

Processing Characteristics of Alpha-Methylstyrene-Methacrylonitrile Copolymer

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Synopsis

Processing behavior of alpha-methylstyrene-methacrylonitrile copolymer has been studied in a Brabender Plasticorder and in a capillary rheometer. The copolymer is thermally unstable at a processing temperature of 230°C; however, addition of 2% ethyl acrylate to the copolymer composition enhances processing stability. The terpolymer is processable in the range of 210° to 250°C. However, it is limited by melt fracture at low shear rates.

INTRODUCTION

In previous publications of this series, we reported on the copolymerization behavior of alpha-methylstyrene with methacrylonitrile,¹ the sequence distribution or monomer unit arrangement in the copolymers,² and the physical and mechanical properties of the AMS-MAN copolymer.³ In this publication, we report on the processing behavior of the AMS-MAN copolymer.

Dynamic processability is the combined effect of melt viscosity and thermal stability. These properties can be independently measured by melt flow rate, apparent melt viscosity, and thermogravimetric analysis (TGA) weight loss under programmed temperature conditions. The Brabender Plasticorder is a useful instrument for assessing dynamic processability by combining flow and thermal stability data. Preliminary processing behavior of the AMS-MAN copolymer was obtained on a Brabender Plasticorder. The Brabender torque rheometer is used as a measure of polymer degradation and to characterize the rheology of polymeric materials. The torque, which is a measure of the load on the mixer, is directly related to the viscosity and thermal stability of the melt being mixed. Torque after flux is indicative of melt viscosity and power requirements under dynamic shear conditions. Recent studies⁴ using the Brabender Plasticorder mixing chamber as a typical melt rheometer have shown that rotor rpm at a rotor speed ratio of 3/2 is approximately equal to shear rate in units of sec^{-1} . At 25 rpm, the dynamic shear in the mixing chamber is typical of shear conditions during Banbury melt-mixing, flow in an extruder barrel at low screw speeds, milling, or calendaring. Thus, the flux and flow information gained from the Brabender mixing measurements should be particularly pertinent to processability in an extruder.

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TABLE I
Thermal Stability of Alpha-Methylstyrene–Methacrylonitrile Azeotropic Copolymer

Temperature, °C	Weight loss after 10 min, %
240	1
259	2
305	5
321	10
332	20

TABLE II
Thermal Stability of Alpha-Methylstyrene–Methacrylonitrile Azeotropic Copolymer

Time of preheat, min	230°C Melt index, g/10 min
5	0.25
20	1.22
30	2.63

MATERIAL

The alpha-methylstyrene–methacrylonitrile (AMS–MAN) copolymer was made by emulsion technique as described previously.¹ The data reported in this paper are for azeotropic copolymer which contains 57 mole-% MAN and 43 mole-% AMS. The copolymer had an inherent viscosity of 1.2 in dimethylformamide at 30°C. The structure of the copolymer is essentially that of an alternating arrangement of the monomer units, i.e., an AMS unit followed by a MAN unit. The monomer unit arrangement or sequence distribution has been discussed in detail in a previous publication.²

RESULTS AND DISCUSSION

Poly(alpha-methylstyrene) and poly(methacrylonitrile) are reported⁵ to decompose in the range of 200–300°C to give high yields of monomer. The polymers decompose by random chain scission to yield polymer radicals which rapidly evolve monomer in high yield by an unzipping process. The low thermal stability of the homopolymers, therefore, made necessary a study of the thermal stability of the AMS–MAN copolymer. Isothermal TGA data in air are shown in Table I. The copolymer exhibits processing stability below 250°C whereas, above 300°C, degradation becomes catastrophic. Melt index data in Table II show the copolymer to be unstable at 230°C.

Polyacrylates decompose to yield little or no monomer. Therefore, incorporation of a small amount (2–5%) of ethylacrylate in the AMS–MAN copolymer reduces the facility (by blocking of the unzipping process) with which AMS–MAN sequences revert to monomer at high temperatures. The unzipping of the AMS–MAN chain is interrupted at the acrylate unit. The added stability thus gained allows higher processing temperatures than otherwise possible without objectionable monomer evolution. These statements are substantiated by the melt index data shown in Table III. The melt index stability data in Table III at 260°C indicate a substantial improvement in

TABLE III
Thermal Stability of Alpha-Methylstyrene-
Methacrylonitrile-Ethyl Acrylate Terpolymer^a

Time of preheat, min	260°C Melt index, g/10 min
10	0.95
15	1.09
25	1.02

^a 2 wt-% ethyl acrylate.

thermal stability for the terpolymer over the copolymer (Table II). In addition, the terpolymer is transparent and colorless. Physical properties of the terpolymer are the same as the copolymer.³

