

Single Phase Polymer Systems: CPVC / Styrene Copolymer Alloys

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Synopsis

Random copolymers of styrene and maleic anhydride are miscible with chlorinated poly(vinyl chloride) [CPVC] in all blended proportions. Miscibility was evident in a single glass transition temperature investigated by thermal and mechanical studies. This degree of miscibility differs from the partial miscibility obtained with PVC/styrene copolymers reported previously, where single phase morphology was present only at low blend proportions. Tailoring of physical properties such as heat resistance, flammability resistance, and processability are achieved by varying the relative proportions of CPVC and styrenic copolymer in this miscible alloy system.

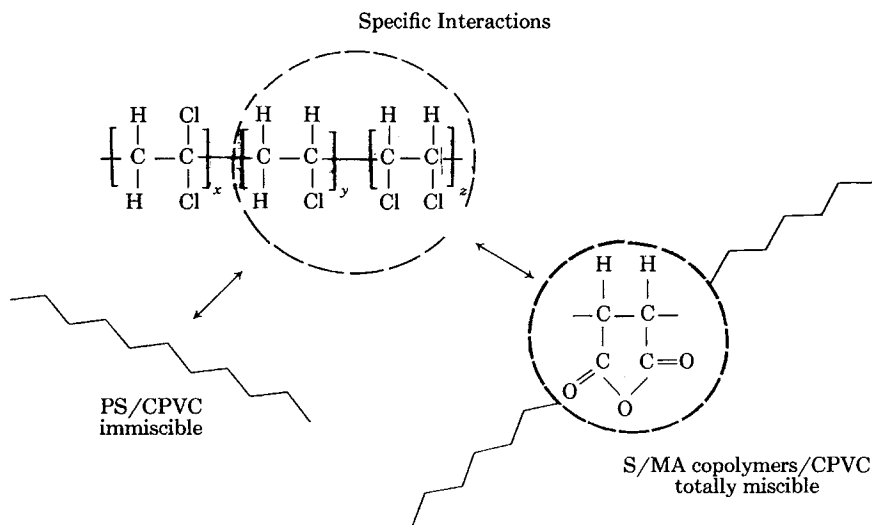
INTRODUCTION

In a continuing series of investigations of styrenic polymer alloys and blends we have completed a study on the miscibility of blends of chlorinated poly(vinyl chloride) (CPVC) and styrene copolymers containing maleic anhydride. Previously, we have reported,¹⁻³ on the miscibility of blends of poly(vinyl chloride) (PVC) and styrene copolymers. These styrene/maleic anhydride copolymers, when blended with PVC, showed miscibility or single phase morphology only at very low concentrations. At higher concentrations this alloy system separated into two altered phases, neither of which was a pure component.

Enhanced miscibility based on the thermodynamics of interaction between the blend components has been covered elsewhere.⁴ As previously found with PVC, the unique polar character derived from the maleic anhydride functionality in Dylark[®] copolymers vs. homopolystyrene provided that improved probability for miscibility with vinyl polymers. Miscibility between styrene/maleic anhydride copolymers and PVC has been extended to CPVC. These CPVC polymers are inherently flame-retardant systems which could possess a wide range of miscibility with oxygen-containing polymers.⁵ This study has shown that CPVC is miscible with styrene/maleic anhydride copolymers in all proportions. This polymer/polymer miscibility is the exception to the general rule of polymer thermodynamics but is potentially commercially significant.

The specific interactions of the CPVC with the styrene/maleic anhydride copolymers not only promotes thermodynamic miscibility but also yields the following macroscopic property effects: improved flow, increased heat resistance, processibility improvements, and reduced impact strength.⁶ Physical properties (e.g., heat resistance) increase in a near linear fashion vs. alloy composition for these miscible, single phase alloys of CPVC/styrenic copolymer in contrast to the sigmoidal dependence for partially miscible,

two phase alloys of PVC/styrenic copolymers.³ The specific interactions permitting miscibility are shown graphically below:



