics of the polymers as well as of the other raw materials used are listed in Table I.

2. Preparation of samples

PVC was mixed with a determined quantity of processing aids (in vol.%) and to this mixture was added 1 vol.% of a lubricant and 2 vol.% of a stabilizer. The same lubricant and stabilizer quantity was added also into pure polymers. All components were at first mixed in a mixer and then milled on a laboratory two-roll mill at temperatures of 155–175°C (according to the modifier quantity) for 10 min. With PVC–PVAc mixtures the PVC was at first plasticized with a lubricant and a stabilizer, and then PVAc was successively added while the mill temperature was being decreased. Two mm thick plates were pressed at temperatures of 170–190°C. After cooling in a cooling press the plates were tempered for a period of 12 hrs at 90°C. PVAc mixtures were tempered for the

TABLE I

Raw materials applied

Trade name	Composition		$\bar{M}_w$	Manufacturer
Solvic 239	PVC		$9,6.10^4$	Solvay Cie, Belgium
Paraloid K120 N	~95% methylmethacrylate, ~5% ethylacrylate		$1,35.10^6$	Rohm & Haas Co., U.S.A.
Degalan V 26	~90% methylmethacrylate, ~10% butylacrylate		$8,34.10^4$	Degussa A.G., FRD
Umakryl 70/30	63% methylmethacrylate, 37% styrene		$1,4.10^5$	Synthesia Semtin, N.C., Pardubice, Czechoslovakia
PS	polystyrene 97%		$3,2.10^5$	Synthesia Semtin, N.C., Pardubice, Czechoslovakia
PVAc	polyvinylacetate		$1,27.10^5$	CHZWP, N.C., Nováky, Czechoslovakia
OP-Wax	lubricant	partly saponified wax of montanic acids		Farbwerke Hoechst, A.G., FRD
Melite 31	stabilizer	dialkyltin merkaptide		Albright and Wilson, GB

same period, however, at 70°C. Dumbbell-shaped samples for tensile tests were cut out from the plates. The test portion of which was 20 mm long with a cross-section 2 × 5 mm. The samples for dynamic-mechanical measurements on the torsion pendulum were prepared by milling from plates.

3. Electron microscopy

The morphology of polymeric mixtures was studied by electron microscope (JEM 6A manufactured by JEOLCO) from ultrathin sections and from replicas of the cutting surfaces. Ultrathin sections (thickness approx. 500 Å) were cut with a diamond knife on an ultramicrotom (Reichert) at room temperature. The replica technique of the cut surfaces provided satisfactory results in evaluating the morphology of polyethylene filled with kaolin.[5] This has been applied in the same way to the given type of compositions. The cutting surfaces were prepared with a metal knife on a sledge microtome at 25°C from which were then prepared the two-stage replicas with polyvinyl alcohol/carbon. In the cutting-off process the material is deformed, and, according to the mechanical properties of the object, there arise in the vicinity of the cutting plane brittle or tough fractures. With the investigated samples of the modified PVC investigated there are tough fractures, whereby the fracture frontline proceeds along the inclusion border which are then uncovered for replication and observation with a transmission electron microscope.

4. Measuring of mechanical properties

Tensile tests were carried out on an adapted tensile tester (Schopper) equipped with a device for tempering samples to measure high deformations. The cross-head speed was 120 mm/min. The calculated strain rate was $\dot{\epsilon} = 0,1$ sec.$^{-1}$ Prior to measuring, the samples were tempered for 20 min. at the given temperature.

From the obtained stress–strain curves was determined the breaking stress σ, breaking strain ϵ and the energy to break E. This energy was determined by measuring the area under the stress–strain curve.

It is necessary to state that the measurements at high temperatures, suffered from a higher error. Despite the fact that the interior of the clamps was precisely machined to the shape of the samples, the slippage of the material from the clamps increased more and more with increasing temperature and this could not be prevented. If the sample was drawn into a fibre, which in many cases was very thin, the final strain was regarded at deformation value when the formation of this fibre started.

Dynamic mechanical measurements were carried out on a torsion pendulum of current design by the method of free oscillation at a temperature range of

20–150°C and frequencies of about 1 Hz. The mutual compatibility of the various polymers was determined from the mutual shift of α-maximum on the tan δ-temperature curve and from the decrease on the dynamic modulus–temperature curve.

5. Measurement of density

Density measurements of the strained parts of samples after breaking were carried out after cooling by means of the floating method in a K_2HgI_4 solution at a temperature of 20°C with a precision of 0,001 g/cm.[3]

III. RESULTS

1. Miscibility of processing aids with PVC

The dynamic-mechanical data for pure processing aids and for their mixtures with PVC are reported in the Figures 1–4. It is obvious that in the range of

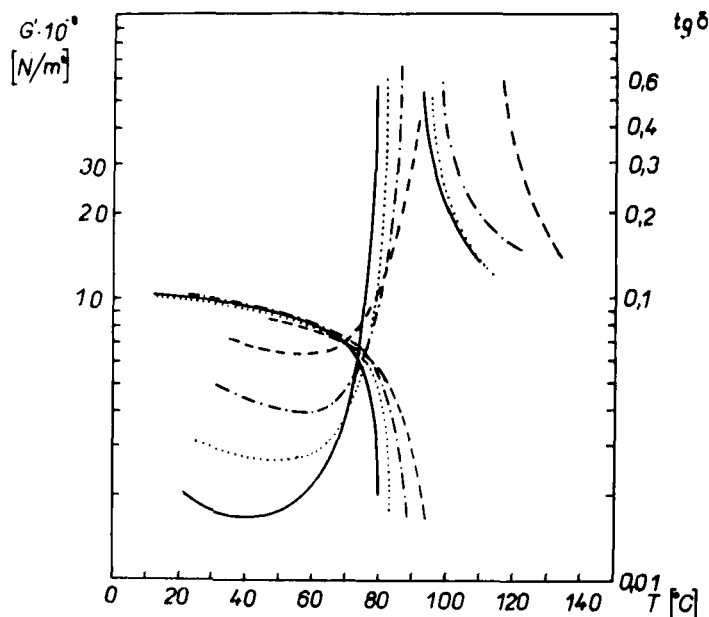FIGURE 1 The temperature dependence of the shear modulus G' and the mechanical damping tan δ for various mixtures of PVC with Paraloid K 120 N.

———— PVC

········ PVC with 20% vol. of Paraloid

— · — · PVC with 40% vol. of Paraloid

— — — Paraloid

measured concentrations a satisfactory miscibility is exhibited by the systems PVC–Paraloid and PVC–Degalan. On the tan δ-temperature curve there appears a new α-maximum of the mixture lying between the original α-maxima of the pure polymers. Likewise the dynamic modulus G' is dropping in one step only.

PVC and Umakryl are miscible only to a limited extent since the transition regions of both original components always remain distinguishable, though shifted towards each other. The dynamic modulus drops with temperature in two steps which are not far from each other (Figure 3). PVC is only slightly miscible with polyvinylacetate, as α-maxima of both components do not approach each other. The decrease of the dynamic modulus occurs in two steps at glass temperature of pure components. The size of the G' drop and the height of the α-maximum for PVAc seems to be dependent only on the PVAc concentration in the mixture (Figure 4).

