

# Multiphase Polymer Systems: PVC / Styrene Copolymer Alloys

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## Synopsis

The compatibility of blends of poly(vinyl chloride) (PVC) and styrene copolymers containing maleic anhydride have been investigated by thermal and dynamic and mechanical studies. Unlike homopolymer polystyrene, these styrene/maleic anhydride copolymers, when blended with PVC, provide a degree of miscibility. Complete miscibility or single phase morphology is present only at low concentrations. At higher concentrations, the alloy system separates into two altered phases—neither of which is a pure component. At intermediate alloy compositions, the phases are relatively constant in polymer composition, but the ratio of phases can vary. These altered phases are dispersed at extreme concentrations and are cocontinuous at levels approaching approximately 60 wt % PVC. The intermixed, altered phases show various degrees of miscibility and provide significant adhesion between the two phases. Physical property improvements are attributable to the partial miscibility of the phases.

## INTRODUCTION

Polymer alloys and blends have been the subject of major investigations over the last 10 years and are continuing with an even greater intensity. The semantic interpretation of whether one has a polymer blend or a polymer alloy depends strongly on the phase behavior of the two-component system. The questions of immiscibility vs. miscibility are key to the assessment of preferred compositions. Miscibility is promoted by the thermodynamics of interaction between the blend components, and these concepts have been covered elsewhere.<sup>1</sup>

Although polymer/polymer miscibility is the exception to the general concepts of polymer thermodynamics, specific interactions between active sites on two polymers have been proposed as a driving force for polymer/polymer miscibility. The miscibility of polymer blends containing PVC has been widely studied.<sup>2-5</sup> The list of polymers miscible with PVC in Table I have a common carbonyl functionality which provides an interactive site to promote miscibility with PVC. Intermolecular interactions of the  $\alpha$ -hydrogen of PVC with carbonyl groups in various polyesters promote miscibility in these systems.<sup>6,7</sup> Fava and Chaney<sup>8</sup> have reported a small shift in the dynamic mechanical loss spectrum of blends with PVC and modified styrene/maleic anhydride copolymers. The polarity of the chlorine group is also attributed to interactions promoting miscibility.<sup>9</sup> Polystyrene and polyethylene, having no polar carbonyl functions, are immiscible with PVC and support the specific interaction concept as a driving force for polymer/polymer miscibility. However, styrene/maleic anhydride copolymers contain both carbonyl groups and

TABLE I  
Miscibility between PVC and Carbonyl Containing Polymers

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Thermodynamics predict immiscibility between polymers, e.g.,  
 PVC/polyethylene  
 PVC/polystyrene

Miscibility promoted by specific molecular interactions between PVC and oxygen (carbonyl) containing polymers, e.g.  
 EVA  
 E/VA/C=O  
 E/VA/SO<sub>2</sub>  
 E/N, *N*-dimethyl acrylamide  
 E/ethyl acrylate/C=O  
 E/hexyl acrylate/C=O  
 Chlorinated EVA  
 PMMA  
 PBT and copolymers with *p*-(THF)  
 Aliphatic polyesters, e.g., PCL  
 Butadiene/AN  
 MMA/ $\alpha$ -methyl styrene/AN  
 $\alpha$ -Methyl styrene/methacrylonitrile

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the electron withdrawing oxygen in the five-membered ring. These in-chain functionalities not only increase the heat resistance of styrene/maleic anhydride copolymers vs. polystyrene, but are responsible for interactions with PVC that promote partial miscibility.

Polar carbonyl containing copolymers of polystyrene are available from Arco Chemical as DYLARK<sup>®</sup> resins. DYLARK resins are random, nonalternating, high molecular weight copolymers of styrene (S) and maleic anhydride (MA). These S/MA copolymers have heat resistances which increase with the percentage MA content. Commercial grades include compositions with a range of heat resistance and toughness. The inclusion of the polar MA functionality not only increases key properties such as heat resistance but also provides an

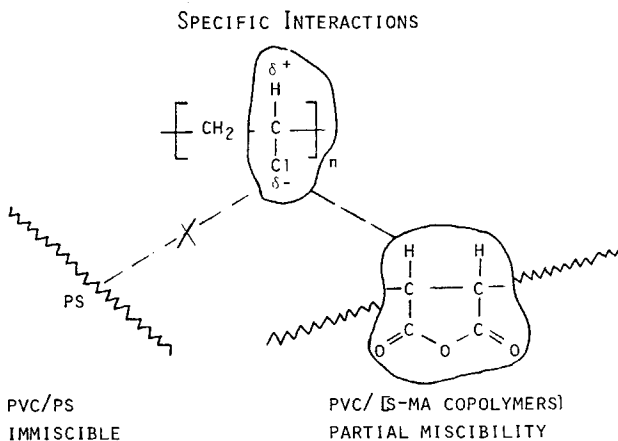


Fig. 1. Specific interactions between S/MA copolymers and PVC.

interactive site to promote miscibility with vinyl polymers which is not accessible to homopolystyrene/PVC alloys.<sup>10</sup> The specific interactions promoting miscibility are graphically depicted in Figure 1 and will be the subject of this paper.

## RESULTS

### Miscibility

DYLARK 332 copolymer (12.5% MA) was melt-compounded with a stabilized PVC compound using a Haake Rheocord equipped with a conical, counterrotating twin screw extruder. Compositions ranging from pure PVC compound to pure DYLARK 332 copolymer were prepared for thermodynamic miscibility determinations by differential scanning calorimetry (DSC). The DSC glass transition temperatures ( $T_g$ ) listed in Table II establish a partially miscible system for DYLARK/PVC alloys by virtue of the consistent displacement from the pure component  $T_g$ 's. This partially miscible system is characterized by two separate  $T_g$ 's at intermediate compositions which are significantly shifted from the  $T_g$  of either pure PVC or pure DYLARK 332 copolymer. These two separate phases exist in these alloys, but neither of the two phases are pure components. The lower  $T_g$  phase is comprised predominately of PVC which is saturated to the limit of solubility or miscibility with the DYLARK copolymer component. Likewise the higher  $T_g$  phase is DYLARK copolymer which is saturated with PVC. The limits of miscibilities (i.e., DYLARK copolymer in PVC vs. PVC in DYLARK copolymer) are not equal or symmetrical. PVC has a greater tendency to accept DYLARK copolymer than the contrary as can be seen from the singular  $T_g$ 's for alloys containing less than 20 wt % DYLARK copolymer. At  $\geq 20\%$

TABLE II  
Partial Miscibility in PVC/(S/MA) Alloy by Thermal (DSC) Methods

Overall alloy composition (% PVC/% S/MA)	PVC control <sup>a</sup>	Glass transition $T_g$ (°C)		S/MA control <sup>b</sup>
		Alloy		
		PVC-rich phase	S/MA-rich phase	
100/0	81.5			
90/10		84.5	—	
80/20		85.5	117	
60/40		86.5	124	
40/60		86.5	125.5	
20/80		86.5	128	
10/90		86.5	129	
0/100				132
40/60% S/MA (8% MA)	81.5	86.5	115.5	120
40/60% S/MA (12% MA)	81.5	86.5	125.5	132
40/60% S/MA (17% MA)	81.5	85.0	133.5	140

<sup>a</sup>PVC compound formulation: 100 parts PVC resin (0.98 IV,  $T_g = 88.5^\circ\text{C}$ ); 2 parts mercaptide tin stabilizer; 1.5 parts calcium stearate. ( $T_g = 84.0$  dry blend;  $T_g = 81.5$  extruded)

<sup>b</sup>DYLARK 332 copolymer.