RESULTS

Miscibility

Dylark 332 Copolymer (86% styrene/14% maleic anhydride) was melt compounded in an extruder with a commercial CPVC compound from B. F. Goodrich (CPVC 3010) for the miscibility determinations in Table I. Glass transition temperatures (T_g) for each of the pure components in these alloys merged to yield single T_g 's which were intermediate between the T_g 's of the pure components. Differential scanning calorimetry (DSC) analyses for the single thermal T_g of each alloy is compared in Table I with the theoretical prediction based on the Fox equation for random copolymers. The agreement between experimental and theoretical predictions for a single T_g system confirms the total miscibility between Dylark/CPVC in all blended proportions. In Figure 1, the glass transitions as detected by the mechanical methods of dynamic mechanical analysis also support the total miscibility between Dylark/CPVC in all blended proportions. DSC analyses for crystal Dylark 232 copolymer (8% MA)/CPVC and Dylark 290 copolymer (17% MA)/CPVC confirm that this total miscibility between Dylark/CPVC is universal across the current range of % MA in Dylark copolymer products. These styrenic copolymers are the typically high molecular weight (MW) materials having peak MW in excess of 125,000 which are commonly used for extrusion and injection molding applications. The magnitudes of MW for both CPVC and styrenic copolymers preclude any entropic driving force for miscibility. Miscibility in the case of these high polymer alloys is projected to be the result of specific interactions.

TABLE I

Alloy compositions, % Dylark 332/ copolymer % CPVC	Miscibility ^a		FR properties, flame retardant alloys		Thermal properties, enhanced heat resistance	
	DSC glass transition T_g (°C)	single T_g , thermodynamically miscible Theoretical ^b T_g (°C)	Dynamic mechanical analysis, loss max temp (°C)	Oxygen Index	W/Dylark 332 copolymer DTUL (°F)	W/Dylark 232 copolymer DTUL (°F)
100/0	130		145	0.20	234	222
95/5	126	129	145	0.21	229.5	218
90/10	126	128	143	0.21	229	211.5
80/20	124.5	126	141	0.22	226.5	217.5
60/40	123	123	137	0.25	220	214.5
20/80	114	116	130	0.35	208.5	208
10/90	114	114	128	0.45	206.5	206.5
5/95			128	0.51	205.5	202.5
0/100	112.5				203	203

^aInvariant across Dylark copolymer product line.

^bSingle T_g calculated from Fox relation for random copolymers and thermodynamically miscible alloys.

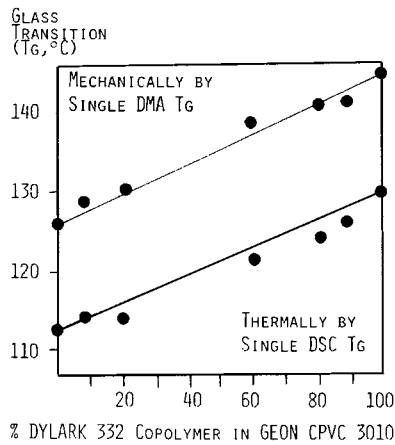


Fig. 1. Thermodynamic miscibility of CPVC/Dylark alloys. True thermodynamic miscibility (single T_g) is in both thermal and mechanical properties; totally miscible in all proportions.

FLAME-RETARDANT PROPERTIES

Oxygen index measurements for the Dylark/CPVC alloys in Table I are seen in Figure 2 to monotonically increase from the oxygen index of 0.20 for pure Dylark 332 Copolymer to the oxygen index of 0.51 for pure CPVC 3010. The actual percent CPVC required to provide flame retardant properties to the Dylark/CPVC alloys was monitored by Underwriter's Laboratory testing (UL 94). Alloys containing $\geq 40\%$ CPVC (i.e., oxygen index ≥ 0.25) passed the UL 94 V-0 requirements at 1/8 in. thicknesses. CPVC contents exceeding 40% CPVC are required for 1/16 in. thicknesses to pass UL 94 V-0 requirements. Inherent flame-retardant properties of CPVC can be maintained in

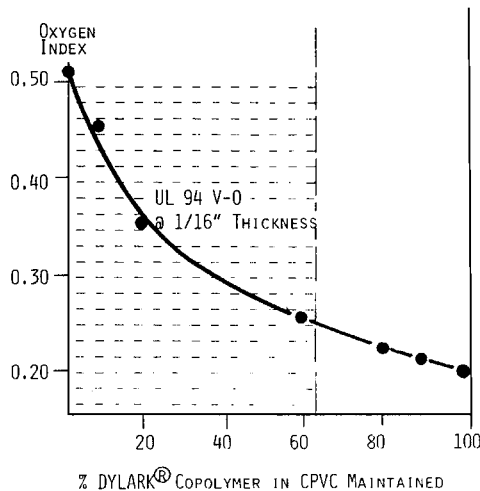


Fig. 2. Flame resistance of CPVC/Dylark alloys. Inherent flame resistance of CPVC is maintained in alloys up to 60% Dylark copolymer contents.

alloys with Dylark copolymers indicating a range of commercial utility in flame-retardant applications given the alloy composition restrictions in Figure 2.

