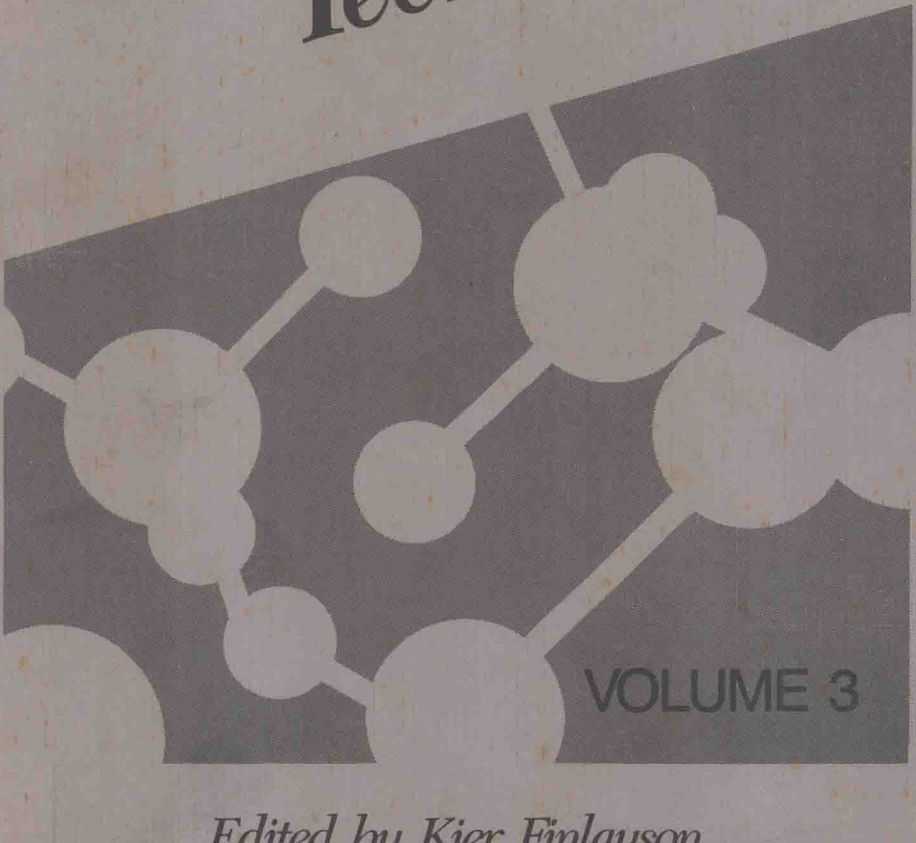
Advances in Polymer Blends and Alloys Technology



Edited by Kier Finlayson

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VOLUME 3

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EDITOR'S NOTE: The development of new plastic materials through compounding of polymer blends and alloys has gained attention over many years. New methods are being developed for combining dissimilar polymers, and studies are being conducted to understand the structure and morphology of these multiphase polymers.

There are established blends that are known to provide desired physical and chemical properties, and there are ongoing developments to control reactions occurring during the blending process to determine the miscibility and other properties.

This third volume in a series presents a cross section of the activity in this increasingly important field.

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1

Practical Benefits of Polymer Blending

RUDOLPH D. DEANIN*

PRODUCTION, PUBLICITY, AND research publications on polymer blends have been growing exponentially for the past 45 years (Table 1). The field is so broad and diverse that we need to survey its practical significance. What are the practical benefits that account for this vigorous growth? It is convenient to carry out this survey in 2 stages: (1) established practice and (2) recent developments.

ESTABLISHED PRACTICE [2,3]

Processability is often improved by polyblending (Table 2). In most cases the improvement is measured in terms of increase in melt flow. For blow molding and thermoforming, it is often an increase in melt extensibility and/or elasticity. In polyurethane rubber, on the other hand, addition of thermoplastic ABS reduces melt elasticity and produces smoother melt flow.

Increased Modulus results when a rigid plastic is added to an elastomer (Table 3). This produces much tougher rubbery products.

Lower Modulus results when an elastomer is added to a rigid plastic (Table 4). Here the elastomer acts as a polymeric plasticizer, less efficient than monomeric plasticizers, but extremely more permanent.