In order to complete the picture the PVC–polystyrene mixtures has been used, which are known to be incompatible.[6]
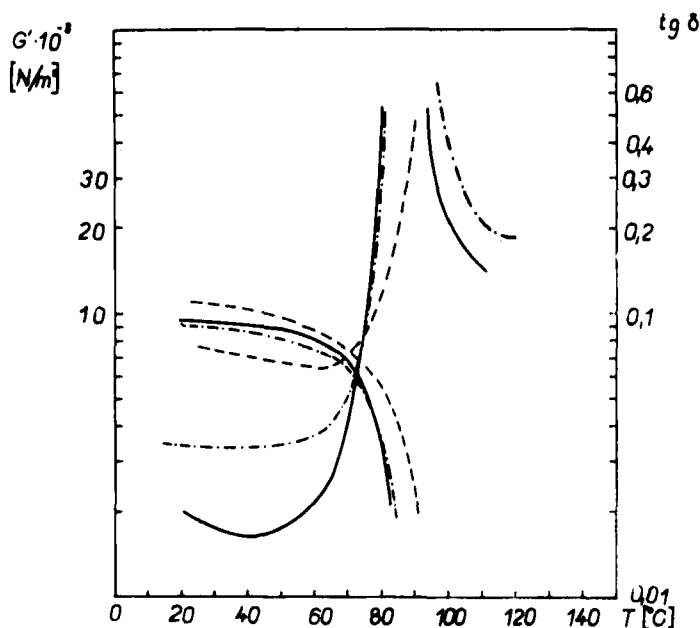

FIGURE 2   The temperature dependence of the shear modulus G' and the mechanical damping tan δ for various mixtures of PVC with Degalan V 26.

———————   PVC
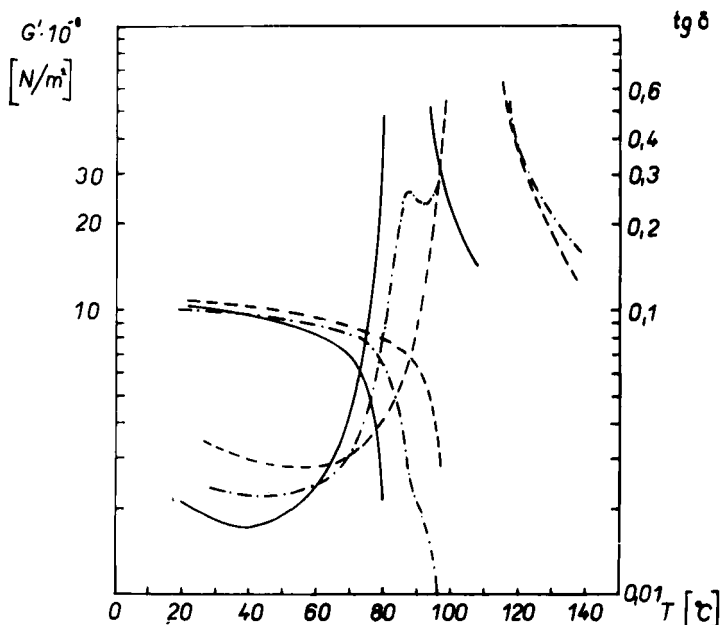— · — ·   PVC with 40% vol. of Degalan
— — —   Degalan

FIGURE 3 The temperature dependence of the shear modulus G' and the mechanical damping tan δ for various mixtures of PVC with Umakryl 70/30.
——————— PVC
— · — · PVC with 40% vol. of Umakryl
— — — Umakryl

2. The morphology of polymeric mixtures

The morphology of PVC itself (Figure 5) and of its mixtures with different processing aids is obvious from micrographs made from two preparations (Figures 6–10). The fundamental agreement of the results of the ultrathin sections and of the replicas of the cutting surfaces excludes any preparative artifacts. A comparison will show that both these preparative methods not only confirm but also complete each other. In the case of PVC itself and PVC compositions with well miscible polymers, the microheterogeneity of the system is more apparent from the surface relief of the cutting surface (Figures 5b, 6b). In the case of PVC compositions with slightly miscible polymers, however, it is more evident from the contrasting picture of the ultrathin sections (Figures 8a, 9a, 10a). With growing miscibility of components, the difference of their electronically optical densities (the contrast) is, in fact, decreasing, and the less expressive heterogeneity becomes more or less apparent from the relief of the cutting surface, since it is constantly affecting the cutting process in a subtle way. The PVC is depicted on the pictures by dark planes at the cuts and by relief forms on the cutting planes respectively. The differentiation of these
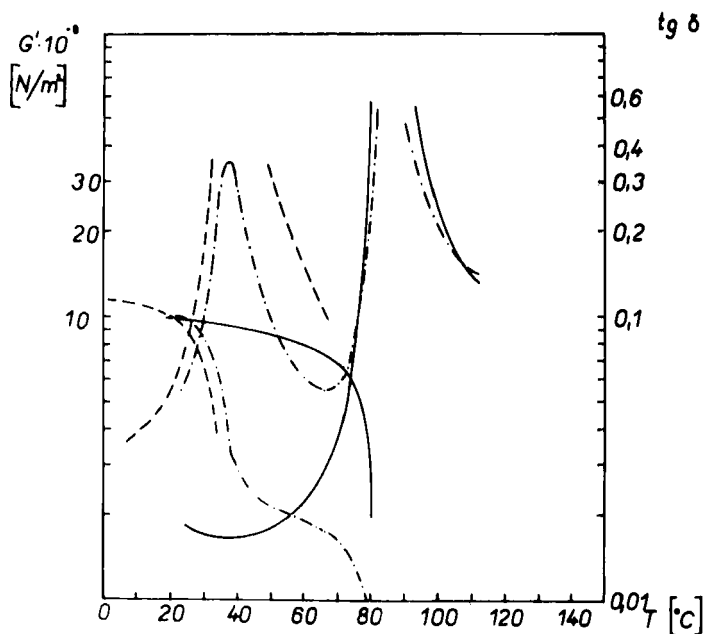
FIGURE 4   The temperature dependence of the shear modulus G' and the mechanical damping tan δ for various mixtures of PVC with polyvinylacetate.
————— PVC
— · — · PVC with 40% vol. of polyvinylacetate
— — — polyvinylacetate

nonhomogeneities from the vicinity may be regarded as the qualitative measure of the mutual miscibility of components.

According to the criterion mentioned the miscibility of polymers with PVC decreases in the same order (Figures 6–10) as was found from measurements of the dynamic-mechanical properties. The inclusions are well defined in PVC compositions with poorly miscible polymers, where as in composition with miscible Paraloid the border of the inclusions are not visible (Figure 6b).

Supermolecular heterogeneity exists in PVC itself. Certain density fluctuations of blackening are apparent on the ultrathin sections (Figure 5a—the artifact-like white spots are holes developed during the cutting process). The structure of the incompletely broken down PVC particles is however clearly visible from the surface replicas in Figure 5b. Besides the globular particles smaller than 1 μm, we may find also particles under 500 Å which seem to be arising from the break-down of the globular particles. The presence of the second polymeric component supports the particle break-down of the PVC matrix since the shear stresses are higher during processing. Pictures confirm that under the same processing conditions, PVC in mixtures is more homogeneous than in pure form (Figure 6b).
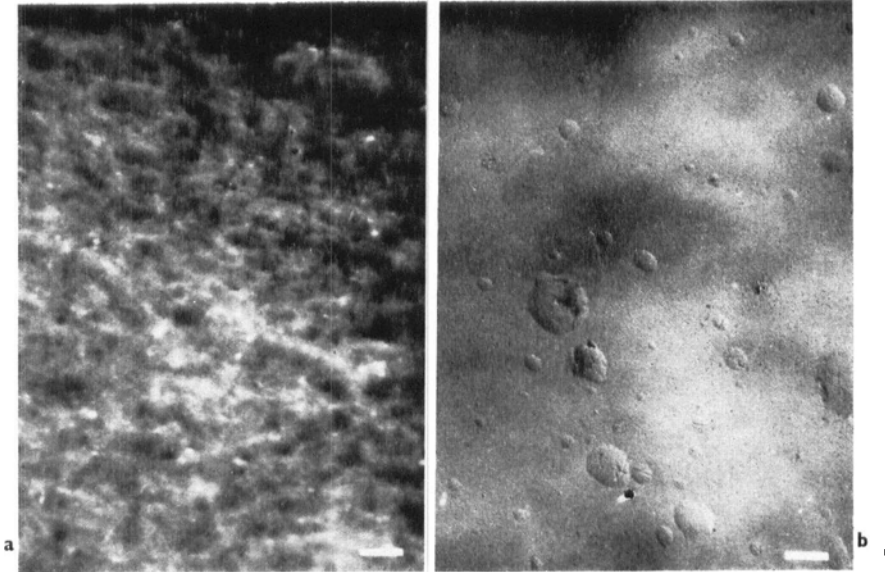
FIGURE 5   Electron micrographs of the ultrathin section (a) and the replica of cutting surface (b) of polyvinylchloride.
Bar scale — 1 μm.

