

BEHAVIOR OF COPOLYMERS, BLENDS AND ALLOYS

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Abstract - While poly(vinyl chloride) possesses an excellent balance of cost and properties, it is often modified by the incorporation of comonomers, monomeric and polymeric plasticizers, and polymers of various kinds. In this way the processability, state, mechanical properties and environmental behavior can often be improved. This lecture reviews the principles that underly such modifications and discusses applications of these principles, with emphasis on recent developments.

INTRODUCTION

Second only to polyolefins in production volume, poly(vinyl chloride) (PVC) has an excellent combination of low cost, versatility, and properties (1). When properly formulated, PVC can be obtained in both flexible and rigid forms that are strong and relatively inert to a wide range of environmental conditions. However, improvements in processability, heat distortion temperature, impact strength, and service life have long been sought. Thus much attention has been given to the modification of PVC, originally by copolymerization, and more recently by blending or "alloying" with other resins. As the emphasis of polymer science and technology continues to move away from wholly new monomers and towards modification of old ones (2), even greater attention to both the basic and applied aspects of PVC modification may be expected.

The purpose of this paper is to review the principles that underly the modification of PVC by copolymerization and blending, to discuss typical examples of current interest, and to indicate probable directions for future work. For recent reviews, see Kleiner (3), Förster and Herner (4), Olabisi et al. (5,6), and Paul and Newman (7); for standard works on PVC see Nass (1), Sarvetnick (8), and Koleske and Wartman (9). Useful information is also provided in reference (10), and by Brydson (11), Roff and Scott (12) and Nielsen (13).

PRINCIPLES OF PVC MODIFICATION

Regardless of whether copolymerization or polyblending is used, the general aim is the same: to improve some property without undue loss in others (see, for example, Table 1). Also, it is sometimes possible to achieve a synergistic improvement to a level higher than that of either component. Typically, the aim is to alter the viscoelastic response of the polymer, e.g., to raise or lower the glass temperature (T_g) or heat-distortion temperature (HDT), to lower the melt flow point or melt viscosity, to increase ductility and hence formability, or to increase the fracture energy. (Other properties such as weatherability, solubility, and pigment-binding or adhesive character may also be affected, but are beyond the scope of this review, except insofar as a modifier for viscoelastic or mechanical purposes also affects other properties.)

Interestingly, different laws of additivity apply depending on the degree of homogeneity. At the ends of a continuum of homogeneity (let us say on a scale of ~ 10 nm), we have of course two extreme cases: homogeneous and compatible, and heterogeneous and incompatible. Each of these two classes may subsume both copolymers and blends. In fact many real systems exhibit partial compatibility; for example, the glassy but not the rubbery component of a glassy-rubbery graft polymer may be compatible with another glassy matrix.

Variations in compatibility

Many experimental methods have been used to establish criteria for miscibility and compatibility. These include evaluation of mechanical, dilatometric or dielectric transitions, differential scanning calorimetry, thermo-optical analysis, visible and electron microscopy, scattering techniques (light, neutrons, and X-rays), ternary solution methods, chromatographic techniques, and various kinds of spectroscopy. For detailed reviews, see references (6) and (7). The characteristics and consequences of compatibility and incompatibility are outlined below.

TABLE 1. Some typical modifiers for PVC (after ref. 4)

Modifier	%	To Improve	Modifier	%	To Improve
MBS	5-15	impact strength	MMA	1-4	processing, thermoforming
AMBS	5-15	impact strength	AMA	1-4	processing, thermoforming
ABS	5-15	impact strength	AMS/AN	1-4	processing, thermoforming
EVA	5-10	impact strength	PA	-	de-adhesion, processing
CPE	10-20	impact strength	VC/VA	to 30	thermoforming
MBA	5-15	impact strength	SAN	7-12	foam extrusion
PA	5-10	impact strength	SAN	to 50	HDT
EPDM	-	impact strength	AMS/SAMB	50-50	HDT, toughness
ABS + plasticizer	-	toughness	NBR	30-50	chemical resistance; NBR plasticizes and toughens

ABS = acrylonitrile/butadiene/styrene; AMA = acrylate/methacrylate; AMS = α -methyl styrene; AMBS = acrylonitrile/MBS; CPE = chlorinated polyethylene; EPDM = ethylene/propylene/diene; MBA = methacrylate/butyl acrylate; MBS = methacrylate/butadiene/styrene; PA = polyacrylate; VC/VA = vinyl chloride/vinyl acetate copolymer; NBR = acrylonitrile/butadiene rubber.

Homogeneous mixtures. In this case, two constituents A and B are completely compatible. With a copolymer the corresponding homopolymers must be compatible, or if not, the reactivity ratios and polymerization conditions must be such that long sequences of one monomer unit are avoided. Such mixtures will be transparent (if A and B are amorphous), only one phase will be discernible under the electron microscope, and only one sharp T_g will be found. In general, properties will represent some kind of average of the constituent properties weighted by the proportion of each component. Thus the T_g will be intermediate (see Fig. 1a), possibly, but not necessarily, following one of the standard equations for mixtures (14). However, peaks may occur in ultimate properties such as tensile strength when one component is brittle and the other ductile (Fig. 2); the ductile component can often delay the onset of flow-induced fracture (see also below).

Polymers that are compatible with PVC (at least at some concentrations and compositions) include poly(methyl methacrylate), chlorinated PVC, poly(butylene terephthalate), some polyester oligomers, poly ϵ -caprolactone, and a variety of copolymers such as ethylene/vinyl acetate, ethylene/ethyl acrylate/CO, butadiene/acrylonitrile (with some reservations) and α -methyl styrene/acrylonitrile. The glassy components of ABS, methacrylate/butadiene/styrene, and butadiene/acrylonitrile copolymers are also compatible with PVC (5,6). Blends of PVC with the fire-retardant condensation product of tetrachlorobisphenol A have been shown to be compatible over a wide range of compositions (15a). For more complete discussion and detailed listings see Olabisi et al. (ch. 5, ref. 6), and Krause (15).

Inhomogeneous mixtures. In contrast, completely inhomogeneous mixtures exhibit quite complex behavior, depending on the property being measured. As with any composite (16-19), the properties depend on the proportions of A and B, on their properties, on the degree and nature of the interfacial adhesion, on the phase continuity, and often on the phase size. If adhesion is poor, strength and modulus will be reduced. If adhesion is good, the modulus will fall between upper and lower bounds corresponding to weighting of the constituent properties in series or in parallel, respectively; for particulate phases, Kerner's equation (or a variant) often holds approximately (Fig. 3). Strength will be reduced unless the dispersed phase can initiate crazing or shear yielding in the matrix (16). Regardless of the adhesion, each component will exhibit its own T_g . In practice, the use of polymers that are truly incompatible usually yields poor properties (20). An exception is the use of block or graft copolymers, which exhibit good interfacial adhesion due to the covalent linkages between the phases; in effect these may act as compatibilizing agents.

In-between mixtures. If the components of a polymeric mixture are partially miscible in each other, then a range of viscoelastic behavior may be encountered, depending on the scale of the heterogeneity. This is so with a variety of mixtures, including plasticized polymers, polyblends, and copolymers in which long sequences of one component are incompatible with the other component (13). With a plasticized composition, a single T_g will be observed, as is seen with a single-phase system (see Fig. 1a). However the transition will be broadened, reflecting a broadening of the relaxation spectrum (13,22). Similar behavior is observed with copolymers whose distribution of composition is broad and whose long sequences are incompatible. At the other end of the scale of heterogeneity, e.g., in a partially compatible polyblend, two T_g s may be detected, one from each phase, but if some miscibility is present, the peaks in $\tan \delta$ or loss modulus are moved closer together and become progressively suppressed in intensity, reflecting the ability of the high- T_g component to raise the T_g of the low- T_g component, and vice versa (19). Thus, as mentioned earlier, there is a continuum of viscoelastic response from a single broad transition to more-or-less discrete but shifted

and broadened T_g s (Fig. 4).