Strength of elastomers is increased by addition of rigid plastics (Table 5). Addition of polypropylene to EPDM, and of PVC to nitrile rubber, converts them into strong thermoplastic elastomers. Addition of high-styrene/butadiene resin or phenolic resin to rubber during compounding greatly increases the strength and toughness, so that the added polymers are referred to as "reinforcing resins."

In interpenetrating polymer networks of acrylic, polyester, and polyurethane polymers, synergistic improvement of tensile strength has often been observed.

Paper presented at IUPAC International Symposium on Macromolecules, Montreal, PQ, July 13, 1990.

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Table 1. U.S. sales of commodity polyblends 1989 [1].

Polymers	Millions of Pounds
ABS	1243
PPE/PS	176
PP/EPDM (10% of PP)	725
HIPS (2/3 of PS)	3456
Rigid PVC (1/2 of PVC)	4154
Total blends	9754
Total U.S. plastics	58,228
Blends as percent of total	17%

Table 2. Practical benefits of established polyblends.

Processability

Base Polymer	Added Polymer
PVC	NBR
PVC	ABS
PVC	AN/BD/AMS
PPO	HIPS
PSF	ABS
PC	PE
PC	ABS
PC	PET
PC	PBT
PC	CPTI
PUR	ABS

Table 3. Practical benefits of established polyblends.

Increased Modulus

Base Polymer	Added Polymer
NBR	PVC
PUR	ABS

Table 4. Practical benefits of established polyblends.

Lower Modulus	
Base Polymer	Added Polymer
PVC	CPE
PVC	NBR

Table 5. Practical benefits of established polyblends.

Strength	
Base Polymer	Added Polymer
EPDM	PP
NBR	PVC
Rubber	ST/BD
Rubber	Phenolic

IPNs of acrylics, polyesters and polyurethanes.

Table 6. Practical benefits of established polyblends.

Impact Strength	
Base Polymer	Added Polymer
PP	EPDM
PP	Butyl
PS	Rubber
SMA	PC
SAN	PBD
SAN	NBR
ABS	PVC
ABS	PC
PVC	CPE
PVC	EVA
PVC	NBR
PVC	ABS
PVC	Acrylic
PPO	HIPS
Epoxy	CTBN
T.S. Polyester	CTBN
Nylon	ET/X
Phenolic	NBR

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Table 7. Practical benefits of established polyblends.

Lubricity	
Base Polymer	**Added Polymer**
Acetal	PTFE
PC	PTFE
Nylon 66	PTFE

Table 8. Practical benefits of established polyblends.

Abrasion Resistance	
Base Polymer	**Added Polymer**
ABS	PUR
Acetal	PTFE
PC	PTFE
Nylon 66	PTFE

Table 9. Practical benefits of established polyblends.

Low-Temperature Impact Strength	
Base Polymer	**Added Polymer**
PP	Butyl
PP	EPDM

Actually most of the high-impact systems listed earlier.

Table 10. Practical benefits of established polyblends.

Increase T_g and HDT	
Base Polymer	**Added Polymer**
HIPS	PPO
ABS	AN/BD/AMS
ABS	SMA
ABS	PSF
ABS	PC
PVC	AMS/AN

Table 11. Practical benefits of established polyblends.

Flame Retardance	
Base Polymer	Added Polymer
PE	CPE
ABS	PVC

Impact Strength is the most frequently reported benefit from polyblending (Table 6), and accounts for the largest volume of commercial practice. The improvement of impact strength is an extreme example of synergism, which is not yet completely understood. In most cases, the overall benefit is the combination of high modulus and heat deflection temperature from the matrix phase, plus the high ductility and impact strength from the finely-dispersed rubbery domains of the impact modifier. When polycarbonate is added to a commodity plastic, it actually contributes to all these properties simultaneously.

Lubricity of engineering plastics for gears and bearings can be increased greatly by addition of 5–20% of PTFE powder (Table 7).

Abrasion Resistance generally benefits from increased lubricity, and the improvement can be very dramatic (Table 8). This again is demonstrated by the addition of PTFE powder to engineering plastics. When polyurethane rubber is added to ABS, it brings its own inherent abrasion resistance along to the polyblend.

Low-Temperature Impact Strength of polypropylene was first improved by adding butyl rubber, later and more successfully by EPDM (Table 9). This was actually the major improvement in its progress to commodity growth. Probably most of the impact modifiers (Table 6) actually also improve impact strength at low temperatures, but this is not as often reported in the literature.