DYLARK copolymer contents, PVC becomes saturated with DYLARK copolymer, and the alloy splits into two phases. Progressively increasing the wt % DYLARK copolymer in the overall alloy composition does not significantly alter the composition of each saturated phase—only the relative quantity of each phase present in the total alloy mass. This concept of the phase structure in partially miscible alloys of DYLARK/PVC is verified by estimating the phase compositions from the shifted  $T_g$  values, using the following adaptation of the simple Fox relationship<sup>11</sup> for  $T_g$  of random copolymers:

$$\text{phase 1 = PVC-rich phase: } W_{1,\text{PVC}} = \frac{T_{\text{PVC}}}{T_{\text{S/MA}} - T_{\text{PVC}}} \left( \frac{T_{\text{S/MA}}}{T_1} - 1 \right)$$

$$\text{phase 2 = S/MA-rich phase: } W_{2,\text{PVC}} = \frac{T_{\text{PVC}}}{T_{\text{S/MA}} - T_{\text{PVC}}} \left( \frac{T_{\text{S/MA}}}{T_2} - 1 \right)$$

where  $T_{\text{PVC}}$ ,  $T_{\text{SMA}}$ ,  $T_1$ ,  $T_2$  = glass transition temperatures for PVC, S/MA, phase 1, and phase 2, respectively,  $W_{1,\text{PVC}}$  = weight fraction of PVC in phase 1 which is the lower  $T_g$  phase or PVC rich phase, and  $W_{2,\text{PVC}}$  = weight fraction of PVC in phase 2 which is the higher  $T_g$  phase or DYLARK-copolymer-rich phase. Relative contents of each phase in the overall alloy can be calculated using the following equations derived by applying constraints of mass balance and knowing the composition of phases ( $W_{1,\text{PVC}}$  and  $W_{2,\text{PVC}}$ ) and overall weight fraction of PVC in the alloy ( $W_{\text{PVC}}$ ):

$$X_1 = \text{phase 1 content} = (W_{\text{PVC}} - W_{2,\text{PVC}})/(W_{1,\text{PVC}} - W_{2,\text{PVC}})$$

$$X_2 = \text{phase 2 content} = 1 - X_1$$

The results of this phase analysis are shown in Figure 2. Approximately 12% DYLARK copolymer can be added to PVC before phase separation occurs compared with approximately 6% PVC into DYLARK copolymer. Between 6% PVC and 88% of PVC in alloys, the relative amounts of the two phases switches from a majority phase 2 (high DYLARK copolymer content, high  $T_g$ ) to a majority of phase 1 (high PVC content, low  $T_g$ ). At these intermediate PVC contents, the physical and thermal properties would be expected to be sigmoidally dependent on overall alloy composition as predicted by a rule of mixtures relationships based on the relative contents and properties of phases 1 and 2.

The partial miscibility between PVC and S/MA copolymers (DYLARK copolymers) is not dependent on the % MA levels. In Table II, the partial miscibilities of 40% PVC/60% S/MA copolymers by DSC are similar from 8% MA to 17% MA. The following extents of partial miscibility between PVC and S/MA copolymers were calculated from the shifts in DSC glass transitions and confirm the independence of PVC miscibility within the commercial

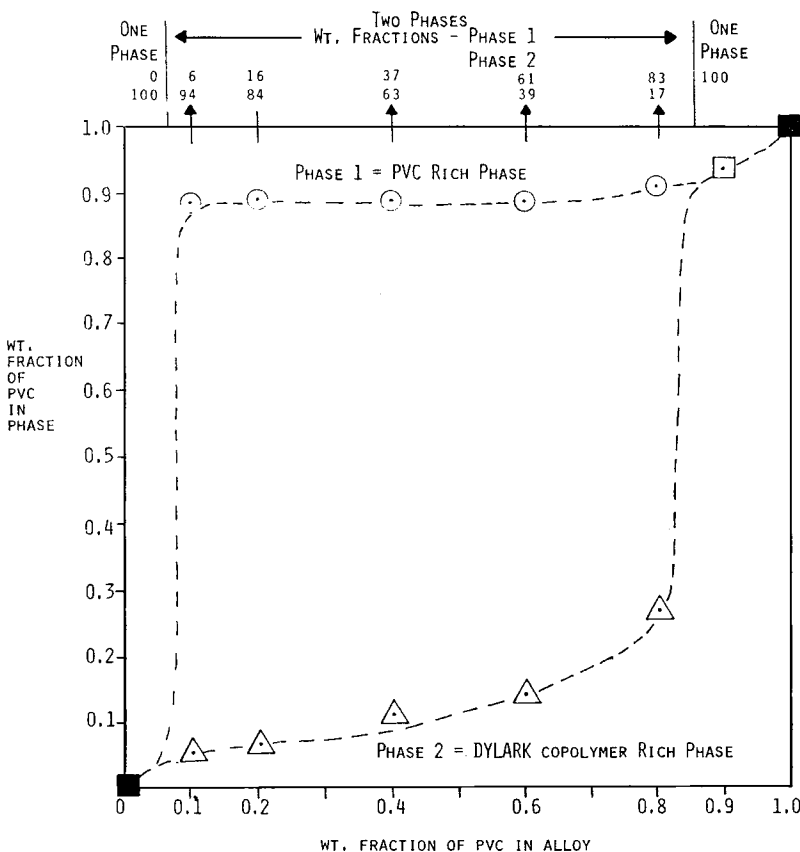


Fig. 2. Partial miscibility in (S/MA)/PVC alloys.