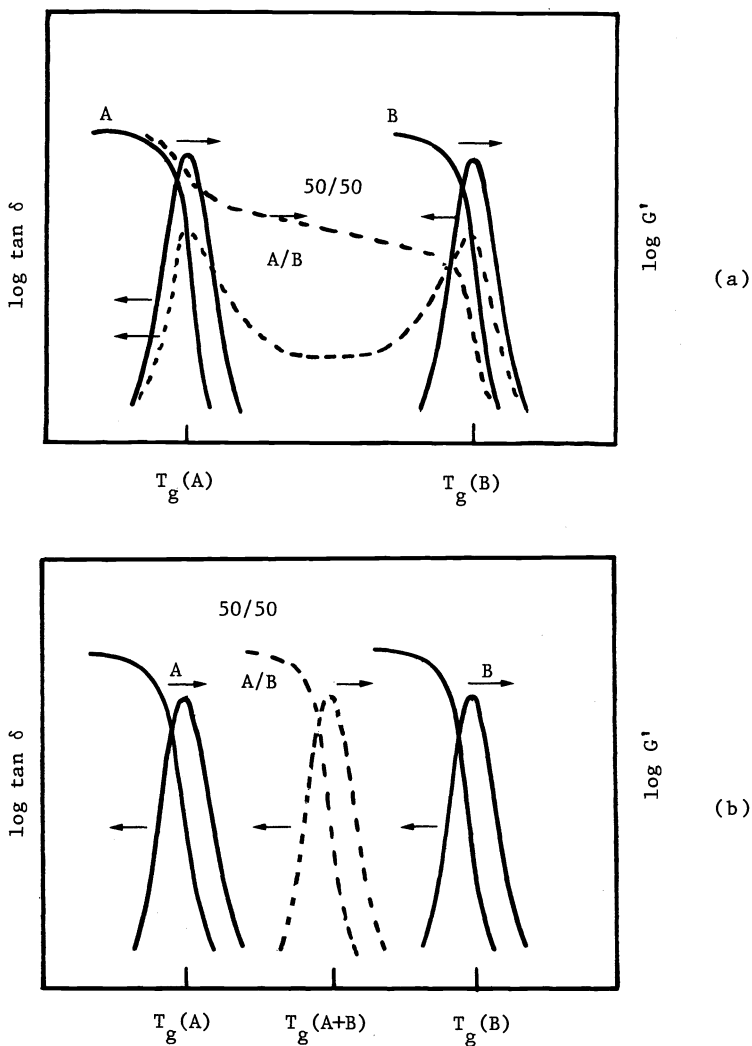


Fig. 1. Generalized behavior of the dynamic mechanical properties of a miscible blend (a) and a two-phase, incompatible blend (b): —, pure components; ----, mixture [after Olabisi et al. (6)].

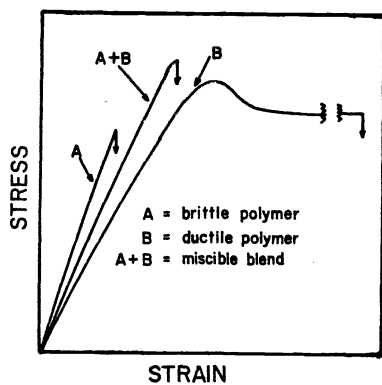


Fig. 2. Typical stress-strain behavior for a miscible mixture of a brittle polymer (A) with a ductile polymer (B). Note that the miscible blend (A+B) exhibits higher tensile strength than either component [after Olabisi et al. (6)].

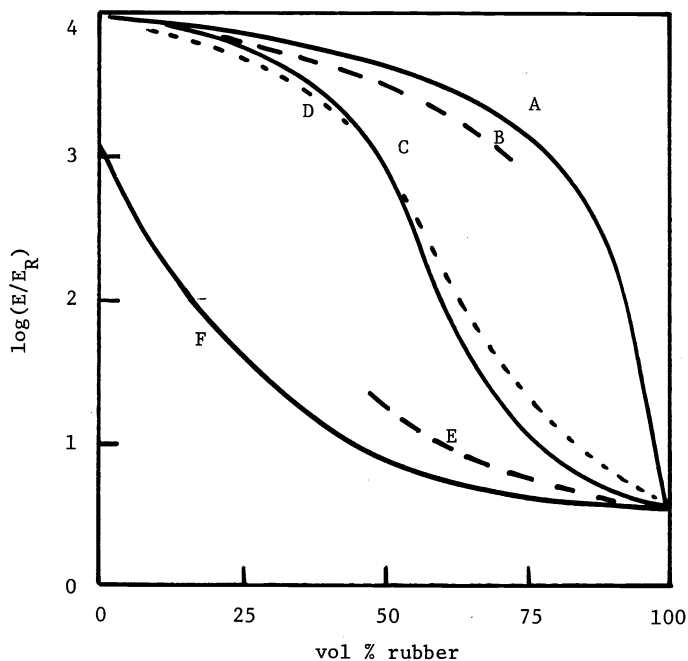


Fig. 3. Dependence of relative modulus of glassy polymer/rubber blends on rubber content, where E is the modulus of the composite and E_R the modulus of the rubbery phase. Curves A and F are as predicted by the unmodified Kerner equation; Curves B and E are typical experimental data and predictions of modified Kerner and van der Poel equations. For Curves A and B, the glassy polymer is the continuous phase; for Curves E and F, the rubber is the continuous phase. Curve C shows modulus-composition dependence for a series of homogeneous copolymers corresponding to the heterogeneous blends in monomer compositions. Curve D corresponds to the prediction of several models to account for systems in which both components behave essentially as discrete but continuous phases. [after Dickie (21)].

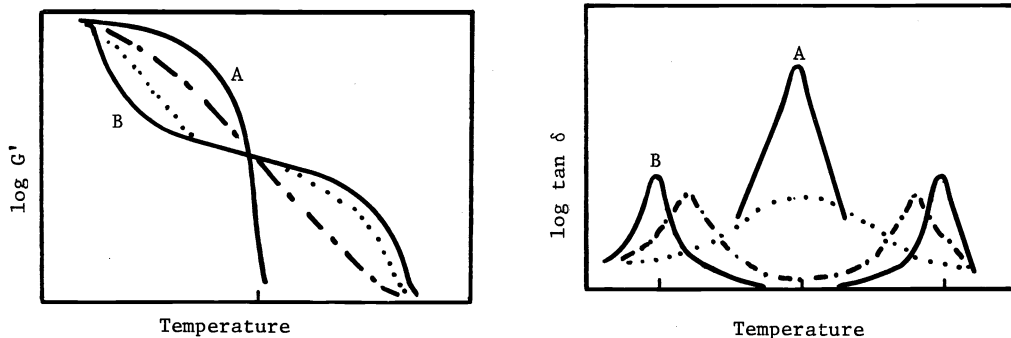


Fig. 4. Typical modulus and mechanical loss ($\tan \delta$) behavior for polymer blends: (A), miscible; (...), partially miscible with a broad spectrum of heterogeneity; (·-·-·-·-·), partially miscible; (B) heterogeneous. [after Olabisi, et al. (6)].

Typical semi-compatible polymeric additives for PVC include the following (6,15): ABS, methacrylate-butadiene-styrene terpolymers (MBS), ethylene/vinyl acetate copolymers (EVA), EVA/VC graft copolymers, vinyl acetate/VC, some polyurethanes, and chlorinated polyethylene (CPE). (In some cases, the polymer may be compatible only in certain ranges of composition and temperature.)

In fact, for good impact strength, partial compatibility of a glassy/rubbery polymer is preferred. In this case a discrete rubbery phase is desirable, in order to reduce the notch sensitivity of both "brittle" and inherently ductile polymers such as polystyrene or poly(methyl methacrylate) and PVC or polypropylene, respectively (16,17,19). At the same time a weak interface is generally undesirable [with some possible exceptions (23)], for operation of the most common toughening mechanisms requires that stresses be transmitted effectively across the rubber/plastic interface. Hence either some chemical bonds or at least some

interfacial mixing is desired.