FIGURE 6   Electron micrographs of the ultrathin section (a) and the replica of cutting surface (b) of PVC mixture with 40% vol. of Paraloid.
Bar scale — 1 μm.

FIGURE 7   Electron micrographs of the ultrathin section (a) and the replica of cutting surface (b) of PVC mixture with 40% vol. of Degalan.
Bar scale = 1 μm.
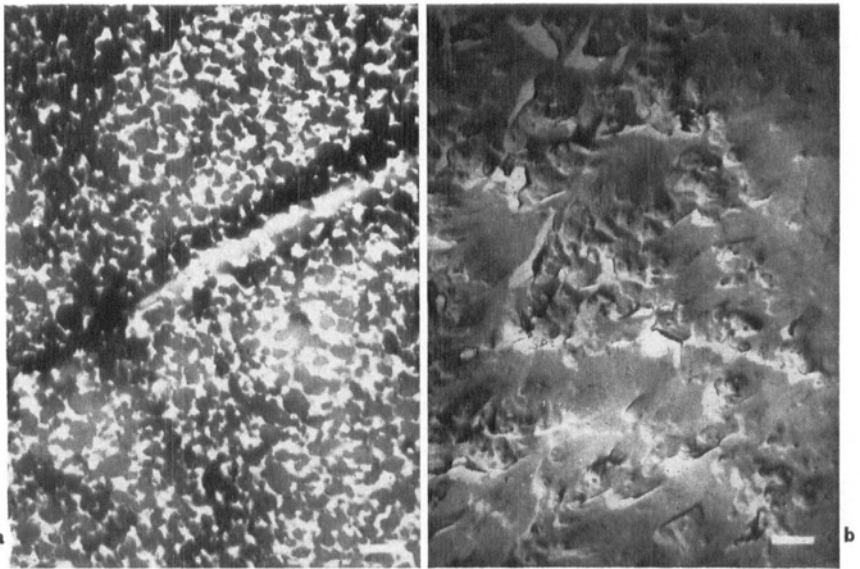
FIGURE 8   Electron micrographs of the ultrathin section (a) and the replica of cutting surface (b) of PVC mixture with 40% vol. of Umakryl.
Bar scale = 1 μm.
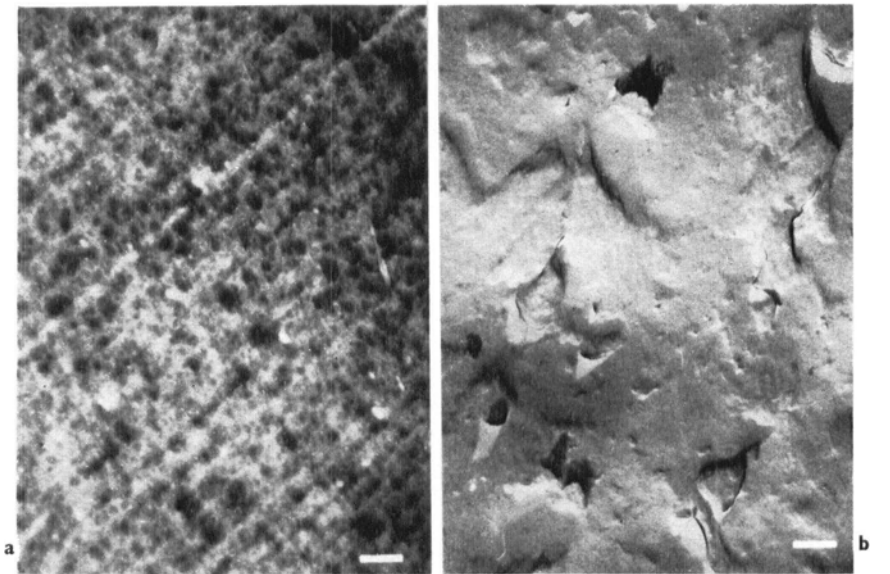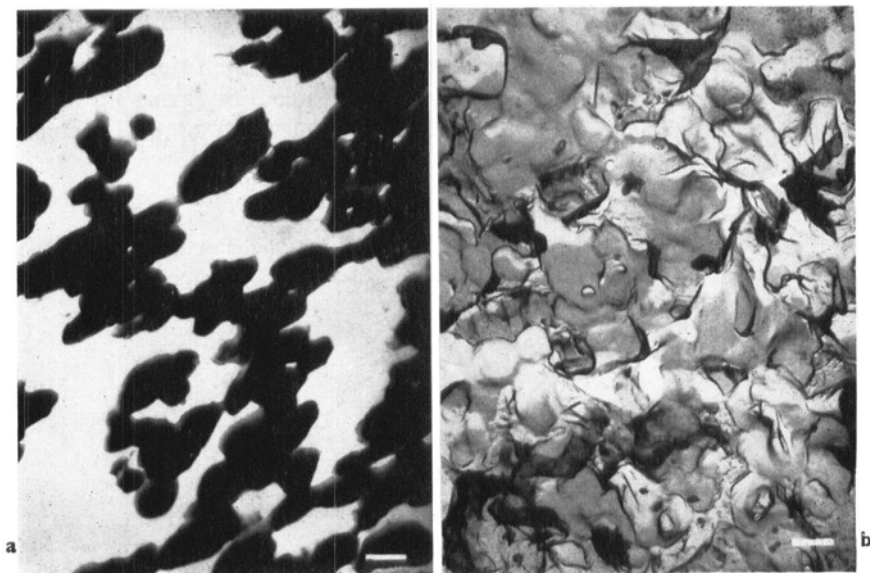
FIGURE 9   Electron micrographs of the ultrathin section (a) and the replica of cutting surface (b) of PVC mixture with 40% vol. of polystyrene.
Bar scale = 1 μm.
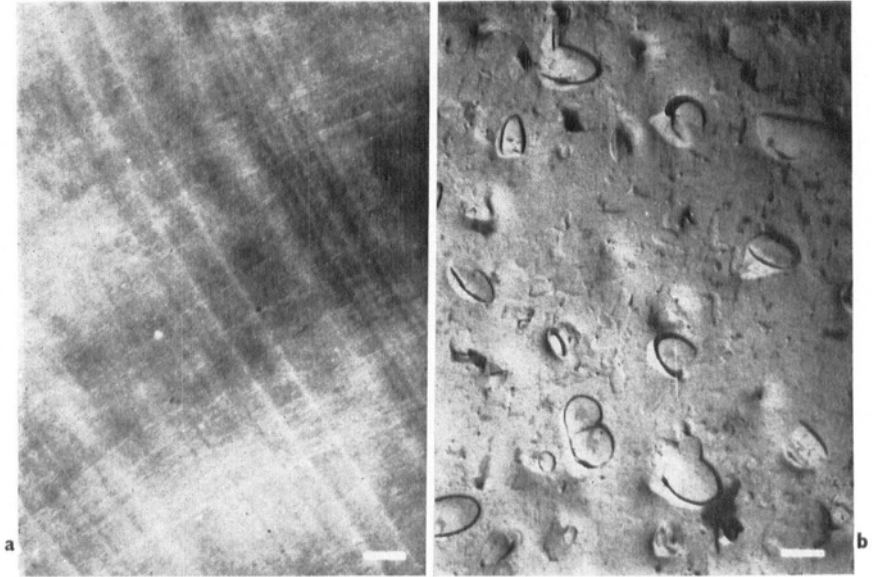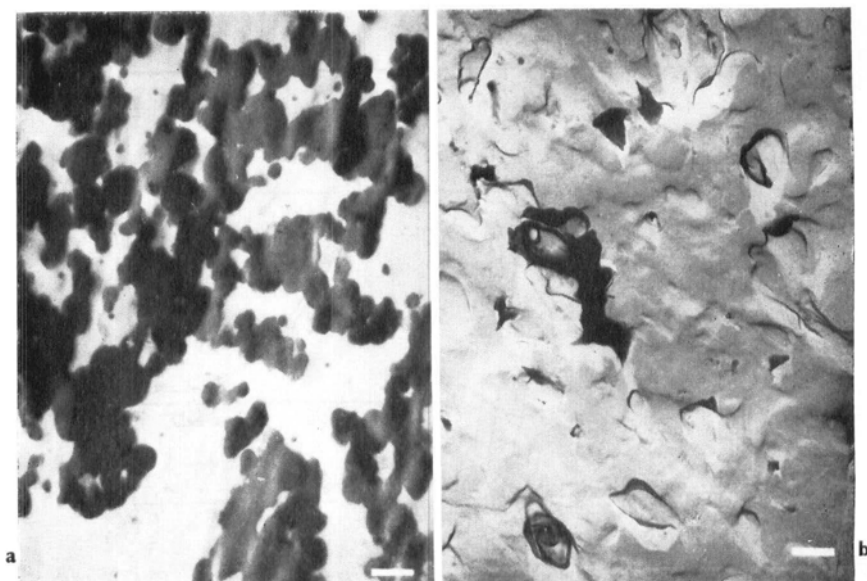
FIGURE 10   Electron micrographs of the ultrathin section (a) and the replica of cutting surface (b) of PVC mixture with 40% vol. of polyvinylacetate.
Bar scale = 1 μm.
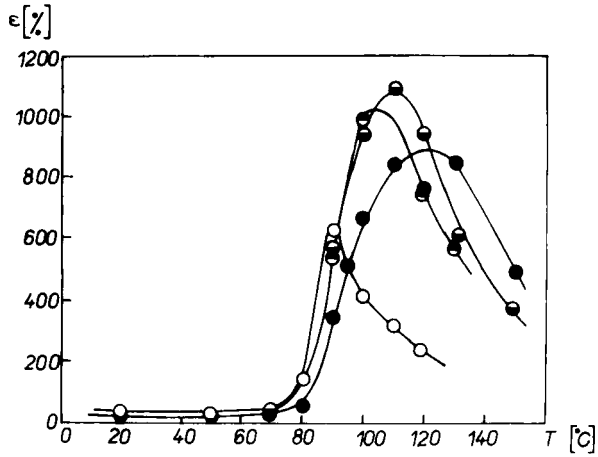
FIGURE 11   Temperature dependence of breaking strain ϵ for mixtures PVC–Paraloid.
○ PVC
◐ PVC with 20% vol. of Paraloid
◒ PVC with 40% vol. of Paraloid
● Paraloid