DYLARK copolymer range of % MA contents:

Wt % PVC in Phases for 40% PVC Alloys/60% S/MA Copolymers

	Phase 1	Phase 2
S/MA (8% MA)	85.8	10.7
S/MA (12% MA)	88.8	11.5
S/MA (17% MA)	93.1	9.7

Partial miscibility in DYLARK/PVC alloys is also evident by dynamic mechanical analyses (DMA) in Table III. The DMA transitions shift in exactly the same fashion as the DSC transitions. Thus, partial miscibility is apparent by both thermal and mechanical methods. Partial miscibility in the two phases of DYLARK/PVC alloys provides for a chemical similarity which promotes significant adhesion between phases. From a practical viewpoint, this adhesion between phases accounts for the significant macromechanical properties observed for these alloy systems.

Spectroscopic techniques have been used to document not only the existence of miscibility between PVC and polar styrenic copolymers but

TABLE III  
 Partial Miscibility in PVC/(S/MA) Alloy by Mechanical (DMA) Methods

Overall Alloy Composition [% PVC/% S/MA (12.5% MA)]	DMA Transition (°C)			
	PVC Control <sup>a</sup>	Alloy		S/MA control
		PVC-rich phase	S/MA-rich phase	
100/0	96			
90/10		99	—	
80/20		100	125	
60/40		105	126	
40/60		108	135	
20/80		108.8	144	
10/90		—	143	
0/100				144

<sup>a</sup>PVC compound formulation: 100 parts PVC resin (0.98 IV); 2 parts mercaptide tin stabilizer; 1.5 parts calcium stearate.

additionally the molecular origin or driving force for miscibility. Fourier transform infrared (FTIR) spectra of DYLARK/PVC alloys indicates a shifting of the absorption frequencies for the  $\alpha$ -hydrogen of PVC and the anhydride bridge structure of the maleic anhydride functionality in DYLARK copolymers. The frequency shifts or energy state changes for these two structures are the result of specific molecular interactions which promote miscibility. No frequency shifts or interactions occurred for molecular structures other than the two structures described above. The specific molecular interactions promoting miscibility are depicted in Figure 1 and were experimentally observed to be strongest (i.e., largest frequency shifts) at intermediate DYLARK/PVC alloy compositions.

Miscibility between S/MA copolymers and other vinyl polymers containing chlorine substituents (i.e., chlorinated polyethylene, chlorinated PVC, and vinylidene chloride copolymers) will be reported later. The miscibility between S/MA copolymers and these chlorine-containing polymers is consistent with the structural composition of these vinyl polymers.

### THERMAL / MECHANICAL PROPERTIES—NONIMPACT MODIFIED

The DYLARK/PVC alloys analyzed for miscibility in Tables II and III were injection-molded into ASTM test specimens for thermal and mechanical property testing as non-impact-modified alloys. The resulting thermal/mechanical properties in Table IV demonstrate the favorable property balance effected by the partial miscibility between DYLARK/PVC and the significant macroadhesion between alloy phases.

#### *Heat Resistance*

Heat resistance, as measured by deflection temperature under load (DTUL) at 264 psi, projects a practical temperature exposure limit to avoid warpage and dimensional distortion for molded articles in end-use applications. The

TABLE IV  
Thermal/Mechanical Properties of DYLARK/PVC Alloys

	DTUL (°F) 1/8 in. thick		Flexural properties		Tensile properties		
	As molded (°F)	Annealed <sup>a</sup> (°F)	Modulus (X 10 <sup>-5</sup> psi)	Strength (psi)	Modulus (X 10 <sup>-5</sup> psi)	Strength (psi)	Elongation (%)
Alloy composition							
%PVC/%DYLARK							
copolymer (12% MA)							
100/0	157	162	4.50	13,400	3.12	7890	27
90/10	159	166	4.83	14,600	3.25	8250	24
80/20	160	167	4.83	15,000	3.27	8750	16
60/40	175	197	5.22	17,000	3.24	9680	45
40/60	200	231	5.07	15,500	3.26	9290	4
20/80	214	238	5.43	14,000	3.34	7600	3
10/90	212	236	5.34	13,200	3.39	6870	2
0/100	223	241	5.35	16,400	3.31	6960	2
40/60% DYLARK 232	188	223	5.22	14,900	3.19	9130	4
copolymer (8% MA)							
40/60% DYLARK 332	200	231	5.22	14,900	3.19	9130	4
copolymer (12% MA)							
40/60% DYLARK 290	206	237	5.41	15,300	3.29	8880	4
copolymer (17% MA)							

<sup>a</sup>Annealed for 48 h at 90°C.

elevated heat resistance inherent in the high heat, S/MA styrenic copolymers can be used as a heat distortion additive for PVC compounds to provide a continuous tailoring of alloy heat resistance (see Fig. 3). The unannealed DTUL of PVC compounds monotonically increases from 157°F to the 170–200°F range for 40–60% S/MA styrenic copolymer contents. At a 157°F DTUL, PVC compounds are not capable of withstanding temperature exposures experienced in electrical/electronic housing applications but can be upgraded by alloying with S/MA copolymers into broader end-use markets. At 40% styrenic copolymer levels with 170°F DTUL, DYLARK/PVC alloys can be classified as low end engineering thermoplastics. At 60% styrenic copolymer contents and 200 + °F DTUL, DYLARK/PVC alloys approach hot water application requirements. Annealed DTUL yield consistently inflated ratings compared to unannealed or as molded ratings. These inflated annealed DTUL values are commonly cited in commercial literature for heat resistance comparisons. However, the unannealed DTUL are a more practical projection for the limit of end-use temperature exposure since molded articles are seldom annealed before being installed directly into end use service.

The sigmoidal shape of the DTUL vs. alloy composition graph in Figure 3 reflects the miscibility/phase relationships discussed in the previous section. At either extreme in alloy composition the heat resistance changes are gradual as would be expected for miscible, one-phase systems. At intermediate alloy compositions, the relative amounts of these two separate phases in these DYLARK/PVC alloys yield the steep sigmoidal dependence expected from a rule of mixture relationship. The commercial significance of this phase separation is evident by comparing the +3°F increase in DTUL for 20% DYLARK copolymer addition into PVC vs. the +18°F increase at 40%