Increased T_g *and HDT* can be observed when a more rigid molecule is added to a less rigid one (Table 10). The improvement is approximately proportional. The more rigid polymer must either be miscible or else form its own matrix phase, in order to produce optimum benefit.

Flame Retardance can be improved by adding a more combustion-resistant polymer (Table 11). When chlorinated polyethylene is added to polyethylene, it reduces the amount of additional flame-retardant that will be required. When PVC is added to ABS, it contributes so much chlorine content that it solves one of ABS's major problems.

Table 12. Practical benefits of established polyblends.

Transparency	
Base Polymer	Added Polymer
PVDF	PMMA
PVDF	PEMA

Table 13. Practical benefits of established polyblends.

Chemical Resistance	
Base Polymer	Added Polymer
PP	Butyl
PP	EPDM
PMMA	PVDF
PEMA	PVDF
PC	PET
PC	PBT
PC	CPTI

Transparency is usually one of the major sacrifices in polyblending. In rare cases the polyblender may actually report an improvement (Table 12). Here the addition of acrylic polymers presumably reduced the crystallinity of the polyvinylidene fluoride.

Chemical Resistance may occasionally be improved by polyblending (Table 13). The problems and the improvements are quite diverse. Environmental stress cracking of polypropylene can be resisted by addition of the ductility of butyl and EPDM elastomers. Solvent crazing of polycarbonate can be resisted by addition of crystalline polyesters. Solvent sensitivity of acrylics may be reduced by addition of crystalline polyvinylidene fluoride. Both the mechanisms and the extents of these improvements may vary widely.

Low Cost is too often quoted by the trade journals as a major reason for polyblending. In commercial practice, some polyblending operations may actually produce a modest decrease in cost (Table 14), but this is rarely if ever the major reason for making the polyblend. In most cases, the compounder makes a polyblend for sound technical reasons; if it also lowers the cost a bit, this is an additional benefit.

Miscellaneous benefits of polyblending are reported occasionally in the literature (Table 15). These are all valid qualitative improvements, and require alert market development specialists to make use of them. Their success depends upon the quantitative benefits they may offer in specific areas.

Table 14. Practical benefits of established polyblends.

Low Cost	
Base Polymer	Added Polymer
PMMA	PET
PSF	ABS
PC	ABS
PC	SMA
PC	PET
PUR	ABS

Table 15. Practical benefits of established polyblends.

Miscellaneous		
Base Polymer	Added Polymer	Practical Benefit Added
ABS	PUR	Elastic recovery
PC	SMA	Heat aging resistance
PC	CPTI	Gamma radiation resistance
PET	PMMA	Less shrinkage & warping
PBT	Phenoxy	Filler acceptance

RECENT DEVELOPMENTS

That was the status of established commercial practice. For a survey of the bustling current activity in the field, the most useful sources are the ACS and SPE preprints and *Modern Plastics* magazine and encyclopedia. An 18-month scan from January 1989 to June 1990 gives us a good grasp of where the action is.

It should be noted that many polymer blends require the addition of compatibilizers to give them useful properties. The literature often ignores this or only skims it superficially. This is a more obscure and secretive subject for future study.

Processability improvement is still sometimes reported in terms of increased melt flow, but the variety of more sophisticated measures is impressive (Table 16). Polyolefin extrusion was improved by addition of fluoroelastomers. "Dynamically vulcanized rubber" (EPR, EPDM, ethylene copolymers, chlorinated polyethylene, natural and nitrile rubber) domains are cross-linked in the presence

Table 16. Practical benefits in recent R&D.

Processability		
Base Polymer	Added Polymer	Ref.
PE	Fluoroelastomer	[8]
PP	Fluoroelastomer	[8]
LLDPE	VDF/HFP + PEG	[14]
Dyn. vulc. rubber	PE or PP	[48]
ABS	PC	[31]
PVC	ABS	[29]
PPO	HIPS	[5]
PES	LCP	[27]
Polyarylate	LCP	[27]
PUR	ABS	[46]
PUR	Phenoxy	[11]
HiMW T.P. PI	LoMW T.S. PI	[36,37]

Table 17. Practical benefits in recent R&D.