HEAT RESISTANCE

Dylark copolymers provide enhanced heat resistance over polystyrene homopolymers with deflection temperatures under load (DTUL, ASTM D-648) ranging from 222 to 234°F for current Dylark copolymer products. CPVC also claims enhanced heat resistance over poly(vinyl chloride) with DTUL for CPVC 3010 being in excess of 200°F vs. 158°F for PVC. Alloys of Dylark/CPVC maintain heat resistance properties of both pure components as indicated by the monotonic increase in DTUL for the alloys in Table I based on both Dylark 232 (8% MA) copolymer/CPVC and Dylark 332 (14% MA) copolymer/CPVC. These DTUL values were measured on unannealed, 1/8 in. thick, compression molded specimens but indicate that low level addition of Dylark copolymers can only enhance the basic heat resistance of CPVC compounds. The relative extent by which the basic heat resistance of CPVC compounds can be enhanced varies with the type of Dylark copolymer selected for alloying. Higher heat Dylark copolymers containing higher % MA contents are preferred. Dylark 290 (17% MA) copolymer, the highest % MA product available, proved to be the most effective heat resistance promoter for CPVC compounds, as can be seen from the graphical comparison of DTUL in Figure 3.

Miscibility between Dylark/CPVC permits the heat resistance of alloys to be monotonically tailored by alloy composition. Higher % MA products such as Dylark 290 copolymer (17% MA) are preferred for optimum enhancement in alloy heat resistance.

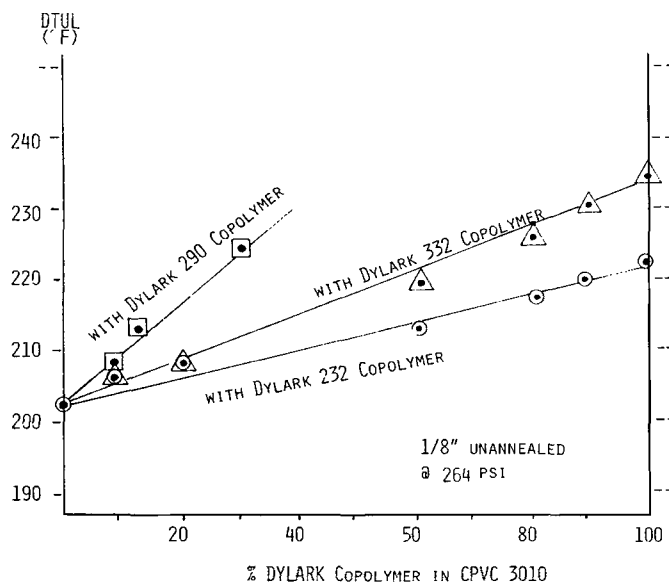


Fig. 3. Heat resistance of CPVC/Dylark alloys. Dylark copolymer increased the heat resistance of CPVC by the "rule of mixtures" linear relationship.

MELT RHEOLOGY

Dylark copolymers not only decrease the melt viscosity when added to CPVC compounds, but also provide for a continuing decrease in melt viscosity at higher processing temperatures. Melt viscosities using an Instron capillary rheometer with a capillary having a length/diameter ratio of 19.9 are compared in Figures 4, 6, and 8. In Figure 4, the highest viscosity curve is for an extrusion grade CPVC compound (CPVC 3007). Adding successively larger ratios of crystal Dylark 332 copolymer (14% MA) results in a progressive lowering of melt viscosity at all shear rates. The melt viscosity of a typical injection molding CPVC compound (CPVC 3015) is also plotted in Figure 4 as open square symbols and is approximately equal in viscosity to 10% Dylark

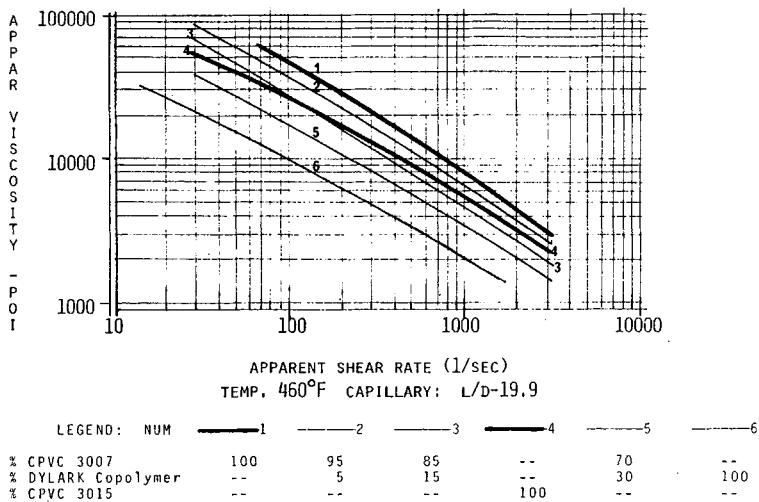


Fig. 4. Instron rheometry of CPVC/Dylark alloys.