FIGURE 12   Temperature dependence of breaking stress σ for mixtures PVC–Paraloid.
○ PVC
◐ PVC with 20% vol. of Paraloid
◒ PVC with 40% vol. of Paraloid
● Paraloid
At right-hand detail of dependence for pure components.

3. Mechanical properties

The temperature dependencies of the breaking strain ϵ, of the breaking stress σ and of the energy to break E are shown for the system PVC–Paraloid in the Figures 11–13, for the system PVC–Degalan in Figures 14 and 15, and for the

FIGURE 13   Temperature dependence of energy to break E for mixtures PVC–Paraloid.
○ PVC   ◑ PVC with 40% vol. of Paraloid
◕ PVC with 20% vol. of Paraloid   ● Paraloid
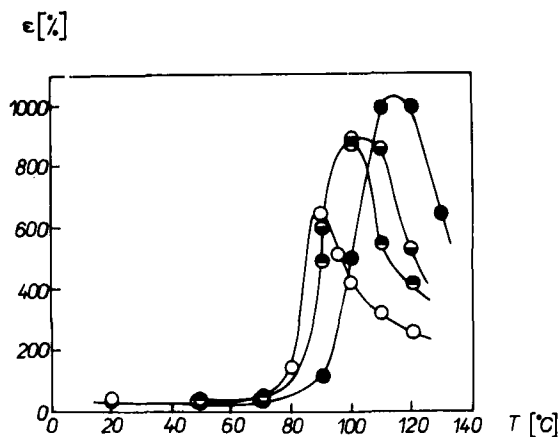
FIGURE 14   Temperature dependence of breaking strain ϵ for mixtures PVC–Degalan V 26.
○ PVC   ◑ PVC with 40% vol. of Degalan
◕ PVC with 20% vol. of Degalan   ● Degalan
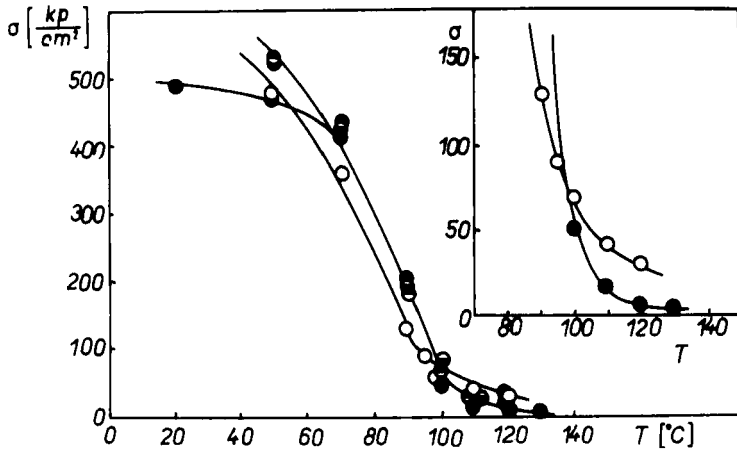
FIGURE 15   Temperature dependence of breaking stress σ for mixtures PVC–Degalan V 26.
○   PVC   ◒   PVC with 40% vol. of Degalan
◓   PVC with 20% vol. of Degalan   ●   Degalan
At right-hand detail of dependence for pure components.
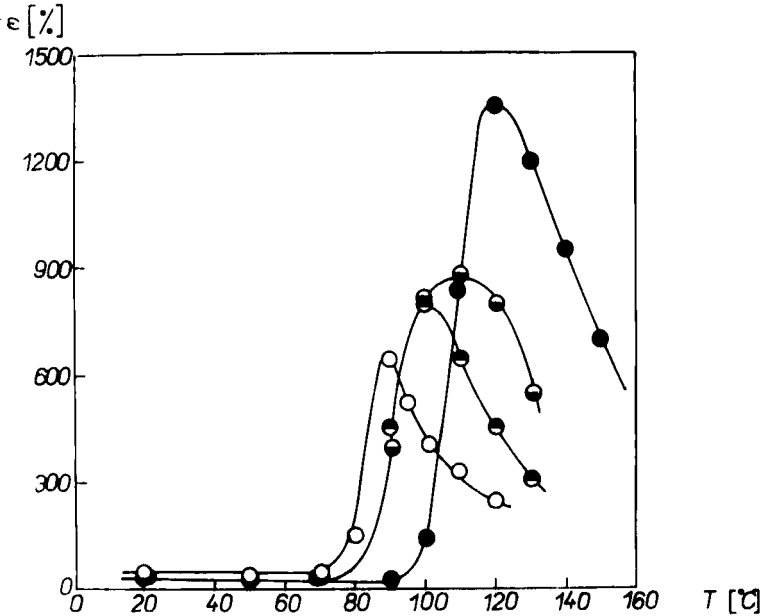
FIGURE 16   Temperature dependence of breaking strain ϵ for mixtures PVC–Umakryl 70/30.
○   PVC   ◒   PVC with 40% vol. of Umakryl
◓   PVC with 20% vol. of Umakryl   ●   Umakryl