Higher Modulus		
Base Polymer	Added Polymer	Ref.
PP	LCP	[13]
PVC	Acrylic/glutarimide	[16]
Polyacetal	LCP	[6]
PEEK	LCP	[6]
Polyethersulfone	LCP	[6]
PPS	LCP	[6]
PC	LCP	[6]
PUR	ABS	[46]
PUR	Phenolic	[7]
Amorphous polyamide	LCP	[6]
Polyetherimide	LCP	[6]
Polybenzimidazole	Polybenzothiazole	[23]

of a thermoplastic polyolefin matrix which provides the melt processability. Polyester and polyesteramide liquid crystal polymers exist in the melt as small organized regions instead of tangled random coils, giving easier melt flow, and contributing this when blended into amorphous engineering plastics. ABS and phenoxy resin convert the rubbery polyurethane melt into smooth thermoplastic flow, and low-MW acetylene-terminated polyimide oligomers improve the flow of high-MW "thermoplastic" polyimides, then cross-link and thermoset to give best end-use properties.

Higher Modulus was produced in a number of systems by a variety of mechanisms (Table 17). Liquid crystal polymers, mainly hydroxybenzoate and hydroxynaphthoate copolyesters, first provided improved melt flow, and then *in situ* formed micro-fibrillar reinforcing structures which increased the modulus of the matrix polymers. When PMMA was partly transimidified to the glutarimide copolymer, it served to stiffen PVC. Addition of rigid ABS and phenolic resins to flexible polyurethanes of course increased their stiffness. Polybenzothiazole, long recognized as a rigid rod polymer, is now listed as a liquid crystal polymer and increases modulus in the same way.

Lower Modulus was observed when thermoplastic elastomers were added to LLDPE (Table 18). Presumably the butadiene and ethylene/butylene blocks were

Table 18. Practical benefits in recent R&D [10].

Lower Modulus	
Base Polymer	Added Polymer
LLDPE	SBS
LLDPE	SEBS

reasonably miscible with the amorphous phase of the LLDPE, increasing its volume and therefore its softening effect.

Strength was increased in quite a number of polymer systems, and by quite a variety of different mechanisms (Table 19). When thermoplastic elastomers improved LLDPE, they may have modified its crystallinity, or the styrene domains may have served as reinforcing filler. While HDPE was immiscible with HIPS, styrene-ethylene/butylene diblock copolymer appeared to orient across the interphase, producing synergistic improvement. Polybutene probably modified the crystallization of polypropylene. Ethyl cellulose liquid crystals provided micro-fibrillar reinforcement of dynamically vulcanized elastomers. The stiff molecules and hydrogen-bonding of acrylic/glutarimide copolymer reinforced PVC. Liquid crystal polymers provided micro-fibrillar reinforcement in a number of engineering plastics. ABS and PVC brought their strength to polyurethanes, and interpenetrating polymer networks of rigid styrene and acrylic polymers increased the strength of castor oil polyurethanes.

Ultimate Elongation was increased in a couple of reports (Table 20). Polybutene would plasticize polypropylene. The effect of ethyl cellulose on dynamically vulcanized elastomers was more obscure.

Elastic Recovery of polyolefins was an inverse benefit from the development of dynamically vulcanized elastomers (Table 21). Whereas polyethylene and polypropylene can easily pass their yield points and permit permanent distortion, ad-

Table 19. Practical benefits in recent R&D.

Strength		
Base Polymer	Added Polymer	Ref.
LLDPE	SBS	[10]
LLDPE	SEBS	[10]
HDPE + HIPS	SEB diblock	[4]
PP	Polybutene	[41]
Dyn. vulc. rubber	Ethyl cellulose	[39]
T.P. elastomers	PTFE	[35]
PVC	Acrylic/glutarimide	[16]
Polyacetal	LCP	[6]
PEEK	LCP	[6]
Polyethersulfone	LCP	[6]
PPS	LCP	[6]
PC	LCP	[6]
PUR	PS	[42]
PUR	ABS	[46]
PUR	PVC	[7]
PUR	PMMA	[42]
PUR	PAN	[42]
Amorphous polyamide	LCP	[6]
Polyetherimide	LCP	[6]
Polybenzimidazole	Polybenzothiazole	[23]

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