The most generally accepted mechanism for toughening (16,17,19) in rubber-modified plastics is actually a combination of multiple and delocalized crazing (induced at the rubber particles under the influence of a tensile (dilatational) load) with shear banding (induced at the particles or at the ends of a craze). Crazing is undoubtedly favored at low temperatures and high strain-rates, while a shear response is favored the higher the temperature and the lower the strain-rate. While there is still some controversy over mechanistic details (16, 18), it certainly seems clear that rubber particles embedded in ductile matrixes bring out the inherent ductility (e.g., as manifested in cold-drawing) of polymers such as PVC and polypropylene, even in the presence of a notch.

Aging and weathering of polyblends

All polymers undergo physical and chemical effects on aging and exposure to various environments. The effects include: long-term segmental relaxations (physical aging) that result in decreased creep compliance (24); depolymerization (25); oxidation and consequent embrittlement (16,26); and other degradations such as dehydrohalogenation in PVC (27), which may or may not involve oxygen. The effects of physical aging are normally accepted during service, though they may be reversed by raising the temperature to above T_g or by raising the stress to the yield stress. Depolymerization can be inhibited by capping the end-groups of molecules that are susceptible to unzipping of the chain, using a functionality that can block the process; alternately, comonomers can serve to block an unzipping process. Oxidative effects are most common in polymers containing C=C bonds; stabilizers are commonly used to interfere with the free-radical chains involved. With halogen-containing polymers, stabilizers are also used to block the dehydrohalogenation process.

Since many polyblends contain rubbers that in turn contain C=C bonds, oxidative degradation must be seriously considered even if the matrix is relatively inert under normal service (16,19,26). Such degradation can seriously impair properties such as impact strength, even if only a thin surface layer is involved (16). Moreover tests of strength at room temperature may be misleading, for deleterious effects may occur only at low temperatures. Hence much attention has been given to the use of saturated polymeric modifiers.

APPLICATION OF PRINCIPLES OF MODIFICATION TO PVC

Plasticization in copolymers and blends

The internal plasticization of polyvinyl chloride with vinyl acetate has long been practiced (1,11,12) in order to enhance processability. With a polymeric T_g of $\sim 29^\circ\text{C}$, vinyl acetate lowers the T_g of PVC by $\sim 0.6^\circ\text{C}/\text{wt}$ percent vinyl acetate added (Note a). Copolymerization with small proportions of ethylene or propylene (28,29,30) has also been used to enhance processability; the more-or-less-randomly distributed propylene mers may at times enhance thermal stability by blocking dehydrohalogenation. Presumably copolymerization also reduces the crystalline melting point to some degree. [For a recent study of molecular motion in VC/VA thin films, see ref. (31).]

When relatively large proportions of an essentially incompatible comonomer (i.e., incompatible once polymerized) are used, the T_g is broadened if the copolymerization rate constants are such that a broad range of compositions (and hence sequence lengths of the second monomer unit) is obtained. An example is the case of the copolymerization of vinyl chloride and methyl acrylate (Fig. 5).

Of course the shift in T_g due to plasticization may also affect the modulus (rigidity); if the resultant T_g is close to room temperature, the modulus itself may be lowered. Thus a second reason for plasticization is to produce a copolymer whose T_g is below room temperature, as in a flexible vinyl resin. It should be noted, however, that copolymerization is not as effective in reducing T_g as the introduction of an equivalent volume fraction of a monomeric plasticizer, for the T_g of the latter is typically very much lower than that of the polymer corresponding to a comonomer. However, monomeric plasticizers tend to migrate out of PVC—a problem resulting in deleterious effects such as embrittlement or contamination of a food-stuff. Thus much attention has been given to the development of polymeric plasticizers. These are polymers that have low T_g s and that are compatible with PVC. In practice, small proportions of a low-molecular-weight or monomeric plasticizer may also be added to enhance blending. [For recent reviews, see references 6 and 33.]

Major features of the blending of plasticizing polymers with PVC to lower T_g and reduce stiffness to yield flexible materials will now be summarized. The use of small proportions to improve processability without significant loss in rigidity is discussed below (see Processing Aids).

Note a: As mentioned above, standard expressions for the T_g of blends of A and B such as the Fox equation ($1/T_g = w_A/T_{gA} + w_B/T_{gB}$, where w is the wt fraction) may require modification in order to obtain the best fit to experimental data for PVC blends (28).

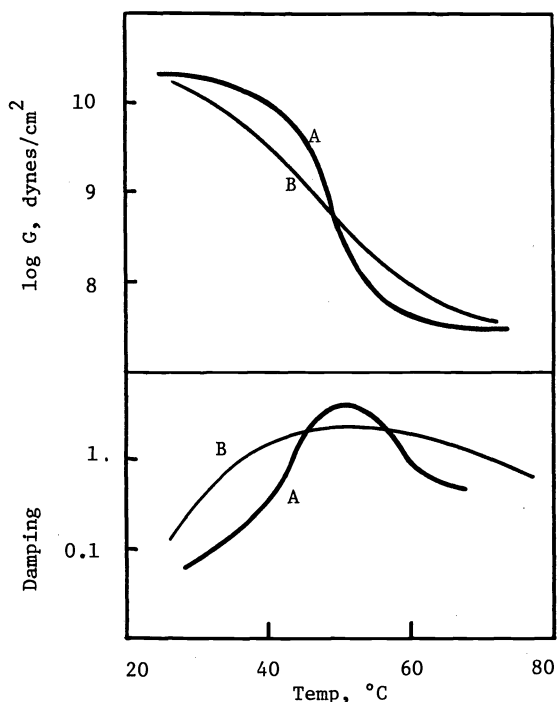


Fig. 5. Dynamic mechanical spectra for VC/MA copolymers: A, homogeneous; B, heterogeneous [after Nielsen (32)].

The earliest example of a miscible polyblend of PVC with a polymeric plasticizer was the development of PVC/nitrile rubber blends (i.e., blends with NBR, acrylonitrile/butadiene copolymers) (6). The blends are typically characterized by good aging and solvent resistance, high permanence of the rubber, and flex-crack resistance. At acrylonitrile concentrations of between ~10% and 25%, the blend is partially incompatible (see Toughened Resins, below); as the acrylonitrile proportion increases to 40% miscibility increases. In fact, this blend is still used today. Recent studies by Jordan et al. (34) describe the mechanical and viscoelastic behavior of such blends (along with the behavior of vinyl chloride/vinyl stearate copolymers). Landi (35) has investigated the use of liquid NBRs, and Deanin et al. (36) have noted that NBR can be added to plasticized PVC without sacrifice in abrasion resistance. There are, however, some problems with processing (6) and powdered dry blends are sometimes used.

Oligomeric polyesters [e.g., poly(ethylene adipate)] have also been used extensively for some time (6,33,37); their higher-molecular weight analogs are reported to be effective as plasticizers, and hence may well be miscible too. Higher molecular weights aid in reducing extractability. Recently, much attention has been given to ethylene copolymers and other polyesters. Because of the ability of the α -hydrogen in PVC to form a hydrogen bond with the proton-accepting C=O group in an ester, compatibility of ester groups with PVC is quite favorable. [For detailed discussions, see Hammer (33).]

At vinyl acetate concentrations between 65 and 70 wt percent, ethylene/vinyl acetate (EVA) copolymers are quite miscible with PVC (38). To evade some processing problems with the EVA compositions desired, the incorporation of carbon monoxide or sulfur dioxide (each of which offers proton-accepting C=O groups) has been suggested (38-40). If carbon monoxide is present, vinyl acetate can also be replaced with ethyl acrylate; also, the ethylene content can be increased. At least one of these copolymers is known to be offered commercially (6). A comparison of the ability to lower T_g is given in Fig. 6.