system PVC–Umakryl in the Figures 16–18, and finally for the system PVC–polyvinylacetate in Figures 20–22. The resulting temperature dependencies of the breaking strain for selected mixtures are listed in Figure 19.
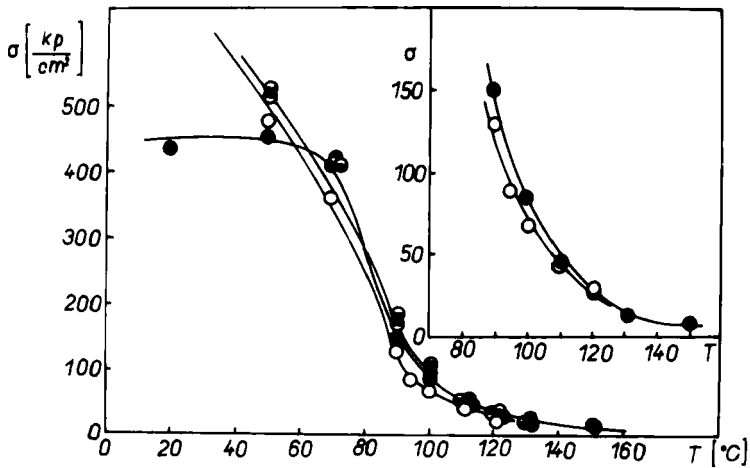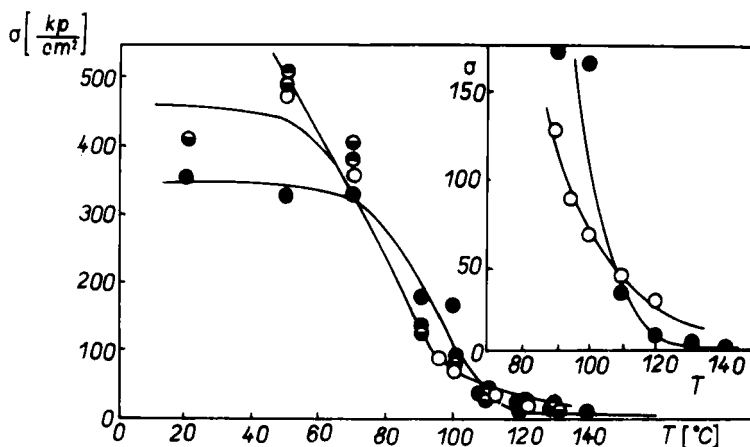
FIGURE 17   Temperature dependence of breaking stress σ for mixtures PVC–Umakryl 70/30.
○   PVC   ◒   PVC with 40% vol. of Umakryl
◓   PVC with 20% vol. of Umakryl   ●   Umakryl
At right-hand detail of dependence for pure components.
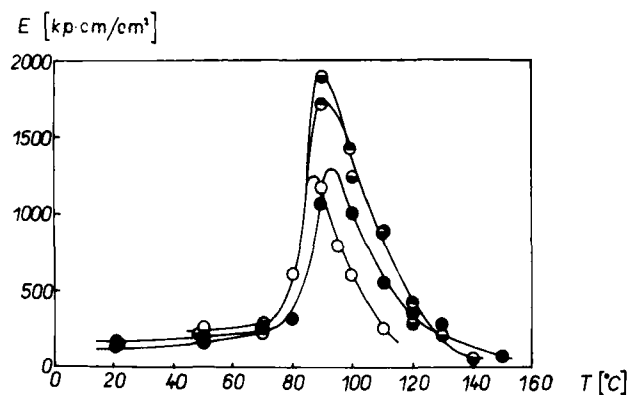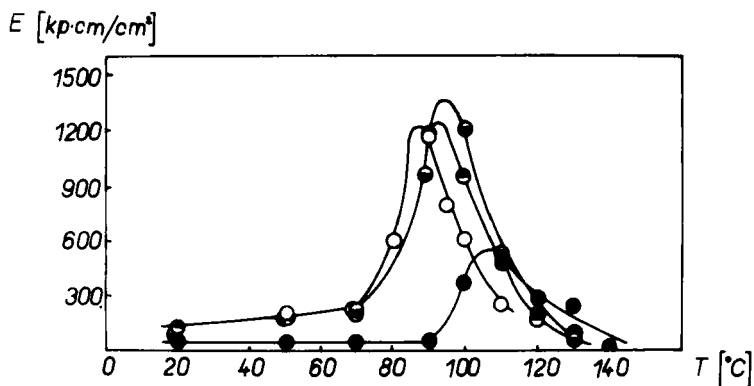
FIGURE 18   Temperature dependence of energy to break E for mixtures PVC–Umakryl.
○   PVC   ◒   PVC with 40% vol. of Umakryl
◓   PVC with 20% vol. of Umakryl   ●   Umakryl

H
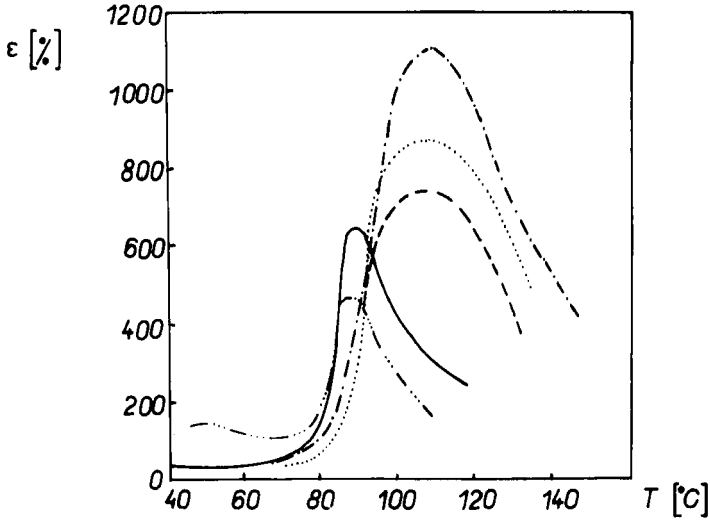
FIGURE 19   Temperature dependence of breaking strain ϵ for mixtures of PVC with 40% vol. of different processing aids.