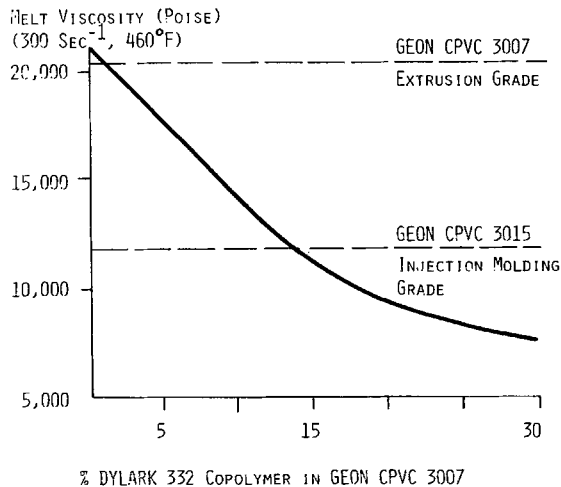


Fig. 5. CPVC/Dylark alloys rheological properties. Dylark copolymer reduces the melt viscosity of CPVC.

332 copolymer/90% extrusion grade CPVC alloy. The systematic lowering of the melt viscosity of CPVC by Dylark copolymers is shown in Figure 5. This relatively low level addition of Dylark copolymers to extrusion grade CPVC compounds enhances flow to a greater extent than the traditional flow modifiers used in commercial CPVC injection molding compounds. The flow modification of CPVC with Dylark copolymers is achieved without the sacrifice in heat resistance, which is expected for the traditional flow modification additives. Thus, the flow modification of CPVC contained in Figure 5 is supplemented by the increased heat resistance described in Figure 3.

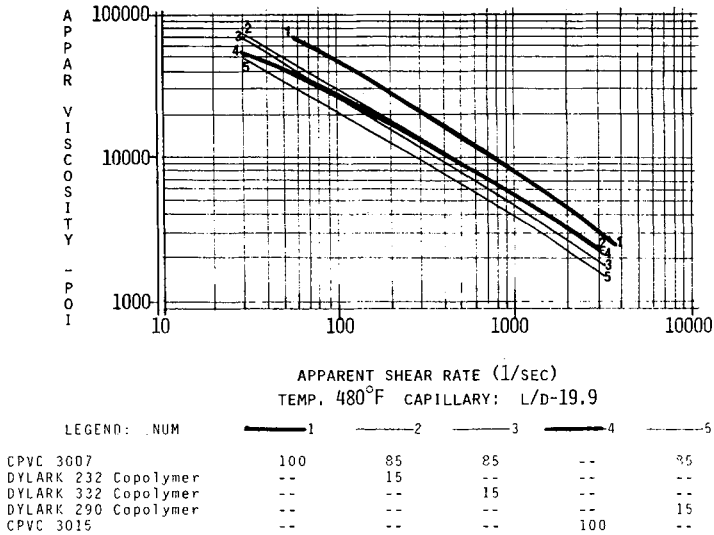


Fig. 6. Instron rheometry of CPVC/Dylark alloys.

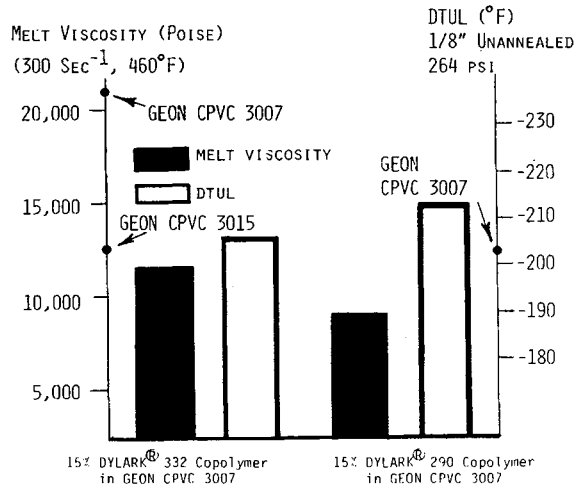


Fig. 7. CPVC/Dylark alloys alloy efficiency. Dylark 290 copolymer is the most efficient in viscosity reduction and heat resistance enhancement.