As shown in Fig. 7a, the T_g of PVC is reduced about 60°C by the incorporation of a 50/50 blend with an ethylene/ethyl acrylate/carbon monoxide terpolymer (71.8/10.5/17.7). The single sharp peak in $\tan \delta$ indicates a high degree of compatibility; interestingly, the secondary (β) transition of PVC is essentially suppressed. Generally, similar behavior was noted for terpolymers based on vinyl acetate. In contrast (Fig. 7b), blends with ethylene/ethyl acrylate copolymer (82/28) exhibited separate peaks for both the PVC and the copolymer, as is expected for a two-phase system.

Poly(ϵ -caprolactone) also serves as a compatible polymeric plasticizer for PVC as well as for other polymers though poly(β -propiolactone) is incompatible (41-43b). However, slow crystallization or phase separation is a complicating factor (42,44); a small amount of

monomeric plasticizer is used to minimize this phenomenon (33). Ethylene/ ϵ -caprolactone copolymers are stated (43) to be useful permanent plasticizers for PVC. In any case, the relative effectiveness of the plasticizers is in the order of the T_g s for the three groups presented in Fig. 6. Chlorinated PE (% chlorine = 65.2% and chlorinated EVA (% chlorine = 38%) are also compatible plasticizers (6); chlorinated PE is stated to be less efficient than typical ethylene copolymers (6) [for discussion of its compatibility, see ref. (45)].

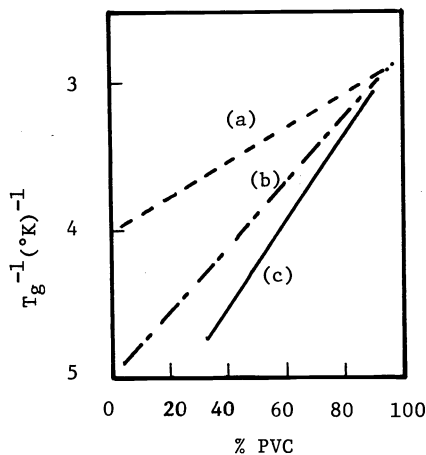


Fig. 6. Effect of (a) ethylene copolymers (38,40), (b) poly(ϵ -polycaprolactone) (41), and (c) PVC/dioctyl phthalate [after Hammer (31)].

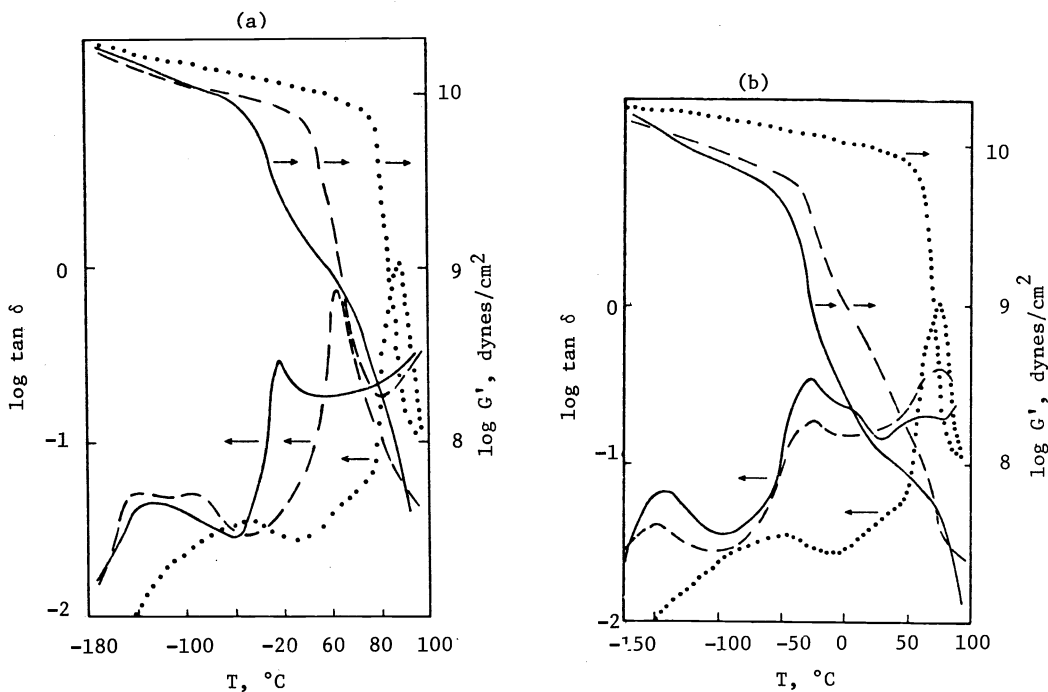


Fig. 7. Mechanical loss and shear modulus-temperature data for ——— E/EA/CO (71.8/10.5/17.7), - - - - 50/50 blend of E/EA/CO (71.8/10.5/17.7)/PVC (QSQF-7), and PVC (QSQF-7). (b) Mechanical loss and shear modulus-temperature data for ——— E/EA (82/18), - - - - 50/50 blend of E/EA (81/28)/PVC (QSQF-7), and PVC (QSQF-7). [Robeson and McGrath (37)].

Certain polyurethanes may act as polymeric plasticizers. Thus thermoplastic polyurethanes based on poly(ϵ -caprolactone) are compatible with PVC (46), but their ability to lower T_g is limited by the hard urethane blocks. A similar limitation exists with poly(butylene terephthalate)-poly(tetrahydrofuran) block copolymers (47,48) though excellent properties are reported for blends with PVC (6).

Heat distortion temperature (HDT)

For many purposes the T_g (and hence HDT) of PVC is inconveniently low ($\sim 80^\circ\text{C}$). While the T_g can be increased by copolymerization with a higher- T_g monomer or by post-chlorination, much recent attention has been given to the blending of PVC with an essentially compatible, higher- T_g polymer. In principle, the T_g could be also raised by incorporating a higher- T_g immiscible polymer. However, this would be possible only if the higher- T_g polymer were the continuous phase; compatibilization at least at the interface would also be required to avoid the deleterious effect of poor interfacial bonding. Hence the use of compatible systems is preferred. Two other characteristics are also desirable: similar flow characteristics during compounding, and freedom from adverse effects on properties such as toughness, color and stability.

Several polymers having T_g s higher than that of PVC are known or believed to be compatible with PVC. Styrene/acrylonitrile (72:28) copolymers (HDT $\sim 95^\circ\text{C}$) are evidently compatible, and are listed as HDT improvers at concentrations up to 50% (4). Poly(methyl methacrylate) (PMMA) is another interesting example of the importance of tacticity in determining compatibility. Thus, while isotactic PMMA is quite incompatible with PVC at all concentrations (50), syndiotactic PMMA ($T_g=115^\circ\text{C}$) is compatible with PVC up to a 1:1 mole ratio. Evidently the helical isotactic conformation hinders the donor-acceptor interaction between carboxyl and chlorine. Atactic PMMA appears to be compatible only over a restricted range of compositions (15,51). Polycarbonate (PC), while not wholly compatible with PVC, does raise the T_g (52). However, since the T_g s of SAN and PMMA are not much higher than that of PVC, only small increases in T_g of the blend are possible ($\sim 7^\circ\text{C}$ for the case of a 50/50 blend with SAN).

Thus there has been much more interest in polymers based on styrene derivatives. While *t*-butyl styrene/acrylonitrile copolymers (6) have been considered, most attention appears to have been given to copolymers of α -methyl styrene (AMS) [for a review see ref. (6)], and especially to AMS/acrylonitrile copolymers (53), which are probably compatible with PVC (6). Compatibility of AMS/methacrylonitrile/ethyl acrylate terpolymers has been reported, and a single T_g of 100°C reported for a blend with PVC (54). The grafting of AMS to PVC has also been reported at this meeting (55). With a T_g of $\sim 170^\circ\text{C}$ for AMS, significant increases in T_g are possible with modest proportions of the modifier.