— · — · — ·   PVC with Paraloid   —————————   PVC
. . . . . .   PVC with Umakryl   — · · · — · · ·   PVC with polyvinylacetate
— — — — —   PVC with polystyrene
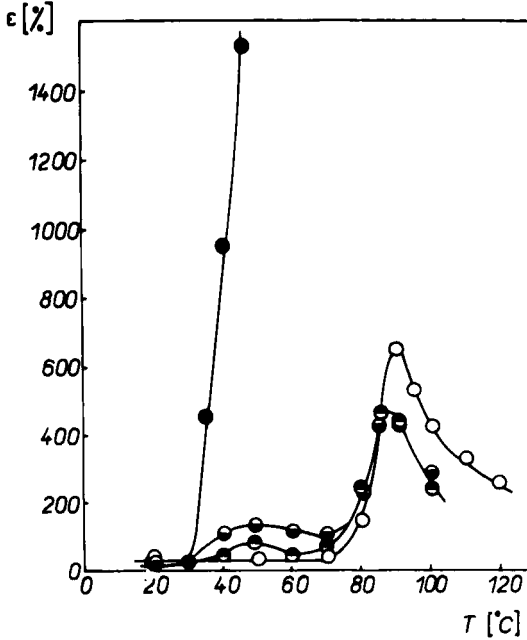
FIGURE 20   Temperature dependence of breaking strain ϵ for mixtures PVC–polyvinyl-acetate.

○   PVC   ◖   PVC with 40% vol. of polyvinylacetate
◓   PVC with 20% vol. of polyvinylacetate   ●   polyvinylacetate
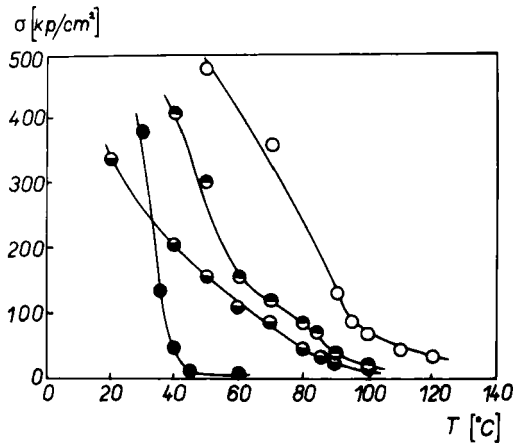
FIGURE 21   Temperature dependence of breaking stress σ for mixtures PVC–polyvinyl-acetate.

○   PVC   ◑   PVC with 40% vol. of polyvinylacetate

◓   PVC with 20% vol. of polyvinylacetate   ●   polyvinylacetate
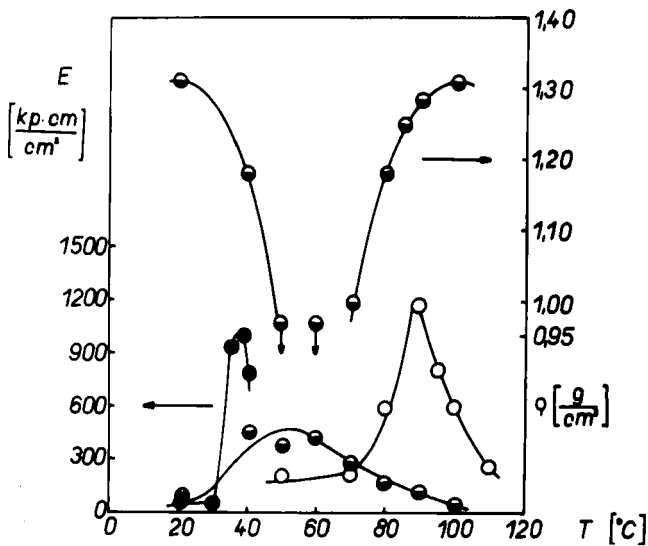
FIGURE 22   Temperature dependence of energy to break E and of density of strained part of samples ρ for mixtures PVC–polyvinylacetate.

○   PVC   ◑   PVC with 40% vol. of polyvinylacetate

◓   PVC with 20% vol. of polyvinylacetate   ●   polyvinylacetate

IV. DISCUSSION

1. Pure polymers

The first electron microscope studies have shown that the morphology of the particles of suspension *polyvinylchloride* is formed by about 1 μm sized globules which can be separated from the compact agglomerates by swelling and embedding of the particles for the ultramicrotomy into methylmethacrylate.[7] It was found later on, that the size of these globules depends on the polymerization and processing conditions.[8,9] In addition to these, 100–200 Å large nodules have been recently discovered on the fracture surfaces of PVC after gas discharge etching; their size increases with content of plasticizer.[10] Instead of the nodules the fibrils are regarded by Matsuo and his co-workers[11] as elementary morphological units of the PVC found in ultrathin sections after embedding into methylmethacrylate. Even though the character of the smallest morphological units has not been so far unambiguously determined, there is no doubt, that the break-down process of the original particles of suspension PVC (approx. 100 μm in size) is proceeding in such a way that they are broken down into primary globules (approx. 1 μm) and into 100–300 Å elementary units respectively. This breakdown of the particles in an essential part of the processing procedure and affects even the final properties of the product.[12,13]

It is evident from the above mentioned, that polyvinylchloride in being processed, is forming a system, which may be regarded as a three-dimensional network formed by PVC macromolecules cross-linked by nodules. It may be expected that the interconnexion of the macromolecules by these physical knots affects all processes currently proceeding at molecular level. The capacity of the chains to change its shape and position towards its surrounding is limited in a number of places. It may be assumed that the plastic flow on the molecular level is limited up to the melting temperature of the nodules (approx. 220°C). It is likely that the presence of relatively strong physical knots in the PVC structure affects not only the flow properties of the melt, but also the mechanical properties in the glass or elastic state. In the same manner the PVC structure must affect even the deformation mechanism of its mixtures with other polymers.

Polyvinylchloride itself at temperatures 20–70°C (and the applied straining rate) shows rather considerable deformations (approx. 40%) (Figure 11), at which the crazing mechanism as well as the cold-drawing mechanism becomes effective. The energy to break remains virtually unchanged in this temperature range and is relatively low (Figure 13).

At further increase of the temperature (70 to approx. 90°C) the samples stop necking, deformations proceed in the whole deformed part homogeneously and shortly, prior to breaking, occurs local whitening in the strained part of

the sample. At this temperature interval, when the temperature approaches the glass temperature of the polymer, the conformation deformation (first phase) must obviously become effective as well as the deformation of the crazing type. Deformability in this range rapidly increases (Figure 11), as does the energy to break (Figure 13). The density of the strained part of the sample after breaking and cooling successively decreases (Table II).

Around 90°C the polymer deformability and the energy to break reaches the maximum.

Any further temperature increase brings the PVC into the rubber region. Symptoms of crazing are quickly disappearing, the energy to break is decreasing and on the contrary, the density of the strained part of the sample after breaking is increasing with temperature (Table II). Breaking strain is rapidly declining. True, elastic deformation of the chains proceed more easily than before, however, no change-over into a plastic flow of the various macromolecules can occur. The nodular PVC structure is obviously the cause of the uneven loading of the PVC chains, and is, also the cause of the later overall failure of the material. The same nodular structure, however, is likewise the cause of the relatively high tensile strength above its Tg—Figure 12.

Polymethylmethacrylate, in comparison with PVC, shows the supermolecular structure that is not formed by extraordinarily permanent physical knots,[14] which might, at corresponding temperatures, be of a hindrance to the expressive orientation and of the plastic flow.