Figure 1 shows the effect of temperature on the Brabender curves of torque versus mixing time on AMS-MAN copolymer. The vertical lines indicate the breath of the recorder trace. The broad torque curve indicates the high melt elasticity of the copolymer at the temperatures indicated. Increasing the temperature from 175°C (copolymer softening temperature) through 205°C narrows the torque curve, indicating improved flow and reduced melt elasticity. Torque versus mixing time for the AMS-MAN-EA terpolymer at 210°C and 230°C is shown in Figure 2. At these temperatures, the torque curve is narrow, and substantially improved melt viscosity characteristics are observed. The terpolymer thermal stability and processing stability is indicated in Figure 2 by the smooth horizontal equilibrium torque curve at long

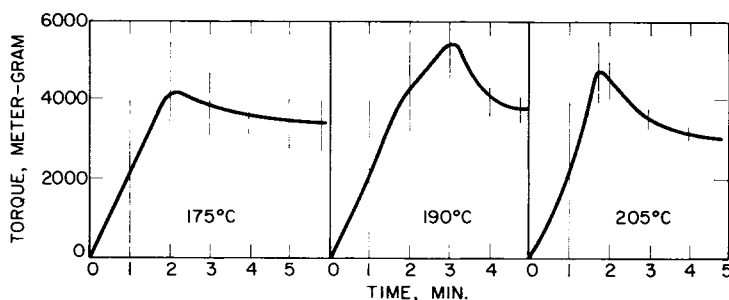


Fig. 1. Effect of temperature on Brabender torque vs. mixing time.

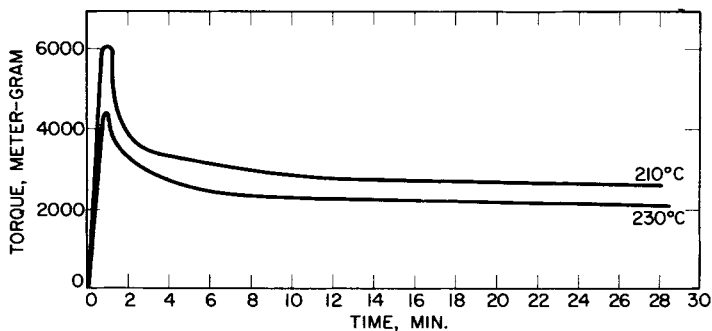


Fig. 2. Dependence of Brabender torque on mixing time.

TABLE IV
Thermal Stability of Alpha-Methylstyrene-
Methacrylonitrile-Ethyl Acrylate Terpolymer

Temp., °C	Fusion time, ^a min	Viscosity change after fusion	Extrudate appearance
230	15	none	clear-void free to 30 min
250	15	none	many voids and trapped air- turns yellow at 30 min

^a Time to reach steady-state viscosity.

times. Terpolymer instability would be indicated by increasing or decreasing torque at longer mixing times.

Melt flow processability characteristics and thermal processing stability were also determined in a capillary rheometer. Processability of AMS-MAN-EA terpolymer was compared with G. E. Lexan polycarbonate. Table IV contains thermal stability data on AMS-MAN-EA. The thermal processing stability and color stability of the terpolymer are good up to 30 min at 230°C based on viscosity-time data. At 250°C, the AMS-MAN-EA extrudate contained trapped gas and turned yellow after 30 min. These data indicate that the maximum processing temperature would be expected to be about 250°C. Figure 3 shows flow curves of AMS-MAN-EA. The terpolymer is processable from 210° to 250°C but is limited by melt fracture at low shear rates. Melt fracture occurs at 8.5 sec⁻¹ at 210°C, 17 sec⁻¹ at 230°C, and 86 sec⁻¹ at 250°C.

Melt fracture is somewhat a misnomer since there is no evidence for any fracture but a gross roughness and irregularity in the extrudate shape with no break in the shear stress-shear rate curve, as one would expect when a real

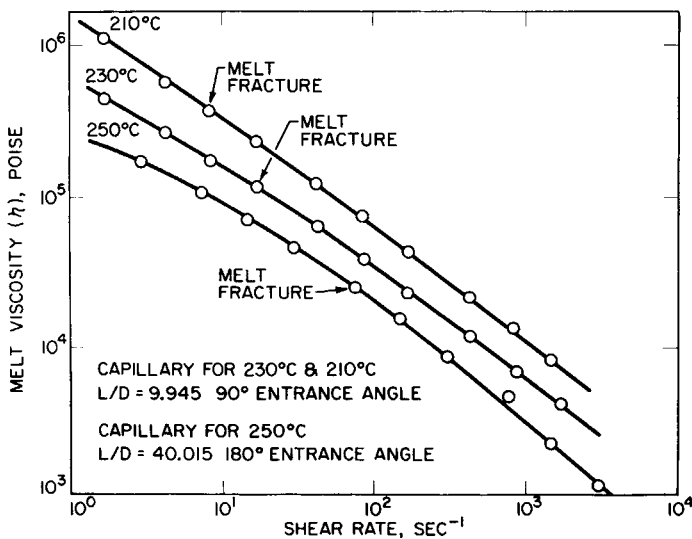


Fig. 3. Effect of temperature on flow curves.