Processing Aids

Melts of rigid PVC typically exhibit high viscosity, high pseudoplasticity, and a tendency towards fracture under stress. The plastification process itself poses difficulties, for PVC cannot be truly melted on a molecular scale without degradation. A domain-like microstructure persists in the "melt"; particle boundaries can serve as easy paths for fracture.

A diverse group of phenomena are related to these tendencies (56-58). For example, the occurrence of melt fracture limits the draw ratio in thermoforming and extrusion blow-molding and causes break-up during calendaring; in general the slow relaxation of the melt leads to a variety of surface defects such as matte and "sharkskin" effects.

To alleviate these problems, a variety of polymers have been proposed (4) — most being of the same chemical types as some of the permanent plasticizers, impact modifiers, or HDT improvers, though used at relatively low concentrations (usually from $\sim 1\%$ to 4%). However, larger proportions may be used to enhance thermoforming and foam extrusion). The goal is usually to achieve the desired effect without changing the T_g to an unacceptable degree. Some of the polymers used have been ABS, MBS, vinyl chloride copolymers, PMMA and acrylic copolymers, and copolymers of AMS with acrylic monomers or acrylonitrile (4) (see also Table 1), with the latter two groups receiving much current attention.

While the precise mechanisms for the improvement of processability may not yet be universally agreed upon (59) several factors appear to be important. In all cases, a significant degree of compatibility is desirable.

In plastification, the processing aid may serve to increase the particle-to-particle friction and to act as a heat flux (58,60); thus the gelation time can be reduced. As has been clearly shown recently (60), molecular weight and composition play major roles. Thus, as shown in Fig. 8a, the higher the molecular weight the longer the gelation time. The implication that high segmental mobility enhances plastification is also borne out by Fig. 8b, which shows an increase in gelation velocity with increasing ethyl acrylate content. In this case "softness" appears to be desirable to enhance the fusion. However, as seen below, this is contradictory to the effect of a processing aid in increasing melt stability.

From the standpoint of melt flow characteristics, it is clear that molecular weight and composition act in a more complex manner (see Fig. 9). The recoverable strain, a measure of extensibility (and resistance to melt fracture) increases at first as M is increased, but then drops off slightly. (Note that the peak in Fig. 9a corresponds to a value of M about 50 times higher than that of the PVC used.) On the other hand, comonomer content has a relatively small effect within the range studied. The lower value for the unmodified PMMA was attributed to poor dispersion of the higher- T_g polymer.

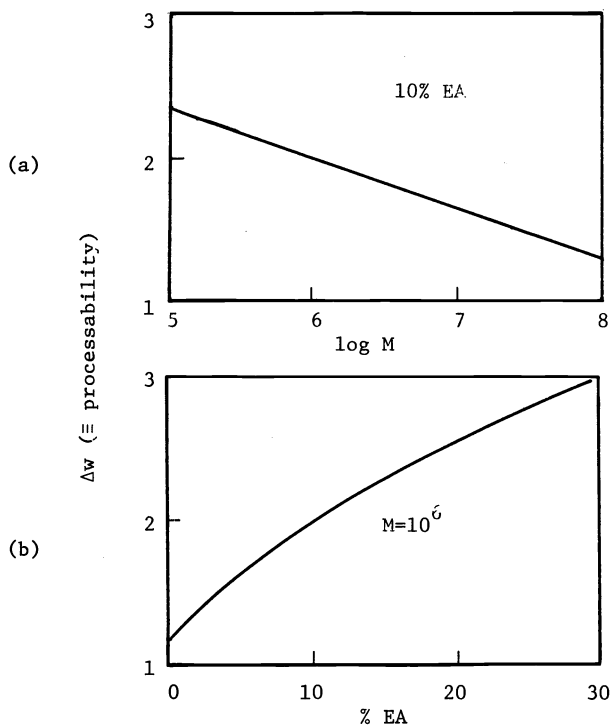


Fig. 8. Effect of (a) molecular weight of an MMA/EA (90/10) copolymer and (b) comonomer composition ($M = 10^6$) on the gelation time of PVC (as indicated by Δw , the decrease in Brabender charge-weight between modified and control specimens). [After Gould and Player (60).]

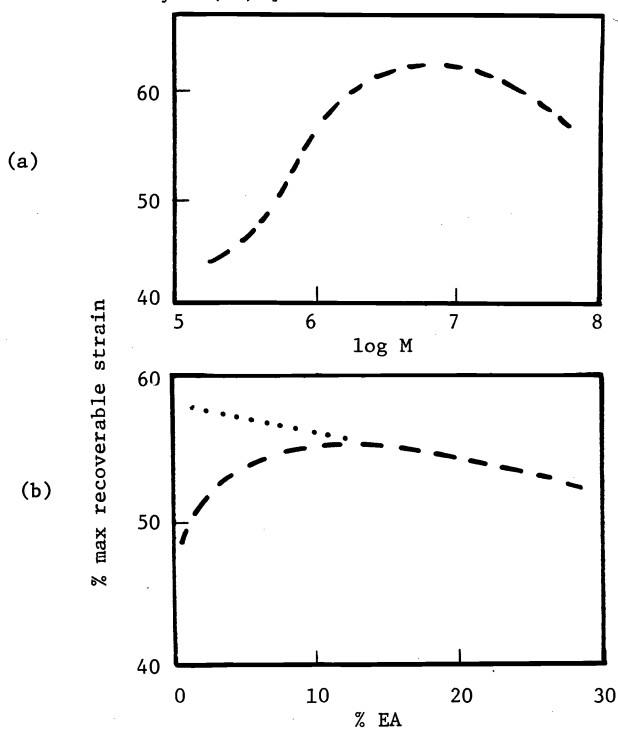


Fig. 9. Effects of (a) molecular weight of an MMA/EA copolymer (90/10) and (b) comonomer composition ($M=10^6$) on maximum recoverable strain (ϵ_r) in PVC. [After Gould and Player (60).]

The beneficial effect of the MMA/EA copolymer on the extensibility of the melt is also obvious in Fig. 10.

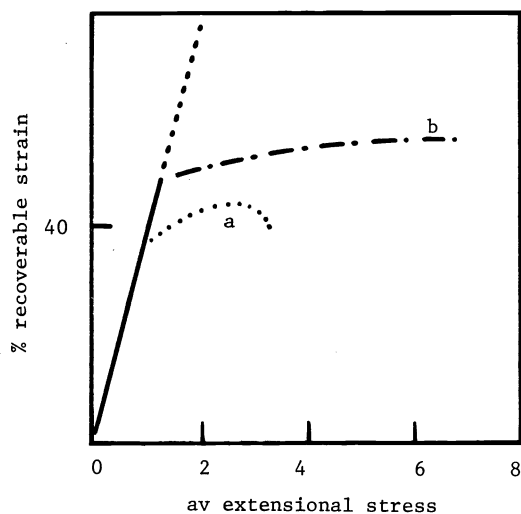


Fig. 10. Post-extrusion swell in PVC using emerging knife-edge die. Relationship between recoverable strain and extensional stress: (a) no EVA; (b) with 3 phr EVA [after Gould and Player (60)].

Thus a high-molecular-weight compatible polymer that has a more homogeneous microstructure than PVC can in effect toughen the inter-particle domains in PVC. To form the gel on plastification, low molecular weight and internal plasticization are facilitative, but once the gel forms, its melt properties are enhanced by a high molecular weight. In turn, the higher molecular weight not only inhibits melt fracture but also delays the onset of bank-marks in calendered sheet, and enhances heat generation and better continuity at the weld-line in an injection-molded article (58,60). With foam extrusion, high molecular weight in the processing aid facilitates plasticization and the generation of uniform cells; as mentioned, the increased extensibility also facilitates drawing during thermoforming or blow-molding (58).

While a measure of compatibility may be desired for the applications just discussed, somewhat lower compatibility may be desirable in order to minimize adhesion to calender rolls. Typically, polyacrylates may be used for this purpose. They serve in part as lubricants, but can also increase the gelation time, due to their partial incompatibility. By adjusting the degree of compatibility, it is possible to extend the range of processing conditions and obtain better film properties as well (58).