At room temperature *Paraloid K 120 N* (copolymer methylmethacrylate/ethylacrylate) shows, in contrast to PVC, a brittle fracture with a corresponding lower deformation (Figure 11). At temperatures of 50–70°C straining crazing symptoms appear, whereas at higher temperatures polymer orientation sets in. Sample splitting which occurs in the longitudinal direction towards stress is very expressive. Energy to break proceeds through the maximum (Figure 13) and the elongation to break increases too. At temperatures above Tg there occurs an elastic deformation with a growing degree of plastic flow. The region of high deformability of Paraloid tends to be quite large due to its high molecular weight (Figure 11). The value of the breaking strain is, in comparison with other modifiers, somewhat lower. The high molecular weight is the cause of a larger amount of entanglements limiting the plastic flow at the given temperature and straining rate. This seems to be also the cause of the relatively high breaking stress of this polymer at increased temperatures (Figure 12).

Degalan V 26 (copolymer methylmethacrylate/butylacrylate) by its chemical structure similar to Paraloid, behaves identically as Paraloid up to the glass temperature. Above Tg its smaller molecular weight as well as the higher bulkiness and the mobility of its side groups make it possible that, simultaneously with its elastic deformation, plastic flow of the macromolecules develops, thus contributing substantially to the increase of the polymer

TABLE II

Densities of the strained parts of samples for the mixtures PVC-processing aids determined at various temperatures of straining

Mixture	Density $\rho_{20°C}$ of straining parts of samples straining at temperature T								
	20°	50°	70°	80°	90°	100°	110°	120°	130°
PVC	1,400	1,397	1,397	1,397	1,385	1,393	1,395		
Paraloid K 120N	1,186	1,181	1,176	1,184[a]	1,185[a]	1,185[a]	1,185[a]	1,186	1,186
Umakryl 70/30	1,140	1,140	1,140	—	1,139	1,139	1,139	1,139	1,140
PVC with 40% vol. of Paraloid	1,309	1,309	1,309	—	1,310[a]	1,310[a]	1,312[a]	1,315	1,315
PVC with 40% vol. of Umakryl	1,273	1,268	1,250	—	1,269[a]	1,271[a]	1,275	1,274	1,273

	20°	35°	40°	45°	50°	60°	70°	80°	85°	90°	100°
Polyvinylacetate	1.195	1,191	1,188	1,195							
PVC with 40% vol. of polyvinylacetate	1,135	—	1,181	—	<1	<1	~1	1,180	1,250	1,285	1,307

Temperature region where the samples are whitening under tensile stress is underlined.

[a] Samples shrink immediately after breaking, whitening is mostly disappearing. Densities of the samples drawn at those temperatures are, in fact, lower.

deformability in this region (Figure 14). For the same structural reasons, however, the region of high breaking strain is expressively narrower than with Paraloid. Likewise the breaking stress is, at higher temperatures substantially lower (Figure 15).

Umakryl 70/30 (copolymer methylmethacrylate/styrene) differs from the previously mentioned polymer by the higher content of the bulky side groups. The polymer is incapable of a larger orientation. Up to 90°C it breaks by a brittle fracture with a corresponding low deformation. Between 100–120°C there occurs a strong increase in deformability, whereby the influence of the plastic flow on deformation is obviously even more important than with Delagan (Figure 16). Even in this case low breaking stress data have been recorded above Tg—Figure 17. It is evident from Figure 18 that even the energy to break is very low in this temperature region, substantially lower than with PVC and Paraloid.

2. PVC mixtures with processing aids

Paraloid, as has been shown by the dynamic-mechanical results, is miscible with PVC (Figure 1). Micrographs indicate the PVC–Paraloid system to be quite homogenous, whereby it seems that the presence of Paraloid enhances the decomposition of the primary PVC particles (cf. Figures 5b, 6b). It cannot be assumed, however, that there occurred any molecular mixing of both polymers.

It is likely that generally the mixture of modifier with PVC must contain some microregions of pure PVC (at least various areas of nodules with their nearest surrounding), where each macromolecule is again surrounded by macromolecules of the same kind and that it reacts towards impulses from outside in the same manner as in the pure component.

It is most likely that there exist, in addition to these regions, some microregions containing predominantly (or solely) macromolecules of the second component, and finally microregions forming a borderline of both phases where the molecular mixing actually occured, when molecules of one type are partly or entirely surrounded by molecules of the other type. The structure of the microregions, their size and the share of the whole mixture, which these occupy, will be controlled by the miscibility of both components, their molecular weight, their mutual ratio in the mixture and by the preparation conditions of the mixture.

In the extreme case, presented by a small quantity of a compatible modifier (e.g. by Paraloid), there may occur only regions of the first and third type in the mixture. In the case of partly compatible polymers there will exist regions of all three types, whereas in the case of incompatible ones, transition regions will be limited or entirely absent.

Mechanical properties (Figure 11) remain virtually unaffected by the addition of Paraloid into PVC in the range of temperatures up to 70°C. The properties remain the same, but an intensively white neck forms on the samples. The first differences tend to appear if the temperature exceeds 70°C. Whitening is more intensive than with PVC (corresponding to higher decreases in density —Table II), the energy to break is higher (Figure 13), the achieved breaking strain lower (Figure 11). It is likely, that the presence of Paraloid forming in this temperature region, as a hard phase dispersed in the softer PVC, is supporting the start of the crazing on the phase borderline, which results in the increased energy consumption needed for breaking the sample under relatively low elongation to break.

The remarkable effects of Paraloid appear primarily in the temperature region, where PVC reaches, and immediately afterwards exceeds, its deformability maximum, i.e. at temperatures of 90–120°C. Paraloid is dispersed in the PVC matrix in the space between the PVC nodules and forms a more or less homogeneous mixture.

It is possible to assume, that Paraloid chains orient themselves, due to the stress action and slip on each other. At the same time, then, due to their good adhesion to PVC, they interconnect the PVC matrix. In the case of pure PVC that there might occur the surmounting of the intermolecular forces, the arising of a crack, and finally, the macroscopic fracture of the sample.

The relatively high strength of Paraloid at these temperatures combined with a high cohesion of both components, no doubt, enables the maximal development and exploitation of the deformation capabilities of both components, particularly that of the PVC phase. This most likely explains why in this case the deformation properties of the mixture exceed those of the pure components (Figure 11). Likewise even the maximum value of energy to break the sample exceeds extensively the maxima values of pure components (Figure 13).

It is necessary to assume further, and the micrographs seem to indicate that the Paraloid facilitates the breaking down of the PVC structure up to the point of nodular level. It even improves the deformability of the PVC phase itself. This effect is analagous to the higher milling temperature, which actually brings about not only a higher break down effect of the PVC structure, but at the same time, even a larger elongation to break.[13] The final decrease of deformability at temperatures over 130°C is brought about by two causes. On the one hand, the PVC phase fails in so many places that there arises a lack of modifiers which might "bind" the matrix, and on the other, the modifier in exceeding a certain temperature possesses already a too large plastic flow to be able to fulfil its toughening function.

The increase of the Paraloid concentration (40%) becomes effective first of all that it delays the start of the deformability decrease of the mixture in

dependence on temperature. A higher Paraloid concentration enables "a repair job" of a larger number of defects in the matrix.

The influence of the molecular weight of the modifier on the tensile properties becomes evident by comparing the effects of Paraloid and Degalan. Degalan identically as Paraloid is well compatible with PVC (Figure 2). That means, that its mixture, analogically as with Paraloid, should be considerably homogeneous. Meanwhile the ultrathin sections confirm this opinion (Figure 7a), the micrographs of the fracture surface show a higher heterogeneity than that with Paraloid. This is possible to explain due to lower molecular weight of Degalan, which forms in the mixture with PVC a structure that is, at this preparation technique of samples, more sensitive to brittle fracture initiated by latent primary particles.