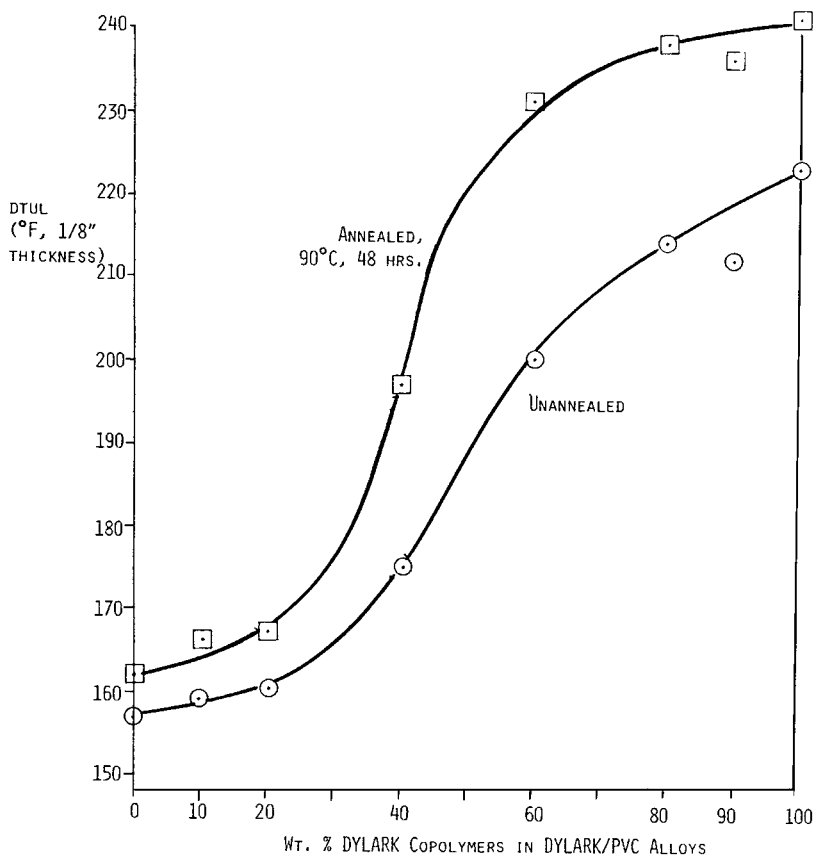


Fig. 3. Heat resistance of PVC enhanced by S/MA copolymers.

DYLARK copolymer contents. At 40% DYLARK copolymer levels, the high  $T_g$  phase has separated to provide an *in situ* reinforcement to thermal exposure. This thermal reinforcement effect is apparent in DTUL comparisons but is even more apparent in thermal aging tests discussed later. DTUL enhancements here are real but underestimate the true potential of DYLARK/PVC alloys to withstand high temperature exposures.

#### Mechanical Properties

The modulus or stiffness of DYLARK copolymer and PVC are maintained in alloys at all proportions (see Table IV). Mechanical strengths by both flexural and tensile testing are preserved in all alloys as a testimony of the significant macroadhesion existing between phases. This adhesion between phases is most apparent in tensile strength or flexural strength testing where the alloy tensile strengths can actually exceed the tensile strength of flexural strength of either pure component. Ductility, as indicated by the tensile elongation to fail, is dictated by the ductility of the major phase. Alloys having the PVC rich phase as the major volume phase are similar in ductility to PVC and vice-versa for alloys having DYLARK copolymer as the major volume phase. DYLARK copolymer resins with improved ductility would



improve the ductility or impact strength in DYLARK/PVC alloys. Impact modified DYLARK/PVC alloys are addressed separately in this report.

## OPTIMIZATION OF PVC BASE RESIN FOR ALLOYING

### *Heat Resistance*

PVC resins have been used in diverse commercial applications due to the extensive compounding technology which has been developed over decades of practical experience in modifying processing/property profiles for end use applications. PVC compound properties are tailored by low level additions of effective additives (e.g., stabilizers, lubricants, plasticizers, processing aids, flow modifiers, etc.) to a particular PVC base resin. However, a wide range of PVC base resins are commercially available to PVC compounds and are rated according to the molecular weight [via inherent viscosity (IV)] among other variables such as particle size and porosity. Molecular weight or IV of the PVC base resin is the predominant PVC resin specification which establishes the melt viscosity and physical property basis from which PVC compound properties can be tailored. PVC resins vary in IV from 0.53 to 1.1 with the following generalized classifications according to end use:

IV of PVC resin	Compound end use
0.53–0.68	Newest generation of injection molding compounds
0.80	Standard injection molding grades for pipe fittings
0.92–0.98	Extrusion compounds for film/profiles
1.0–1.1	Pipe and calendered film

PVC compounds varying in IV of the base PVC resin and DYLARK/PVC alloys based on these PVC compounds were extruded into pellets and injection-molded into ASTM test specimens. Heat resistances (DTUL) of both PVC compounds and DYLARK/PVC alloys in Figure 4 are clearly dependent on the IV of the PVC base resin. The plateau or asymptotic DTUL for PVC compounds is reached at  $IV \geq 0.80$ . The low molecular weight, low IV, or high flow PVC resins proposed as the new generation of PVC resins for injection molding may enhance flow properties but sacrifice heat resistance. More importantly, this DTUL sacrifice for low IV PVC resins is also seen in non-impact-modified alloys of DYLARK 350/PVC (see Fig. 4). Higher IV resins ( $\geq 0.80$ ) are preferred to enhance heat resistance in DYLARK/PVC alloys.

### *Impact Strength*

Toughness or ductility can be rated by Gardner falling weight impact strength (GFWI) or by Notched Izod (NI). GFWI is a two-dimensional, in-plane penetration test which simulates and quantifies the mechanical energy tolerated by molded articles in end use applications. Notched Izod is a one-dimensional test which indicates the ability of a material to dissipate the abnormally high stress concentrations resulting from sharp angled designs in molded articles. In Figure 5, the impact strengths of non-impact modified DYLARK/PVC alloys (0 phr of MBS modifier, curve with circles) are shown

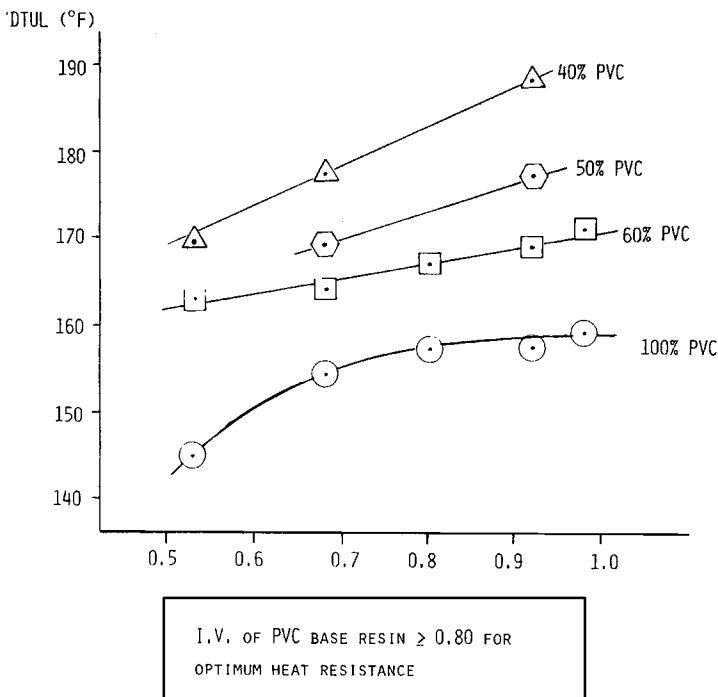


Fig. 4. Heat resistance for (S/MA)/PVC alloys optimized for PVC base resin (PVC/DYLARK 350 alloys). IV of PVC base resin  $\geq 0.80$  for optimum heat resistance.