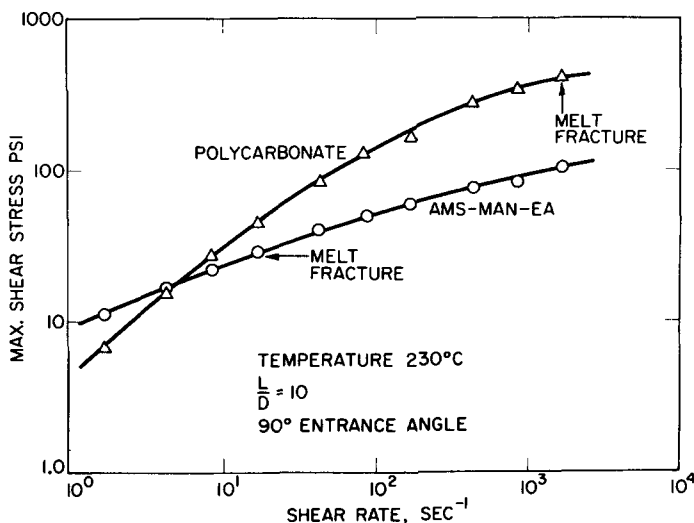


Fig. 4. Maximum shear stress vs. shear rate for terpolymer and polycarbonate.

fracture occurs. Figure 4 shows shear stress plotted against shear rate at 230°C for AMS-MAN-EA and polycarbonate. Lexan polycarbonate is readily melt processable over the temperature range of 230° to 260°C and does not show melt fracture until 1700 sec⁻¹.

Figure 5 (extrudates picture) shows the development of AMS-MAN-EA extrudate irregularity (melt fracture) with increase in shear stress. The irregularity progresses from barely visible spiral grooves on the surface of the extrudate to a discontinuous stage. Comparison of the AMS-MAN-EA extrudate at 230°C and low shear rates (4.30 sec⁻¹, to avoid melt fracture region) shows that die swell (diameter of extrudate/diameter of capillary, d/D)

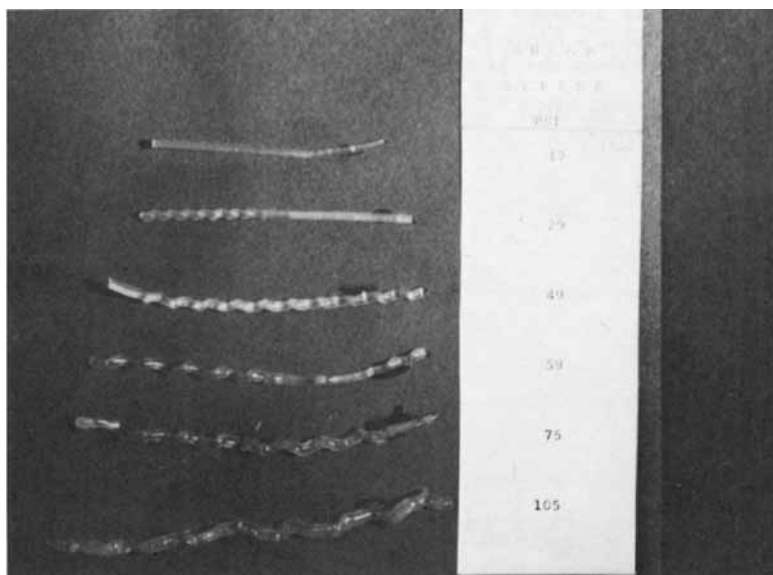


Fig. 5. Terpolymer extrudate melt fracture.

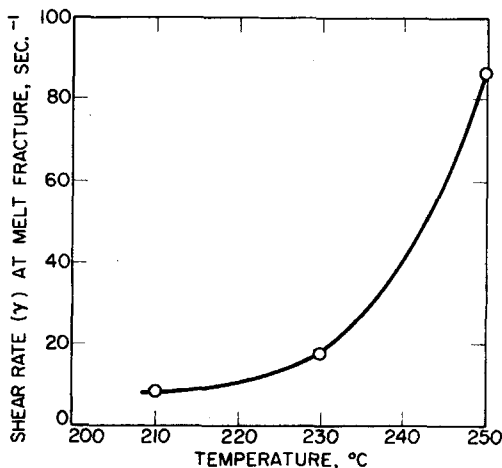


Fig. 6. Dependence of shear rate at melt fracture on temperature.

is about 1.5, whereas for polycarbonate, die swell is 1.0. The melt fracture and die swell observed in the AMS-MAN-EA terpolymer is indicative of high melt elasticity.

Figure 6 is a plot of shear rate at melt fracture versus temperature for the AMS-MAN-EA terpolymer. These data indicate that melt fracture could be avoided at low shear rates at a processing temperature near 260°C.

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