Relative efficiencies of the commercial Dylark copolymer products in flow modification of CPVC are compared in Figure 6. The highest viscosity curve for extrusion grade CPVC 3007 is compared with 15% Dylark/85% CPVC 3007 alloys where the Dylark copolymer component is either Dylark 232 copolymer (8% MA), Dylark 332 copolymer (14% MA) or Dylark 290 copolymer (17% MA). The higher heat resistance, higher % MA Dylark copolymers are more effective in reducing the melt viscosity of CPVC. At 15% levels of Dylark 290 copolymer (17% MA), the melt viscosity of extrusion grade CPVC 3007 has been depressed significantly below the melt viscosity of the commercial

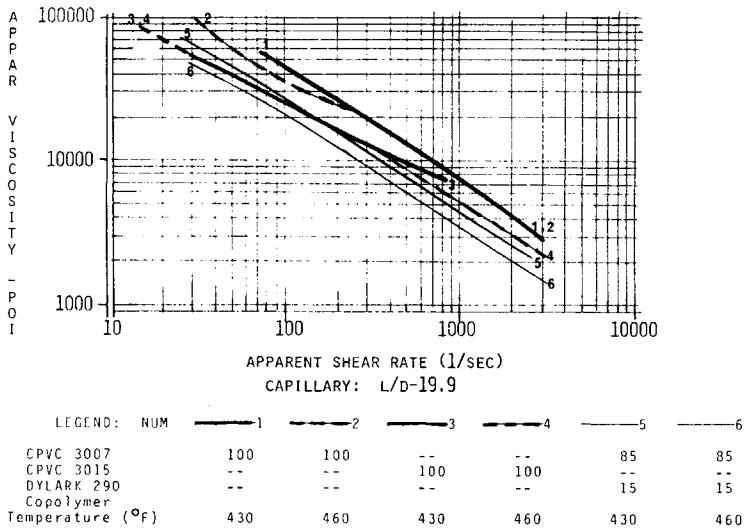


Fig. 8. Temperature dependence for Instron rheometry of CPVC/Dylark alloys.

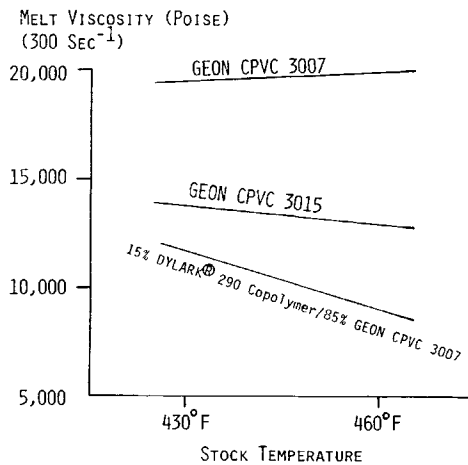


Fig. 9. Temperature dependence of CPVC/Dylark alloys and rheological properties. Viscosity decreases with temperature; wider processing window.

injection grade of CPVC 3015 depicted by the square symbols. Thus, the highest % MA Dylark copolymer, Dylark 290 copolymer (17% MA), is not only the most efficient flow modifier for CPVC (Fig. 7), but was also the most effective Dylark copolymer in enhancing heat resistance (Fig. 3).

Temperature effects on melt viscosities are illustrated in Figure 8. The melt viscosities of CPVC compounds, whether injection molding grades (curves 3 and 4) or extrusion grades (curves 1 and 2), do not decrease significantly with increasing the processing temperature from 430 to 460°F. The 15% Dylark 290/85% CPVC 3007 alloy (curves 5 and 6) does yield the decrease in melt viscosity expected at elevated processing temperatures which broadens the processing window in end use fabrication that has previously limited CPVC compound applications. This effect is demonstrated by the melt viscosity/temperature results in Figure 9.

