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Properties of Alpha-Methylstyrene–Methacrylonitrile Copolymer

J. F. KENNEY,* *Mendham, New Jersey 07945,* and P. J. PATEL,† *Somerville, New Jersey 08876*

Synopsis

Physical and mechanical properties of alpha-methylstyrene–methacrylonitrile copolymer have been determined. The effects of copolymer composition and inherent viscosity (molecular weight) on deflection temperature under load, Izod impact strength, tensile, and flexural properties are reported. The azeotropic copolymer of 57 mole-% methacrylonitrile possessed the best overall properties with a DTUL of 129°C and an Izod impact strength of 0.3 ft-lb/in. notch. The impact strength of the copolymer was improved by graft copolymerization upon a butadiene–methacrylonitrile copolymer. The impact-modified copolymer possessed an Izod impact strength of 6 ft-lb/in. notch and a DTUL of 115°C.

INTRODUCTION

We have reported[1,2] on the emulsion copolymerization behavior of alpha-methylstyrene (AMS) with methacrylonitrile (MAN) and the distribution of monomer sequences in the copolymers. Izod impact strength and deflection temperature under load properties were correlated with the sequence distributions. In this paper, we report further on the properties of the AMS–MAN copolymers.

EXPERIMENTAL

Preparation of the AMS–MAN copolymers has been described previously.[1] The impact-modified copolymer is prepared in the following example. To a 500-ml Fisher-Porter pressure bottle are added a magnetic stirrer, 3.0 g sodium lauryl sulfate, 0.10 g potassium persulfate, 0.01 g sodium meta-bisulfite, 0.05 g disodium hydrogen phosphate, and 200 ml oxygen-free water. Nitrogen is bubbled through the solution for about 5 min, and 0.10 g *tert*-dodecylmercaptan and 25 g methacrylonitrile are added. The bottle is capped, and 84 g butadiene is distilled into the cold bottle. The bottle is heated to 47°C in a warm-water bath with stirring for 24 hr. A 282-g emulsion is obtained for 82% conversion. The emulsion has a solids content of 32%, and the copolymer contains 27 wt-% methacrylonitrile.

To a three-necked flask previously described[1] are added 0.1 g potassium

* Present address: M&T Chemicals Inc., Rahway, New Jersey 07945.

† Present address: Tenneco Chemicals Inc., Flemington, New Jersey 08822.

TABLE I
Dependence of Properties of Alpha-Methylstyrene–Methacrylonitrile Copolymers on Composition

Monomer charge, Mole-% MAN	Copolymer yield, %	MAN in copolymer mole-%	η_{inh}	DTUL	Izod impact, ft-lb/in. notch	Character of molding: Color	Character of molding: Transparency
100	80	100	—	93	0.45	colorless	transparent, very clear
82	91	67	1.70	113	0.43	colorless	transparent, very clear
64	93	60	1.52	124	0.24	colorless	transparent
57	84	57	1.35	129	0.25	colorless	transparent, hazy
50	57	—	1.42	123	0.24	colorless	opaque
50	93	54	1.04	96	0.23	yellow	opaque
50	59	—	0.84	91	—	yellow	opaque
44	48	—	1.43	125	0.23	beige	opaque
44	29	—	0.76	86	0.15	yellow	opaque
37	48	—	1.22	121	0.24	yellow	opaque
37	44	—	0.90	86	0.25	yellow	opaque
37	64	52	0.62	69	—	yellow	opaque
37	13	—	0.60	78	—	yellow	opaque
22	18	47	0.30	—	—	yellow powder	—
0	0	—	—	—	—	—	—

persulfate, 0.01 g sodium meta-bisulfite, 0.05 g disodium hydrogen phosphate, and 225 ml oxygen-free water. To this solution are added 130 g of the butadiene–methacrylonitrile copolymer emulsion prepared above and 0.35 g *tert*-dodecylmercaptan. AMS, 58 g, and MAN, 42 g, are mixed and added to the flask. The polymerization is carried out as described[1] for making copolymer. The yield of rubber-modified copolymer is 110 g. The modified copolymer is stabilized with 1% N-phenyl-B-naphthylamine and milled at 185°C for 10 min. Izod impact strength is 6 ft-lb/in. notch.