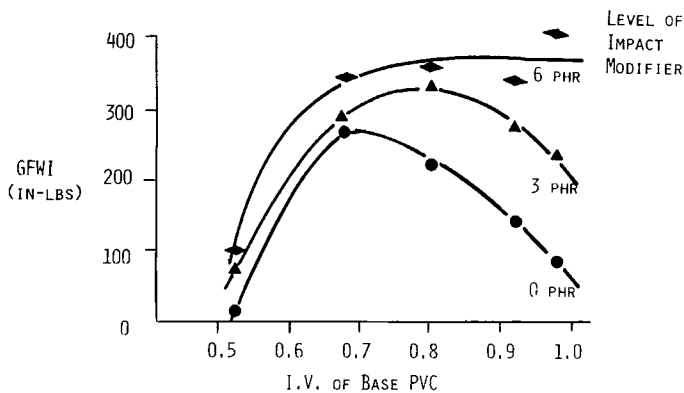


Fig. 5. GFWI of (S/MA)/PVC alloys optimized for PVC base resin; impact modification of 60% nonimpact PVC compound/40% styrene copolymer alloy. Falling wt  $> 400$  in. lb achieved.

using various IV PVC resins. GFWIs are optimal for intermediate IV PVC resins but with the addition of 3 phr ( $\Delta$ ) and 6 phr ( $\diamond$ ) of impact modifier, the GFWI impact strengths of  $> 400$  in. lbs are produced for higher IV based PVC alloys. Impact strength is sacrificed for alloys based on the lowest IV PVC resins at all levels of modifier which represents a significant disadvantage for this PVC base resin in commercial alloys. The addition of 3 and 6 phr of an efficient PVC impact modifier (Acryloid KM653 from Rohm and Haas) systematically increases the Notched Izod impact strength of DYLARK/PVC

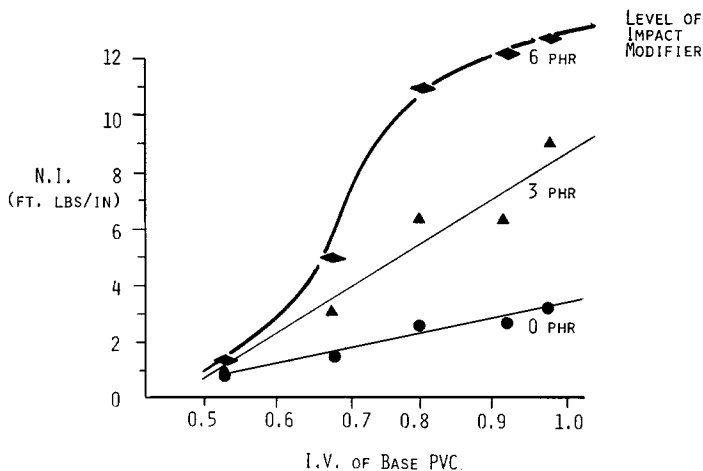


Fig. 6. Notched Izod impact strength of (S/MA)/PVC alloys optimized for PVC base resin; impact modification of 60% nonimpact PVC compound/40% styrene copolymer alloy. Notched Izod > 12 ft lb/in. and falling weight impact 400 + in. lb are achieved. There are better balanced impact properties for moderate MW of PVC resin.

alloys as shown in Figure 6. Exceptional Notched Izods of 12 ft lb/in. are produced only for alloys based on PVC resins having  $\geq 0.80$  IV. At the customary 6 phr loadings of MBS modifiers, only the PVC resins having  $IV \geq 0.80$  in DYLARK/PVC alloys yield exceptionally high NI of 12 ft lb/in. combined with asymptotic GFWI of 400 in. lb. However, no significant improvements in impact strength are realized using PVC resins with an IV greater than the 0.80 IV optimum and can only contribute to high melt viscosities and sacrifice processibility. Optimization of impact strength with respect to IV of the PVC pure resin is also clearly defined for the case of lower IV PVC base resins. The 0.68 IV PVC resin in DYLARK/PVC alloys modified with 6 phr of MBS additive yields the same GFWI as the corresponding alloy with 0.80 IV PVC resin, but the NI drops to 5 vs. the 12 ft lb/in. optimum value. This NI of 5 ft lb/in. for the DYLARK/PVC alloy based on 0.68 IV PVC resin could possibly be enhanced by adding more than the customary 6 phr loading of MBS impact modifier. However, this alloy would still have a depressed DTUL (by virtue of the 0.68 IV PVC base resin) as well as higher cost (due to the increased loading of the expensive MBS modifier). The additional MBS modifier would also mitigate some of the melt viscosity depression projected for the use of an 0.68 IV PVC resin. Thus, 0.80 PVC resin is indeed the optimal PVC resin for DYLARK/PVC alloys based on impact strength (Figs. 5 and 6) and retention of heat resistance (Fig. 4).

#### DYLARK / PVC ALLOYS VS. COMPETITIVE ENGINEERING THERMOPLASTIC PRODUCTS

The mechanical/thermal properties of the optimum DYLARK/PVC alloy formulation is contrasted in Table V with competitive, FR engineering thermoplastics and commercial PVC alloys. Practical heat resistances (DTUL, 1/8 in. unannealed) of DYLARK/PVC alloys and the low end engineering ther-

TABLE V  
Thermal/Mechanical Properties: (S/MA)/PVC Alloy vs. Competitive FR Thermoplastics<sup>a</sup>

	Styrene copolymer/ PVC alloy	Modified PPO	FR HIPS	FR ABS	ABS/ PVC alloy
Specific gravity	1.21	1.08	1.16	1.22	1.21
Notched Izod (ft lb/in.)	8.8	3.1	1.7	3.4	14.1
Falling weight impact strength (in. lb)	480 +	240	40	280	480 +
Deflection temperature Under load 264 psi (°F)	167	170	167	170	137
Flamability (UL94 at 0.125 in.)	V-0	V-0	V-0	V-0	V-0
Flexural modulus ( $\times 10^{-5}$ psi)	3.88	4.04	3.21	3.28	3.21
Flexural strength (psi)	6800	7400	4900	6400	5900
Elongation to break (%)	63	64	46	45	73

<sup>a</sup>Styrene copolymer/PVC alloys mechanical property profiles of typical as-molded specimens. 140°F mold temperature, unannealed test specimens. Miscibility in styrene copolymer/PVC alloys yields engineering thermoplastic property profiles.

moplastics are virtually identical. DYLARK/PVC alloys have a definite heat resistance advantage over other commercial PVC alloys to the extent that DYLARK/PVC alloys are not to be classified as another PVC alloy but rather a low end engineering thermoplastic.