MECHANICAL PROPERTIES

The mechanical properties of CPVC are retained in alloys of Dylark/CPVC as indicated by the mechanical, impact, and heat resistance properties in Table II. Strips were extruded using a laboratory, counter-rotating, conical twin screw extruder (Haake TW100) equipped with a 4 in. coat hanger profile die having a flex lip construction for gauge adjustment. Continuous 4 in. wide strips of approximately 0.060 in. thicknesses were extruded at output rates of approximately 25 lb/h at 125 rpm with stock temperatures of 460°F. Tensile and flexural properties in Table II were determined on die cut specimens from these as-extruded profiles to correspond to end use properties expected for Dylark/CPVC alloys. Tensile and flexural properties of Dylark/CPVC alloys do not differ from the pure CPVC compound properties. Notched Izod impact strengths of CPVC compound and Dylark/CPVC alloys are identical. Gardner falling weight impact (GFWI) strength of CPVC compounds does diminish with the addition of crystal Dylark copolymer. However, GFWI of vinyls and in particular Dylark/vinyl alloys is critically sensitive to the type and level of acrylic impact modifier included in the vinyl compound. The CPVC compound formulary of CPVC 3015 is not known but is not promoted as a high impact CPVC compound. GFWI of Dylark copolymer/vinyl alloys could be optimized by proper selection of the type and level of acrylic impact modifier as well as using a rubber modified Dylark copolymer instead of the crystal Dylark copolymer products used in Table II.

Heat resistance as measured by DTUL (ASTM D-648) must be always compared under identical processing and thermal histories. DTULs in Table II reflect a 20°F increase by incorporating 15% of crystal Dylark 290 copolymer (17% MA) into CPVC 3015, and, most importantly, this enhancement of heat resistance is directly measured from extruded profiles intended for end use application with no subsequent thermal history. Compression-molded DTUL specimens (0.125 × 0.5 × 5 in.) of the products in Table II yielded DTUL values which were as much as 20°F higher than the as-extruded DTUL values listed in Table II. However, the incorporation of Dylark copolymer into CPVC enhances heat resistance regardless of the technique used to measure DTUL.

TABLE II
Profile Extrusions^a: Mechanical Property Comparisons for As-Extruded Profiles

Composition	Impact strength	Flexural properties		Tensile properties			Heat Resistance			
		GFWI (in. lb./mil)	Notched Izod (ft lb./in.)	Modulus ($\times 10^{-5}$ psi)	Strength (psi)	Modulus ($\times 10^{-5}$ psi)	Strength (psi)	Elongation (%)	DTUL ^b (°F)	DTUL ^c (°F)
% CPVC 3015	290									
% Dy/lark copolymer										
0	4.19	0.7	4.39	15,300	2.82	7,900	63	184	201	
5	2.40	0.8	4.53	15,700	2.81	7,700	70	198	203	
10	0.50	0.9	4.38	15,600	2.96	8,100	31	202	208	
15	0	0.7	4.81	16,400	3.02	8,300	55	204	212	
30	0	0.5	4.61	10,600	2.87	6,000	2	212	223	

^aHaake twin screw equipped with a 4 in. coat hanger die having flex lip gauge adjustment of 1/16 in. strip thickness.

^bASTM D-648 at 264 psi, 1/8 in. thickness except for epoxying ends at two 1/16 \times 5 \times 1/2 in. bars to make 1/8 \times 5 \times 1/2 in., as extruded.

^cASTM D-648 at 264 psi, 1/8 in. thickness, compression-molded.

CONCLUSIONS

CPVC is miscible in all proportions with styrene/maleic anhydride copolymers. Miscibility is evidenced in both thermal (DSC) and dynamic mechanical (DMA) methods. The effects of thermodynamic miscibility on the macroscopic physical properties of these alloys are:

- Monotonic tailoring of heat assistance by adjusting ratio of alloy components.
- Melt viscosity of CPVC is reduced and processability is improved by alloying with Dylark copolymers.
- Flame resistance characteristics of CPVC can be maintained in alloys up to about 40% styrene copolymer contents.
- Mechanical properties of pure components are maintained.

The polar character of styrene/maleic anhydride copolymers vs. polystyrene is not only responsible for the partial miscibility in PVC alloys but also promotes miscibility in CPVC alloys

References

1. L. G. Bourland and A. D. Wambach, *J. Vinyl Tech.*, **5**(3), 121 (1983).
2. L. G. Bourland and A. D. Wambach, *Plast. Eng.*, **39**(5), 23 (1983).
3. L. G. Bourland and D. M. Braunstein, *J. Appl. Polym. Sci.*, **32**(8), 6131 (1986).
4. D. R. Paul, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978, Vol. 1, Chap. 1.
5. M. Aubin and R. E. Prudhomme, *Polym. Eng. Sci.*, **24**(5), 350 (1984).
6. L. G. Bourland, U.S. Pat. 4,371,666 (1983) (assigned to Atlantic Richfield Co.).

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