From the point of view of the tensile properties at temperatures up to 100°C the behaviour of PVC mixtures with Paraloid and Degalan respectively is essentially identical. At temperatures over 100°C the effect of Degalan is substantially less expressive. PVC mixtures with Degalan tend to reach lower values in breaking strain and the region of high deformability is expressively narrower than in the case of Paraloid (Figure 14). Proceeding from the previously suggested mechanism, it is quite understandable that the "toughening" capability of the shorter, more mobile Degalan molecules tending expressively towards the plastic flow, is decreasing with growing temperature, more rapidly than at Paraloid. Degalan showing at temperatures of 100–130°C a lower strength than PVC or even Paraloid, does not possess even the satisfactory strength for the effective interconnection of the arising defects of the PVC phase (Figure 15).

It is also for the same reasons that mixtures with Degalan do not reach higher values of breaking strain than that of pure Degalan.

The influence of the limited compatibility of the modifier on the properties of PVC mixtures is demonstrated by Umakryl (Figure 16). In the mixture with PVC below its glass temperature Umakryl supports, likewise as Paraloid and Degalan, the development of crazing, although not deforming by the crazing mechanism itself.

At temperatures above Tg of polyvinylchloride, Umakryl brings about in the mixture an increase of the deformability essentially by the same mechanism as the preceding modifiers. In this case, however, the mixture is already significantly heterogeneous (Figure 8) and Umakryl forms in the PVC its own well observable network. It is likely, that by virtue of the limited compatibility of both polymers, microregions of all three types are being formed. The higher capability for a plastic flow of Umakryl (in comparison with Paraloid), together with a lower compatibility with PVC, is the cause why lower values of the strain to break maximum are reached by the mixture. The region of maximum deformability as well, is at Umakryl relatively narrow, likewise as at

Degalan, owing to the rapidly developing plastic flow. The maximum of energy to break at temperatures of 90–95°C markedly exceeds the maximum of pure Umakryl—Figure 18. Likewise the breaking stress of the mixture in the temperature range of 110–130°C was lower than at PVC—Figure 17.

For demonstrative purposes it is shown further on that the breaking strain increase in the critical temperature region (100–120°C) may be caused even by polystyrene, that means by a polymer incompatible with PVC (Figure 19). Even polystyrene forming with PVC a clearly heterogeneous structure with relatively large microregions of both polymers (Figure 9), forms with PVC a network enabling an increase in deformability. Admittedly, this increase is not so evident as in the preceeding cases, nevertheless, however, the region is substantially increased in which the system shows high elongation—700% (Figure 19).

It is obvious, that even polymers with a very low compatibility with PVC are capable, by means of the indicated mechanism, to increase the deformability of the system. The decisive moment in developing the toughening process, is the sufficient strength of the polystyrene network at temperatures of 100–120°C given by the relative vicinity of the glass temperature of polystyrene.

The fact that the decisive element for the behaviour of the PVC-modifier system is the network strength of the modifier, is demonstrated by the example of the PVC-polyvinylacetate mixture. Polyvinylacetate is incompatible with PVC and its glass temperature lies at 40°C (Figure 4). As can be seen from Figure 10, it also forms with PVC a very heterogeneous structure. Pure polyvinylacetate at temperature above Tg shows a rapidly growing deformability with an increasing portion of plastic flow (Figure 20).

At a temperature of maximum deformability of PVC, polyvinylacetate forms a viscous melt, the deformation behaviour of which cannot be determined by current tensile tests. That is why polyvinylacetate affects the properties of mixtures with PVC in a different way. At temperatures above 40°C its particles act like rubber particles causing prominent crazing combined with whitening of the samples with a very marked decrease in density, and finally with a growth of energy to break (Figure 22). On the strain–temperature dependence there appears at these temperatures a secondary maximum which is dependent on the polyvinylacetate concentration. In agreement with Imasawa and Matsuo,[15] it may be attributed to the significantly developed crazing (Figure 19).

In the region above 80°C there sets in a visible decrease of breaking strain, of breaking stress (Figure 21) and even a decrease of energy to break (Figure 22). Contrary to the previously mentioned modifiers, polyvinylacetate exists here mostly in the form of rather large regions of pure polymer, whereby the melt itself does not possess sufficient mechanical properties to be also able to interconnect the entire system. Even though polyvinylacetate is capable of

considerable elongation—Figure 20—its melt does no longer possess at 60°C a measurable tensile strength. Polyvinylacetate affects the deformation behaviour of polyvinylchloride essentially as a diluent without an active contribution of its own.

V. CONCLUSION

The PVC mixtures with processing aids are mostly composed of three microregions. Two of which are formed by pure components and the third one—the transition microregion—consists of more or less mixed molecules of both components. The capability of the modifier to improve tensile properties of the system at high temperatures (100–130°C) is influenced by the following parameters:

1) The good compatibility of the modifier with PVC enables a homogeneous mixing of both components as well as their good cohesion in the deformation process. It is likely, that modifiers compatible with PVC support moreover the breaking down process of the primary PVC particles up to nodular or molecular level which results in improving the deformability of the PVC phase itself.

2) Thanks to the high molecular weight, the modifier is effective over broad temperature region. Due to the higher concentration of the entanglements, this modifier is not subjected from the temperature point of view, to any premature plastic flow and is capable to interconnect the PVC microregions even at relatively high temperatures.

3) If the glass temperature of the modifier is higher than that of PVC (by approx. 20°C), then the modifier network in PVC may possess at high temperatures a satisfactory tensile strength, which enables in this way its full efficiency.

Provided these important requirements towards the modifier are met the maximum development and exploitation of the deformation capabilities of both components, particularly the deformability of the PVC phase, seems to be possible. The PVC-modifier system in this case does not fail to be effective at those temperatures when pure PVC had lost long ago sufficient cohesiveness.

Acknowledgements

References

1. C. F. Ryan, *SPE J.* **24**, 89 (1968).
2. A. C. Basketl and R. B. MacMillan, BP 106, 2308.
3. C. F. Ryan, *Appl. Pol. Symp.* **15**, 165 (1970).
4. G. Reiff, *Kunststoffe* **58**, 277 (1968).
5. Z. Pelzbauer, *I. Internationale Microsymposium über Polymerkompositionen*, Berlin (DDR), March 1973; *Plaste und Kautschuk* **20**, 748 (1973).
6. R. Buchdahl and L. E. Nielsen, *J. Polym. Sci.* **15**, 1 (1955).
7. H. Prokopová and Z. Pelzbauer, *Chemický průmysl* **15/40**, 30 (1965);
   Z. Pelzbauer, *Staub-Reinhalt. Luft* **27**, 233 (1967).
8. L. I. Vidyaikina, N. A. Okladnov, and B. P. Shtarkman, *Polymer Sci. U.S.S.R.* **8**, 425 (1966).
9. A. R. Berens and V. L. Folt, *Trans. Soc. Reol.* **11**, 95 (1967).
10. D. M. Gezovich and P. H. Geil, *Inter. J. Polymeric Mater.* **1**, 3 (1971).
11. T. Hattori, K. Tanaka, and M. Matsuo, *Pol. Eng. Sci.* **12**, 199 (1972).
12. *Studies on Standardization of Testing Method for PVC Processing*, Part III **8**, Japan PVC Soc. (1966).
13. G. Pezzin, G. Ajroldi, T. Casiraghi, C. Garbuglio, and G. Vittadini, *J. Appl. Pol. Sci.* **16**, 1839 (1972).
14. R. E. Robertson, *J. Chem. Phys.* **44**, 3950 (1966).
15. Y. Ymasawa and M. Matsuo, *Pol. Eng. Sci.* **10**, 261 (1970).