Impact strength of the DYLARK/PVC alloy is considerably higher than any of the other commercial FR engineering thermoplastic products. GFWI of 480 + in. lb and NI of 8.8 ft lb/in. place that DYLARK/PVC alloy into a separate class of ductility beyond that attained with even more expensive engineering thermoplastics such as FR ABS and Noryl N190. The exceptional ductility of DYLARK/PVC alloy is also reflected in the 63% elongation to break. Stiffness and strength of the DYLARK/PVC alloy is much higher than FR ABS or FR HIPS and even approaches the mechanical properties of Noryl N190. This property comparison of DYLARK/PVC alloy with competitive FR thermoplastics in Table V ranks DYLARK/PVC alloys above the cost/performance niche of a PVC alloy and into the category of an FR engineering thermoplastic. By comparison with the other FR engineering thermoplastics, DYLARK/PVC alloy offers exceptional toughness with equivalent heat resistance, stiffness, strength, and specific gravity.

The ability of DYLARK/PVC alloys to perform well in industrial applications is further illustrated in Table VI by the retention of impact strength over a broad processing window. Industrial processing can involve high speed injection rates through small gates creating high shear rates or shear stresses. The impact strength of DYLARK/PVC alloys is unaffected by high shear rate processing in direct opposition to the shear sensitivity evident in competitive products. Thus, the DYLARK/PVC alloy provides not only an exceptional property profile relative to competitive FR thermoplastics, but also a stable processing profile over a wide latitude of processing conditions.

TABLE VI  
Sensitivity of Impact Strength to High Shear Processing<sup>a</sup>

Material	Falling weight impact strength (in. lb)		
	Injection speed	1 cm/s slow	5 cm/s fast
Styrene copolymer/PVC alloy		480 +	480 +
Modified PPO		240	71
FR ABS		280	258
FR HIPS		40	24

increasing shear rate  
 (thin section, small gates,  
 high injection speeds)

<sup>a</sup>Impact strength of styrene copolymer/PVC retained over a wide range of shear rates or processing conditions.

Heat resistance of DYLARK/PVC alloy has been elevated beyond the heat distortion limitations of PVC compounds into the range of heat resistance required by low end engineering thermoplastics. Heat resistance of commercial compounds are traditionally rated by DTUL and often without specifying the DTUL specimen thickness, conditioning history, or fabrication procedures. Heat resistance or DTUL using 1/8 in. thick specimens are shown in Figure 7 to monotonically increase with mold cavity temperature or by high temperature annealing of molded in stresses. Fabricating specimens at higher mold temperatures is equivalent to a post-annealing procedure in that either

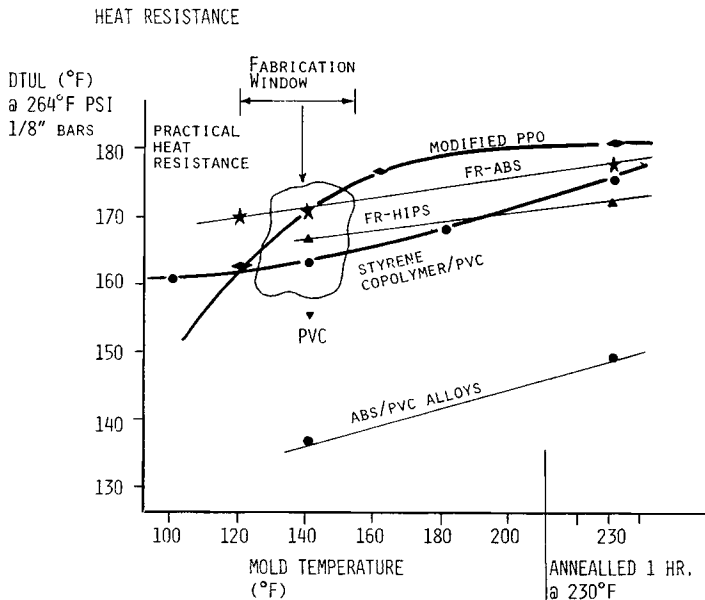
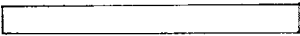
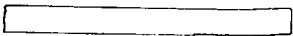

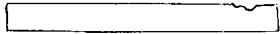
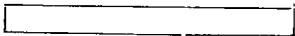
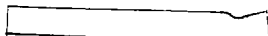


Fig. 7. Practical heat resistance (DTUL) of (S/MA)/PVC alloys equivalent to competitive FR thermoplastics. Practical heat resistance in as-molded end use articles is similar for styrene copolymer/PVC alloys, modified PPO, FR-ABS, and FR-HIPS.

procedure will artificially inflate the DTUL by reducing the molded-in stresses created during fabrication. In practical molding of end-use articles, these molded-in stresses are a natural consequence of industrial fabrication and are not relieved by post-fabrication annealing. Thus, the heat resistance or DTUL measured using  $\leq 1/8$  in. thick specimens fabricated at customary mold temperatures of  $140^{\circ}\text{F}$  is a more realistic estimate of the DTUL attained in practice. Although annealed DTUL values are easily reproduced irrespective of molding or fabrication procedures, these annealed DTUL values reflect the theoretical upper limit in heat resistance for a material rather than the practical limits required by end use applications. Thus, the relative ranking of annealed DTUL for the competitive materials from Figure 7 or by compiling similar values from commercial property sheets is often misleading and certainly is not indicative of the actual heat resistance performance of materials. More importantly, the DTUL of DYLARK/PVC alloys is virtually identical to competitive FR thermoplastics when compared using realistic,  $1/8$  in. unannealed DTUL testing procedures.