Toughened resins

As mentioned earlier, toughening generally requires the incorporation of a rubbery phase that is sufficiently compatible with the matrix to provide a reasonable degree of interfacial adhesion, but sufficiently incompatible to yield a discrete rubbery phase. Thus it was shown that maximum toughening in nitrile-rubber-toughened PVC is obtained at concentrations of acrylonitrile that correspond to partial compatibility (61). CPE, certain polyacrylates, and EVA are also useful in composition ranges corresponding to partial compatibility (6). With terpolymers, the non-rubbery component may well be essentially compatible with the matrix. This is the case for ABS dispersed in PVC (49), and presumably also in MBS blends. Mechanical studies are widely used to characterize the compatibility of the components of toughened PVC, for the mechanical spectrum can often be correlated with impact strength (62). For a recent example in which a combination of mechanical, thermal, and electrical methods was used to characterize transitions in CPE, see reference (63); ^{13}C NMR spectroscopy has also been used to elucidate microstructural details in the same polymer (64).

Toughening Agents. Toughening agents (see Table 1 and ref. 4) include ABS, MBS, NBR (61), EPDM (66), chlorinated polyethylene (CPE), several kinds of acrylics, EVA/PVC graft polymers (65), ethylene/propylene graft copolymers (66) acrylonitrile-MBS compositions (AMBS) and styrene/acrylonitrile/acrylic rubber (67). The non-butadiene-based modifiers also offer the advantage of better weathering behavior (see below), while MBS permits the matching of refractive indexes to give clear formulations. Grafting is frequently advantageous because it provides a means of sensitively balancing compatibility, T_g , toughening capacity, processability, and weatherability (4,65). Interpenetrating polymer networks (IPNs) based on PVC have also been prepared (68,69). A recent example involves the synthesis and characterization of graft copolymers of vinyl chloride with ethylene-propylene and ethylene-propylene-diene backbones by a mass polymerization process (66). Both processability and impact

strength were improved, without much sacrifice in HDT. In any case, the blend must retain a fairly clear-cut two-phase morphology after fabrication (69a-69b); for discussion of the effects of process conditions on some polyacrylates see reference 69a.

EVA/PVC grafts have been known for some time (4,60), and some aspects of their processing and weathering behavior have been discussed above and in Aging and Weathering below. An interesting interpenetrating polymer network (IPN) has also been recently described (69). Usually a vinyl acetate content of 45% is required for adequate impact modification. However, by conducting the grafting of vinyl chloride to EVA while the EVA was swollen but not dissolved in monomers, good impact strengths were obtained with only 25% VA. It was suggested that the IPN gave an acceptable level of compatibility at a lower VA content than would otherwise be the case. Other IPNs based on PVC and nitrile rubber have been prepared and their viscoelastic behavior, but not their impact strength, has been described (68). Since rubber/plastic IPNs resemble finely dispersed polyblends, often exhibit strengths, toughening in the case of PVC is likely if the elastomer phase has a low enough T_g (19).

The ability of some polyester-based polyurethanes to act as permanent plasticizers was mentioned earlier. More recently the effects of polyurethane composition on the mechanical properties of PVC have been described in detail (70); specifically the effects of the glycol type and molar ratio of NCO to OH were examined. In general, ~ 12.5 wt % polyurethane improved both processability and impact strength (the latter by a factor of ~ 2.3 ; however, in some cases, the presence of the polyurethane decreased the thermal stability of the blend (71).

Mechanism of Toughening. So far considerable evidence suggests that the toughening effect of rubbery phases in PVC differs in mechanism from the effect in brittle matrixes like polystyrene PS. While the induction of multiple delocalized crazing in, for example, PS appears to dominate toughening, rubber-modified PVCs typically exhibit a greater degree of shear response in creep (Fig. 11) and in impact loading. It has been suggested that the rubber particles in a ductile matrix like PVC initiate shear bands that control the growth of crazes that could otherwise be the precursors of catastrophic fracture (16,17). Indeed, while crazes have been observed in toughened PVCs (62), they are not often reported (18). The stress whitening sometimes often seen in toughened PVC has been attributed to causes other than crazing. Petrich (72) has proposed that birefringence effects and refractive index mismatches are responsible, while Breuer et al. (73) have noted cavitation inside the rubber particles in MBS-modified PVC.

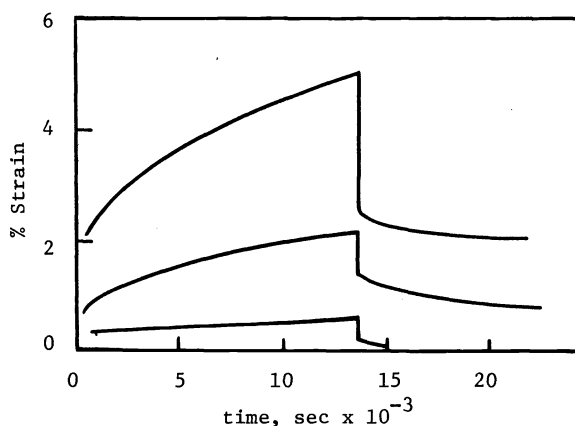


Fig. 11. Tensile creep and recovery of toughened PVC at 20°C under a stress of 36 MPa. Polymer made by blending PVC with 5% ABS concentrate. ΔV , e , and e_3 represent changes in volume, thickness, and length, respectively. Volumetric changes are a consequence of crazing and account for only 5% of the creep in the PVC blend, in comparison with 95% in the case of high-impact PS. [After Bucknall (16).]

As with polystyrene-based systems, the size and degree of dispersion of the rubbery phase is important (18). Thus, with 6-mm specimens of MBS-modified PVC, Purcell (74) reported a 4-fold increase in impact strength as the diameter of the MBS phase was increased 6 times. In contrast, 3-mm specimens exhibited strengths that were higher (equivalent to that of the highest value found at the maximum rubber content in the 6-mm specimens) and independent of rubber content. This behavior surely suggests the ability of rubber particles to induce a change from plane-strain to plane-stress response (thick vs thin specimens). In any case, even though the detailed mechanism of toughening is not unequivocally established, all the evidence is consistent with a major role of rubber in enhancing a ductile shear response under a variety of loading conditions (16-18). The microstructure of the dispersed particles

can also affect processability and impact strength. Thus, EVA/PVC (6/92) graft copolymers possessing a porous structure have been recently shown (75) to give shorter mixing cycles (Fig. 12) and a wider range of processing conditions yielding high impact strengths (Fig. 13).

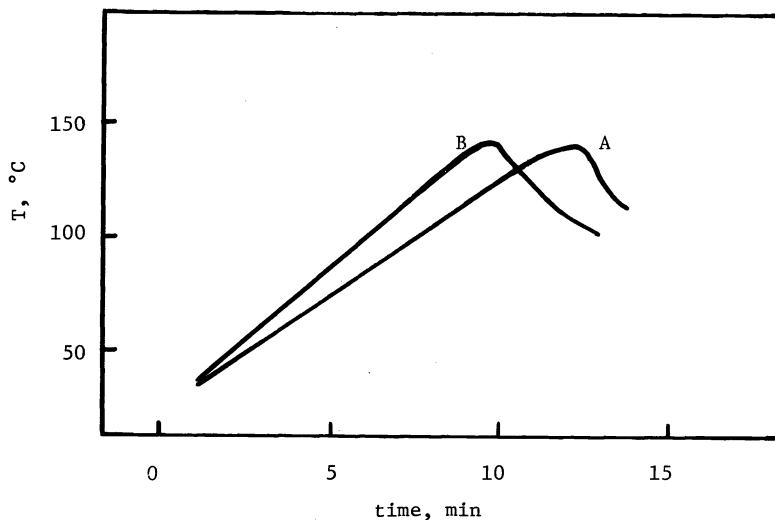


Fig. 12. Conditions required for high-speed mixing of EVA with PVC (6/94): A, non-porous particles; B, porous particles [after Frey et al. (75)].