RESULTS AND DISCUSSION

The effects of copolymer composition and inherent viscosity on such properties as deflection temperature under load (DTUL at 264 psi), Izod impact strength, color, and transparency of a compression-molded sample are shown in Table I. The DTUL increases with decrease in MAN content in the copolymers up to the azeotropic composition. Izod impact strength is low for all compositions. Color and transparency of a compression-molded specimen decrease with decrease in MAN content. DTUL is highly dependent on inherent viscosity and increases with increasing inherent viscosity for a given composition. The azeotropic copolymer (57 mole-% MAN) has the best overall properties with a DTUL of 129°C, colorless, and transparent. Therefore, extensive characterization and property evaluation were carried out on the azeotropic composition. The following data were obtained on this copolymer.

Figure 1 shows the effect of inherent viscosity (molecular weight) on DTUL. A plateau in the inherent viscosity–DTUL curve occurs at an inherent viscosity value of 1.2 corresponding to a DTUL of 128°C. Figure 2 shows a typical Gehman modulus–temperature curve of the copolymer. The temperature corresponding to a modulus value of 10^9 dynes/cm^2 is reported as the T_g at 141°C. A differential scanning calorimeter (DSC) curve is shown in Figure 3. The T_g is indicated at 141°C, fusion or softening point at 175°C, and the onset of decomposition at 223°C. Modulus–temperature and tan

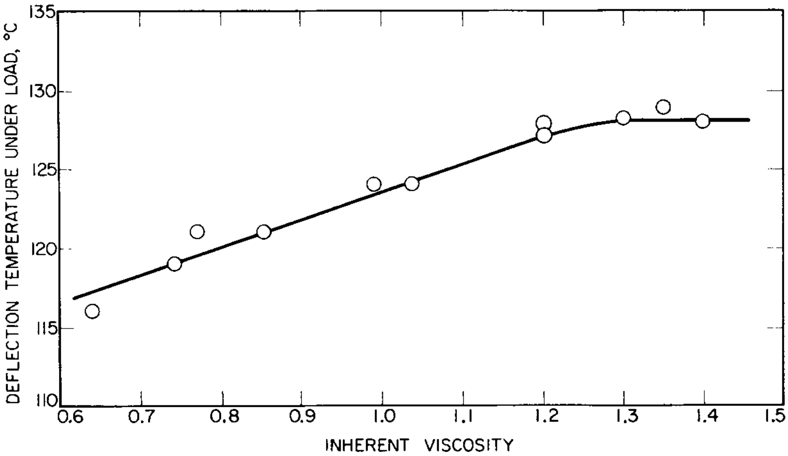

Fig. 1. Dependence of deflection temperature under load on inherent viscosity.

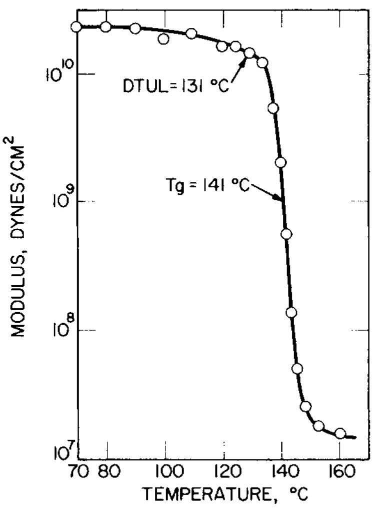

Fig. 2. Modulus–temperature curve of copolymer.

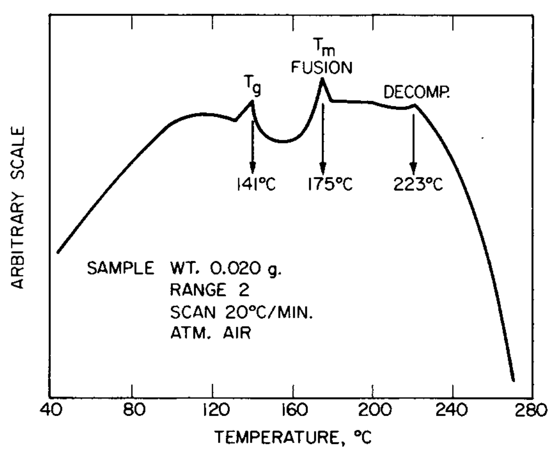

Fig. 3. Differential scanning calorimetry curve of copolymer.