The plastics industry has traditionally used DTUL as the primary measure of heat resistance capability of thermoplastics. Even if the proceeding precautions are exercised in the DTUL specimen preparation and testing procedures, heat resistance can be grossly underestimated for two phase alloys using only the DTUL specification. DTUL is the temperature at which the modulus of a thermoplastic decreases to about  $1.1 \times 10^{-5}$  psi in a three-point bend test and presumably indicates the service temperature at which molded articles would

## HEAT RESISTANCE/DIMENSIONAL STABILITY

MATERIAL	RELATIVE SHRINKAGE OF 1/8" X 5" X 1/2" BAR AFTER 1 HR. EXPOSURE TO 230°F.	DSC GLASS TRANSITION ( $T_g$ , °C)	
STYRENE COPOLYMER/PVC ALLOY		85	122
FR-ABS - CYCOLAC KJW			103
FR-HIPS - STYRON 6075			102.5
MODIFIED PPO - N190			105
ABS/PVC - ETHYL 2160			74
MODIFIED PPO - PX1005			101

PARTIAL MISCIBILITY IN S/MA /PVC ALLOY YIELDS:  
SECOND PHASE (HIGH  $T_g$ ) EXTENDING PRACTICAL SERVICE  
TEMPERATURE RANGE  
DIMENSIONAL STABILITY DURING END USE THERMAL CYCLING  
PRACTICAL HEAT RESISTANCE  
DTUL ( $\leq 1/8$ " UNANNEALED) IS REASONABLE FIRST ESTIMATE  
DTUL UNDERESTIMATES MULTIPHASE ALLOY POTENTIAL

Fig. 8. Dimensional stability of (S/MA)/PVC alloys superior to competitive FR thermoplastics.

evidence extensive warpage and dimensional distortion. Plastic materials do not necessarily distort when the modulus reaches the magical  $1.15 \times 10^{-5}$  psi value, but rather this definition of the distortion temperature provides a standard performance point for testing purposes. DYLARK/PVC alloys, having two high temperature phases ( $T_g = 85^\circ\text{C}$  and  $T_g = 122^\circ\text{C}$ ), will produce an initial drop in modulus at temperatures approaching the  $85^\circ\text{C}$  glass transition of the lower  $T_g$  phase. However, the higher  $122^\circ\text{C}$   $T_g$  phase remains as an *in situ* reinforcement against extensive dimensional warpage. This effect is clearly evident for the thermal aging studies in Figure 8. Only the DYLARK/PVC alloys maintained dimensional stability after aging at  $110^\circ\text{C}$ , indicating a practical heat distortion capability exceeding that of competitive FR thermoplastics and also exceeding that predicted by conventional DTUL measurements. Thus, DYLARK/PVC alloys are superior to competitive FR thermoplastics both in practical heat distortion capability and in impact strengths. DYLARK/PVC alloys offer a definite property advantage in FR engineering applications.

### FLAMMABILITY

The inherent flame retardancy of PVC has been key to its use in the various injection molding applications such as construction and electrical/electronics.

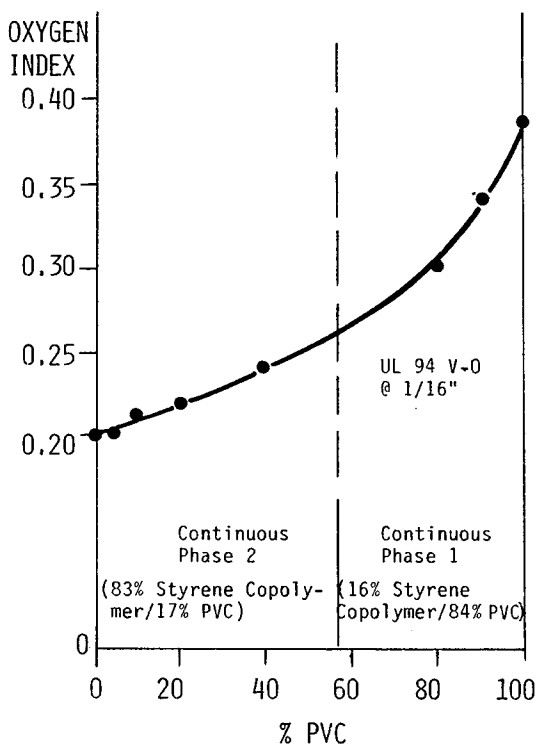


Fig. 9. Fire retardancy of (S/MA)/PVC alloys. The excellent fire resistance of PVC is maintained with 30% additions.

The base PVC resins are 56 wt % chlorine, a very effective flame suppressant. Typical PVC compounds have an oxygen index of 38 and are V-O rated by UL Standard 94. Even when incorporating DYLARK copolymers, impact modifiers, and other additives, our in-house testing has shown that the 40% DYLARK copolymer containing alloys meet the criterion for UL Standard 94 for V-O at 0.099 in. thicknesses and for 5V at 0.125 in. thicknesses. These

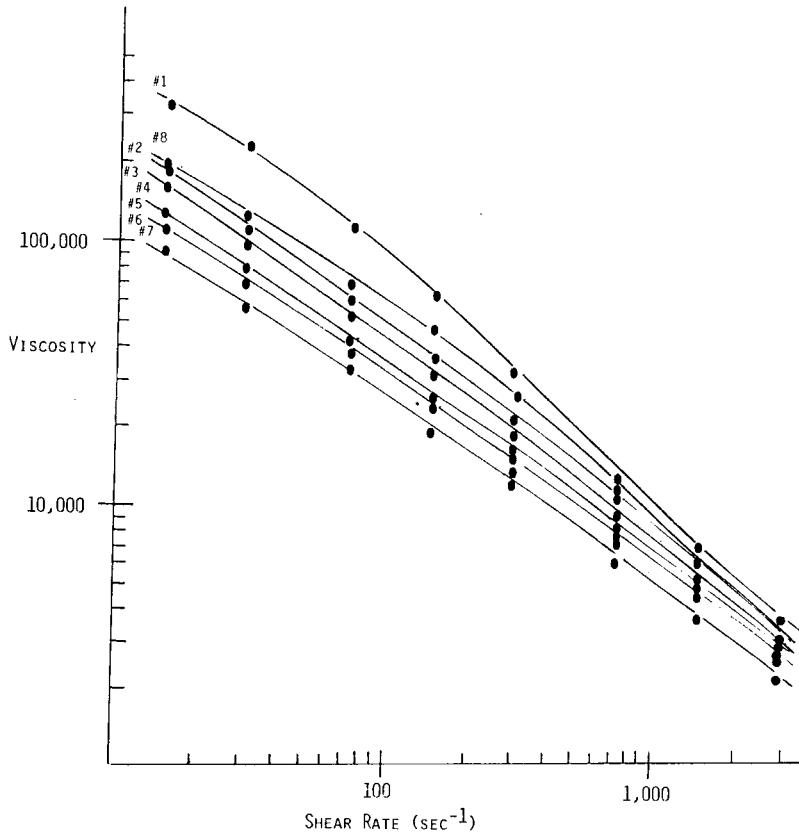


Fig. 10. Melt viscosity of DYLARK/PVC alloys.