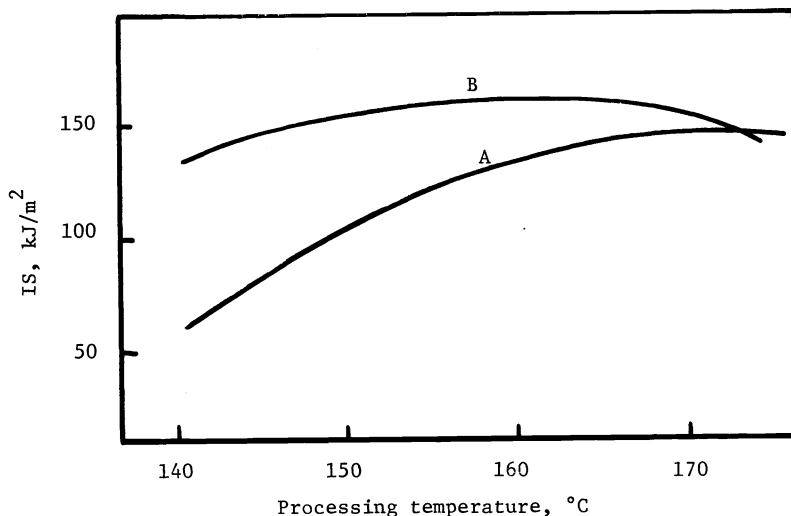


Fig. 13. Processing temperature and impact strength of EVA/PVC (6/94) blends: A, non-porous particles; B, porous particles [after Frey et al. (75)].

Thus grafting and copolymerization can often be judiciously combined to yield a desired combination of low T_g in the elastomer, easy processing, and transparency (75a).

The proportion of modifier used varies between about 5% and 25% depending on the system. In general, as shown in Fig. 14, an optimum proportion for maximum toughening exists (72,76).

As modifier is impregnated into the notch-sensitive PVC, the yield stress is lowered with respect to the fracture stress, and the impact strength rises to very high values in the case of an inherently ductile polymer like PVC. However, beyond a certain modifier content, the role of the PVC is progressively diminished as the composition approaches that of the rubber, which is inherently not as tough as PVC at its best. Thus there is competition between strengthening of the rubbery phase by PVC and weakening of the PVC at high concentrations of rubber (and hence lower moduli).

Modifiers differ widely in their ability to increase toughness. For example, as shown in Fig. 14, 25% of ABS was required to reach an impact strength of ~ 9 J/cm, whereas 7% of EPDM (or $\sim 12\%$ of the graft polymer) was required to reach a similar level (Fig. 15). However, the rubber content of the ABS was only $\sim 5\%$. (Recall also the effects of morphology.)

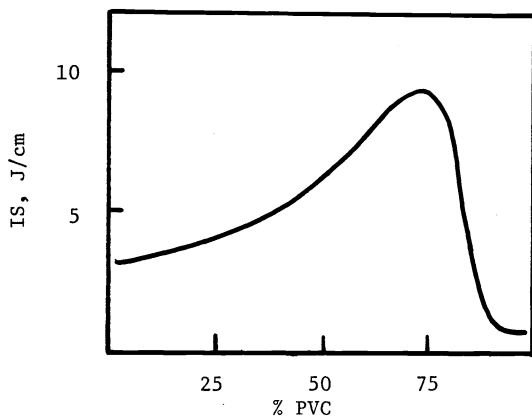


Fig. 14. Notched Izod impact strength of PVC/ABS blends at 23°C showing the maximum in toughness achieved by balancing matrix ductility against rubber content. (After R. D. Deanin and C. Moshar (76).)

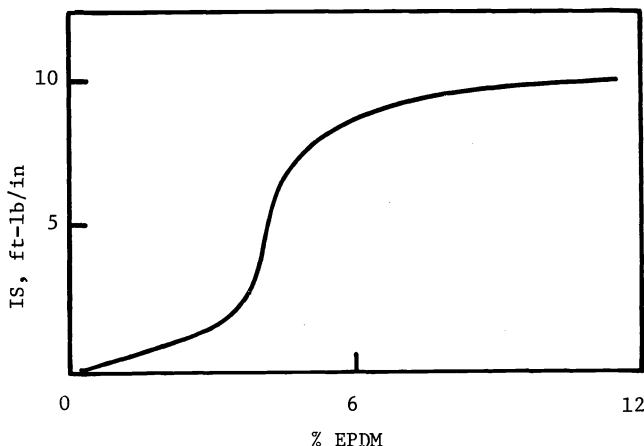


Fig. 15. Notched Izod impact at RT for injection molded high-impact PVC as a function of EPDM content. [After Walker and Slagowski (66).]

Combined effects of molecular weight and rubber content. It is well known that the toughness of a polymer is higher, the higher its molecular weight, though the rate of increase of toughness with M tends to drop off when $M > \sim 10^5$. Considerable evidence shows that both the stability of crazes and the ability to undergo stable yielding and drawing is greater, the higher M . The reason is undoubtedly that higher- M polymers can form entanglement networks that can resist fracture more effectively. Unfortunately, in a rubber/plastic polyblend, the M of the matrix is often decreased when rubber is incorporated, in order to compensate for the increase in viscosity due to the rubber (16). Thus the effects of M and rubber content are often confounded.

However, in a recent study of MBS-modified PVC (77) both Izod impact strength and the fatigue behavior were determined for a series of molecular weights, with the MBS content varied (for each M) from 0 to 14 phr. With respect to impact strength, it was shown that maximum toughening required the molecular weight of the matrix to exceed some minimum value, the critical value being lower the higher the rubber content (Fig. 15). For example, with 10 phr MBS, M_w must be $\sim 10^5$, while with 14 phr MBS, a somewhat lower value of M_w sufficed. On the other hand, with only 6 phr MBS, the transition from low to high values of impact strength (a transition rather analogous to a brittle-ductile transition) had not yet occurred with $M_w \sim 2 \times 10^5$.

Quite different behavior was noted in the resistance to fatigue crack propagation (FCP). While increasing M consistently and dramatically decreased FCP rates under constant loading conditions (Fig. 17), the data for 10 phr and 14 phr were shifted only slightly (though consistently) to the right. Thus, even at a value of M low enough to give little improvement in impact strength (Fig. 16) the fatigue resistance was improved by an order of magnitude. At the same time, little was gained by incorporating more than 6 phr MBS; perhaps the concomitant lowering of modulus counterbalanced the toughening due to the rubbery phase. Also, the greatest relative toughening was observed with the lower values of M .

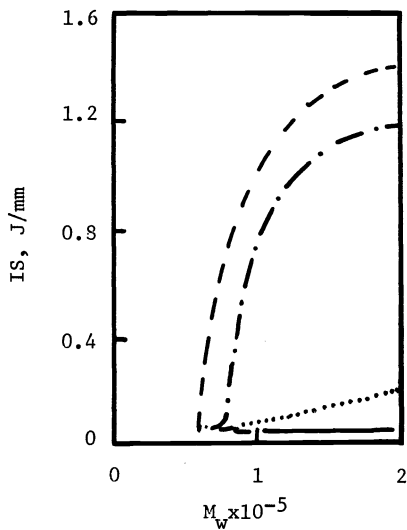


Fig. 16. Effect of MBS content and M of matrix on notched impact strength of PVC blends: phr MBS = 14 (---), 10 (-.-.-), 6 (...), 0 (—) [after Skibo et al. (77).]