TABLE II
Properties of Alpha-Methylstyrene–Methacrylonitrile Azeotropic Copolymer

η_{inh}	Tensile strength, psi	Tensile modulus, psi	Flexural strength, psi	Flexural modulus, psi	Izod impact strength, ft-lb/in. notch	DTUL, °C
1.3	6800	262,000	14,600	638,000	0.25	129
0.8	6390	270,000	11,000	635,000	0.27	120
0.6	4850	260,000	10,000	515,000	0.25	117

TABLE III
Tensile Creep Modulus of Alpha-Methylstyrene–Methacrylonitrile Copolymer

Stress, psi	Temp., °C	Creep modulus, psi × 10^3			
		1 hr	10 hr	100 hr	300 hr
3000	73	420	390	370	330[a]
3000	150	350	300	250	220
3000	200	250	190	120	rupture
3000	250	rupture	—	—	—

[a] Extrapolated results.

δ–temperature curves for AMS–MAN copolymer obtained on a Vibron viscoelastometer are shown in Figure 4. The tan δ–temperature curve exhibits no secondary transitions below the primary transition (T_g) at approximately 130°C.

The effect of inherent viscosity on tensile and flexural properties of the azeotropic copolymer is shown in Table II. Tensile and flexural properties were independent of molecular weight above 0.8 inherent viscosity. The mechanical properties exhibited by the copolymer are typical of styrene-based plastics.

Tensile creep of AMS–MAN copolymer is shown in Table III. Figure 5 shows the effect of temperature on the tensile creep properties at a stress of

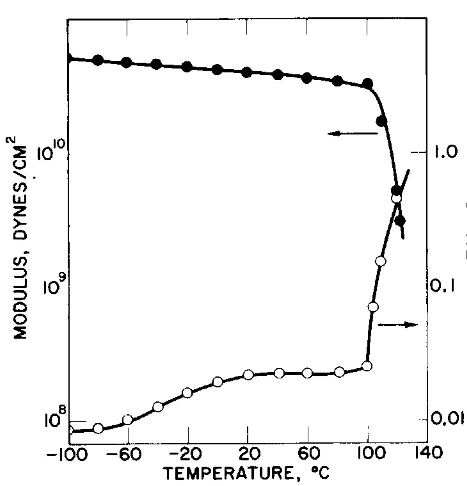

Fig. 4. Modulus–temperature and tan δ–temperature curves of copolymer.

3000 psi. The copolymer exhibits good creep resistance up to at least 75°C, but like most glassy thermoplastics, it is prone to stress craze at high loads. Creep resistance and strength decrease rapidly at about 100°C, and at 120°C the copolymer cannot withstand high loads. The copolymer stress crazed prior to rupture.

IMPACT MODIFICATION

Since the Izod impact strength of the copolymer is only about 0.3 ft-lb/in. notch, the need for improving the impact strength is apparent. The impact strength of the copolymer was improved by polymerizing AMS and MAN in a preformed butadiene–methacrylonitrile copolymer emulsion. The resulting graft copolymer had substantially improved impact strength over the unmodified copolymer at rubber concentrations greater than 18%. The effect of % butadiene–methacrylonitrile rubber in the terpolymer on notched Izod impact strength and on DTUL is shown in Figure 6. Figures 7 and 8 show the effect of mercaptan chain-transfer agent used in the graft copolymerization on impact strength and DTUL at a rubber content of 30%. It is clear that *tert*-dodecylmercaptan is more efficient in enhancing the impact strength.

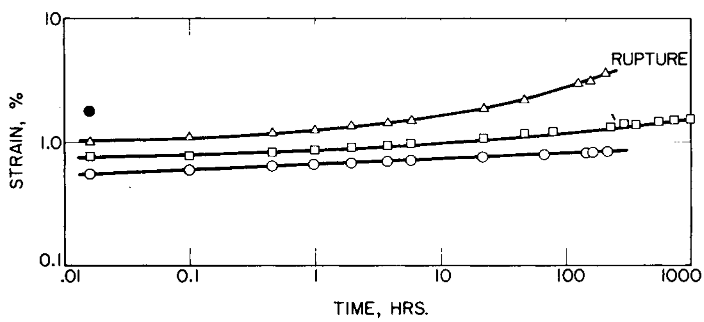

Fig. 5. Effect of temperature on tensile creep. Stress 3000 psi; (○) 73°F; (□) 150°F; (△) 200°F; (●) 250°F.