Curve	Temp (°C)	Composition	
		% DYLARK	% PVC
#1	190	0	100
#2	190	30	70
#3	190	40	60
#4	190	50	50
#5	190	60	40
#6	190	70	30
#7	190	100	0
#8	200	0	100



results indicate that DYLARK/PVC alloys will meet many of the industrial requirements for business machine housings as well as electrical/electronics components. Flame retardency can be tailored by the relative content of PVC as indicated by the oxygen index ratings in Figure 9 for DYLARK/PVC alloys. Oxygen indices of 25 are common for V-O ratings at 1/8 in. thicknesses with an OI of 28 required for a V-O rating at 1/16 in. thicknesses.

### MELT VISCOSITY

Capillary rheology of DYLARK 700 copolymer alloyed with an impact modified, commercial PVC compound are shown in Figure 10 (curves 2-6) for alloy compositions ranging from pure PVC compound to pure DYLARK 700 copolymer. At 190°C the high melt viscosity of this commercial PVC compound based on 0.92 IV PVC (curve 1) is systematically reduced by alloying with the low melt viscosity DYLARK 700 copolymer. The melt viscosity of the commercial, impact-modified PVC compound at 200°C is shown by curve 8 in Figure 10 to reference the magnitude of viscosity depression of PVC by DYLARK copolymer. At 30% DYLARK 700 copolymer contents, the melt viscosity depression of PVC is equivalent to a 20°C increase in melt temperature for the pure PVC compound. Since PVC cannot be commercially processed at 210°C, the DYLARK/PVC alloy offers melt viscosities which are lower than can be achieved by PVC compounds solely using temperature to depress viscosity.

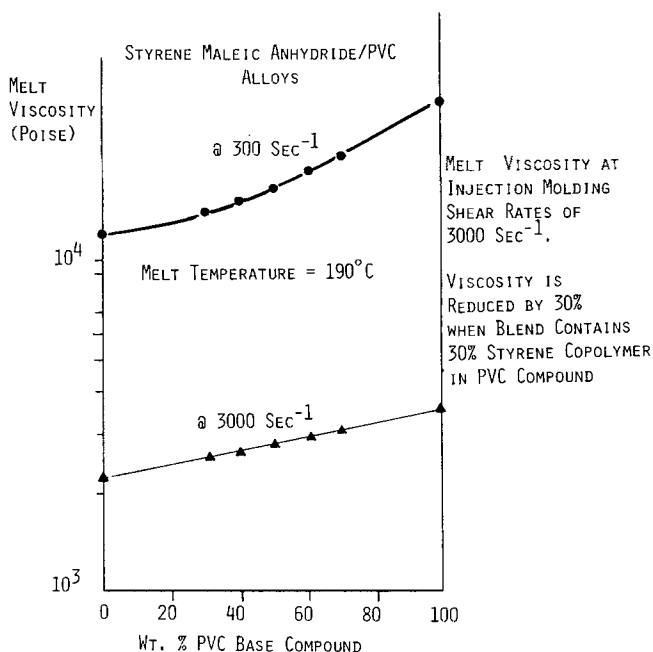


Fig. 11. Melt viscosity reductions; melt viscosity at injection molding shear rates of 3000 s<sup>-1</sup>. Viscosity is reduced by 30% when blend contains 30% styrene copolymer in PVC compound.

The extent of melt viscosity depression depends on the choice of the IV of the base PVC compound, the PVC compound formulation, the % MA in the S/MA copolymer, and the impact modification system for the S/MA copolymer. Since the actual capillary rheology curves in Figure 10 are nearly parallel, melt viscosity depressions can be adequately represented by comparing viscosities at two shear rates:  $3000\text{ s}^{-1}$ , typical of injection molding, and  $300\text{ s}^{-1}$ , typical of extrusion processing. The viscosity data in Figure 10 are graphically represented in Figure 11 to demonstrate the melt viscosity depression of the commercial, impact-modified PVC compound by DYLARK 700 copolymer.

### CONCLUSIONS

S/MA copolymers as well as other polar styrenic copolymers are partially miscible with PVC. Partial miscibility extends mutually to approximately 10 wt % of either component. At higher concentrations, the system separates into a two-phase system with neither phase being a pure component. The two phases differ only in the relative contents of each pure component and are sufficiently chemically similar to exhibit significant macroscopic adhesion between phases. This adhesion between phases accounts for the favorable balance in mechanical properties attained.

The partial miscibility between PVC and these S/MA copolymers provides for a family of heat resistant, fire-retardant alloys spanning the heat resistance range of low end engineering thermoplastics. At approximately 60 wt % PVC, the fire retardancy of PVC is maintained in the alloy, however, the heat resistance is  $10^{\circ}\text{F}$  improved by ASTM tests such as DTUL but is actually superior in practical dimensional stability testing at elevated temperatures.

S/MA copolymers systematically decrease the melt viscosity of PVC to promote flow and processibility in alloy compositions. This flow promotion is accompanied by an increase in heat resistance rather than the usual heat sacrifice from traditional flow additives for PVC.

The adhesion between phases is particularly evident in the exceptional impact strength derived from alloys of S/MA copolymer with PVC. Tough alloys have been produced with GFWI in excess of 480 in. lb and Notched Izod of 12 ft lb/in. These impact strengths are superior to any of the competitive engineering thermoplastics as well as injection molding grades of PVC. Impact strengths of this magnitude for the partially miscible alloys of S/MA copolymers and PVC are insensitive to the processing conditions in contrast to the loss of toughness exhibited by competitive materials at extreme shear rate processing conditions.

The adhesion between phases also is reflected in the retention of the mechanical property profiles of each component in the alloys of S/MA copolymers and PVC. The mechanical property profiles of these alloys are more than competitive with engineering thermoplastics and injection-moldable PVC compounds.

The miscibility between S/MA copolymers and PVC is not as extensive as the total miscibility in all proportions observed in polystyrene/polyphenylene oxide systems. However, this partial miscibility leading to intermixed altered two-phase systems is sufficient to promote the macroscopic adhesion between

these phases to yield an exceptional mechanical property profile. Partially miscible alloys having limited solubilities of components are an important class of new polymer alloys which can provide explanations for the intermolecular interactions which promote total miscibility in polymer systems.

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Received February 14, 1985

Accepted April 5, 1985