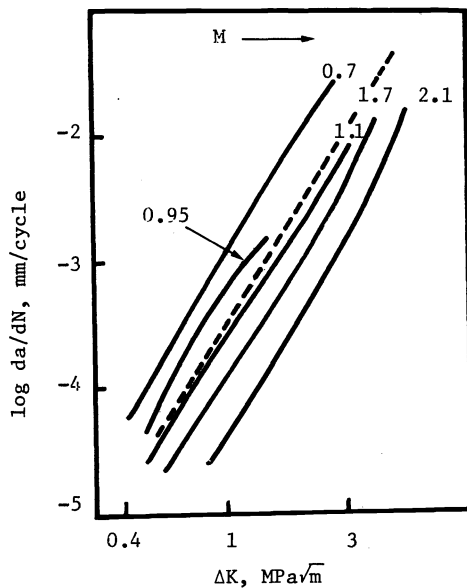


Fig. 17. Effects of M and MBS content on fatigue crack growth rate per cycle (da/dN or 10 Hz) vs the range in the stress intensity factor ΔK (ΔK being proportional to the range in the applied stress, $\Delta\sigma$): (—)Effect of M on PVC containing 6 phr MBS (numbers on the figure represent $M \times 10^{-5}$); (---)effect of MBS (14 phr) on PVC ($M_w = 6.7 \times 10^4$). Similar shifts were noted for other molecular weights [after Skibo, et al. (77)].

Impact and fatigue data have also been reported for blends of PVC with composite acrylic/PVC latex particles made in a 2-stage process by polymerizing vinyl chloride onto preformed acrylic particles (78). While the improvement in Charpy impact strength was at most 3-fold, much much greater improvements in FCP resistance were noted. In this respect, the FCP curves essentially overlapped those of Fig. 17 for MBS/PVC blends.

Indeed, as shown in Fig. 18, the FCP behavior of MBS/PVC (M_w of PVC = 2×10^5 ; 14 phr MBS) is significantly better than that of a commercial polycarbonate. To be sure, this does not necessarily imply a superiority under other loading conditions or with unnotched specimens.

Nevertheless, the results all clearly show the ability of rubber particles to facilitate expression of the ductility inherent in PVC, but not seen in the neat resin due to its notch sensitivity.

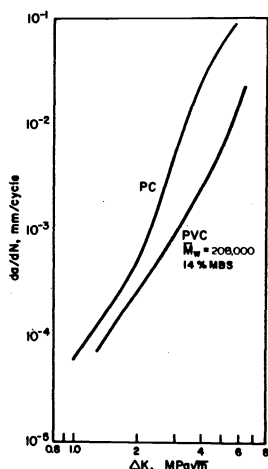


Fig. 18. Comparison of FCP behavior of MBS-modified PVC ($M_w=2.08 \times 10^5$; 14 phr of MBS) with that of a typical commercial polycarbonate. [Reprinted with permission from M. D. Skibo, J. A. Manson, S. M. Webler, R. W. Hertzberg, and E. A. Collins, *Durability of Macromolecular Materials*, p. 311, Copyright 1979 by the American Chemical Society.]

Miscellaneous

It was stated earlier that properties such as tensile strength are not necessarily additive in polyblends if one component is ductile and another not. A good example is the case of a compatible blend of PVC with an AMS/methacrylonitrile copolymer (54). Evidently the higher ductility of the PVC is manifested by an increase in the strain-to-break of the brittle copolymer (as in Fig. 2) that more than compensates for the effect of the decrease in modulus due to the addition of PVC.

Indeed, large-deformation properties such as tensile strength and viscosity may be quite sensitive to subtle variations in compatibility (79). As with the AMS copolymer just mentioned, compatible blends of PVC with AMS/styrene/acrylonitrile copolymers and blends of these copolymers with chlorinated PVC exhibited higher strengths than the individual components. The deviation from values predicted by the rule-of-mixtures was greater, the greater the compatibility. On the other hand, negative deviations were observed, with viscosities, the deviation being greater, the lower the compatibility.

Certain polyurethanes may act as polymeric plasticizers. Thus thermoplastic polyurethanes based on poly(ϵ -caprolactone) are compatible with PVC (44), but their ability to lower T_g is limited by the tendency of the hard urethane blocks to raise T_g . A similar limitation exists with poly(butylene terephthalate)-poly(tetrahydrofuran) block copolymers (45,46), though excellent properties are reported for blends with PVC (6).

For a recent discussion of positive and negative deviations of various physical, mechanical, and rheological properties from a range of PVC blends (with VC/VA copolymers, PMMA, and CPE) as a function of compatibility and phase size, see reference (80). The role of the distribution of the dispersed phase size in PVC/PE blends has also been discussed (81). PVC can also improve the properties of brittle phenolic resins. In this case, the PVC appears to act as a discrete toughening phase (82).

Aging and Weathering

As mentioned above, on aging of PVC as well as other polymers, changes in mechanical and other behavior occur, especially due to physical relaxation and oxidative degradation. Although the effects of purely physical aging (20) in PVC blends have not been clearly described, weathering is well-known to degrade both the appearance and impact strength of PVC and its blends due to the formation of a brittle outer layer (20). The effects are most severe in blends such as ABS that contain unsaturated components; MBS is considered to be less susceptible (11).

The usual approaches to improving weatherability involve serious disadvantages: carbon black protects against ultraviolet light but decreases the impact strength, and antioxidants tend to have limited usefulness over the long term (16). For this reason, saturated elastomers such as polyacrylates have been used as relatively age-resistant toughening agents (11,83). Even these, however are not as resistant as might be desired; also, the T_g of a typical acrylic rubber (-24°C to -55°C) is not as low as that of polybutadiene (as low as -110°C) [a low-as-possible T_g being desirable for the highest possible impact strength (16)]. Chlorinated PE (% chlorine from $\sim 30\%$ to $\sim 40\%$) is also used as an age-resistant modifier

with some sacrifice in T_g and a higher die swell during processing (4). Ethylene/vinyl acetate (typically 55/45 to 60/40) copolymers are also used extensively, again with some loss in T_g .

An extensive study of the natural weathering of a white-pigmented PVC/EVA blend has recently been reported (83); tests were conducted over a 5-year period at 5 regions around the world. Locations were selected to correspond to a wide range of climatic conditions, from hot and dry to tropical. As shown in Fig. 19a, the modified PVC degraded steadily (in terms of notched impact strength) at all locations, but still retained 80% of its original toughness in the two least severe locations, and 60% in the most severe location. Functional performance was judged to be maintained in all cases. In contrast, much more severe deterioration was noted in unmodified controls (Fig. 19b); functional performance was lost after 3-5 years of exposure in the 2 most severe locations. Indeed, at all times and in all locations, the modified resin performed better than the control; indeed polyacrylates are generally believed to block the dehydrochlorination reaction. Promising results have also been reported for SAN/acrylic rubber blends (67).

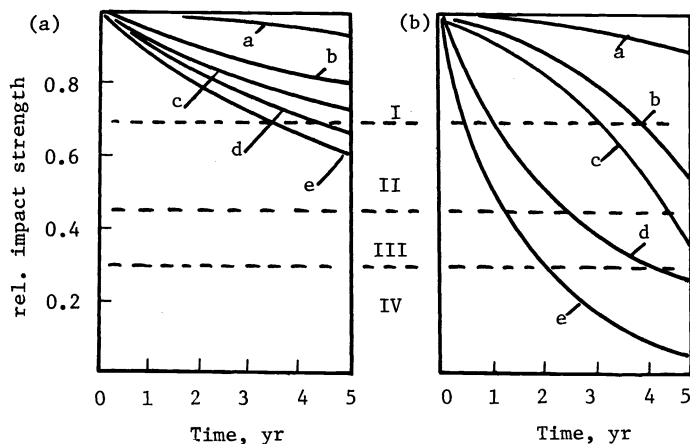


Fig. 19. The deterioration of (a) impact resistant PVC (PVC/EVA) and (b) unmodified control specimens as a function of exposure time at various locations, at which the severity of exposure increased in severity from a to e. Zones I through IV represent respectively: tolerable changes; function maintained; function limited; and function lost [after Menzel (83)].

CONCLUSIONS

Thus the behavior of copolymers and blends depends on the composition, chemical and viscoelastic properties of the components, and compatibility. Further intensive research on phase relationships, special networks such as IPNs, and polyblends capable of improving the HDT processability, plasticization, toughness, and aging may be expected.

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