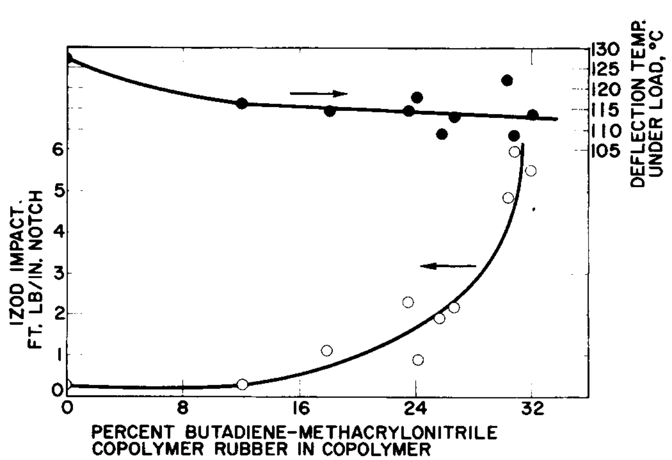

Fig. 6. Effect of rubber content on impact strength and deflection temperature under load.

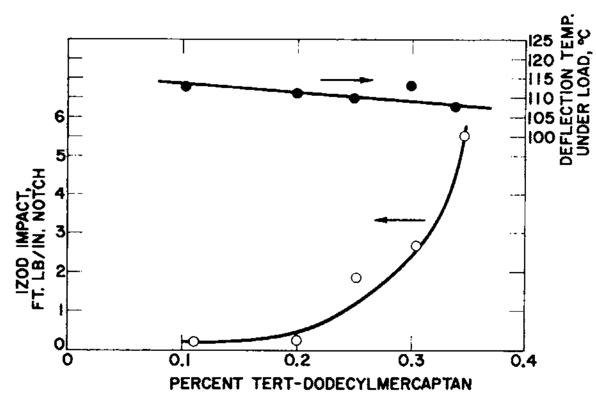

Fig. 7. Effect of *tert*-dodecylmercaptan on impact strength and deflection temperature under load. Rubber content 30%.

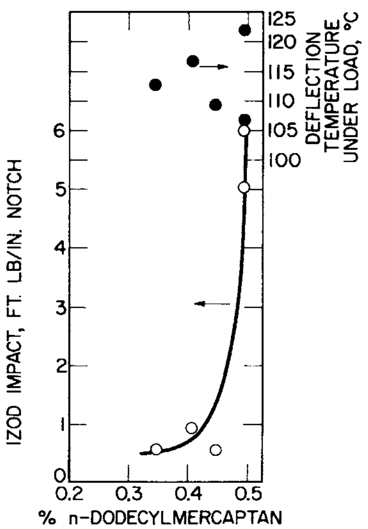

Fig. 8. Effect of *n*-dodecylmercaptan on impact strength and deflection temperature under load. Rubber content 30%.

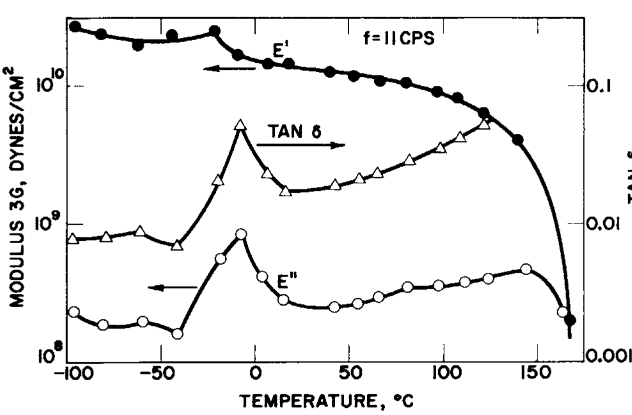

Fig. 9. Modulus-temperature and tan δ-temperature curves for milled rubber-modified copolymer.

The effect of milling the graft copolymer on a two-roll mill at 185°C for 10 min is dramatic. For example, an unmilled sample of impact modified AMS–MAN exhibited an Izod impact strength of 1.1 ft-lb/in. notch and a DTUL of 108°C, whereas a milled sample from the same batch exhibited an Izod value of 6.0 ft-lb/in. notch and a DTUL of 115°C. It was thought that the reason for this behavior was due to heterogeneity in the unmilled sample. In an attempt to explain this behavior, the modulus–temperature and damping–temperature curves on the milled and unmilled samples were obtained on the Vibron viscoelastometer. It was expected that the unmilled sample would exhibit a broadening of the modulus–temperature and tan δ–temperature curves, indicating heterogeneity in the sample. However, the curves were identical for unmilled and milled samples, as shown in Figure 9.

A two-phase system is readily apparent from Figure 9 with two glass transition temperatures, one for the butadiene–methacrylonitrile (62/38) copolymer rubber at −10°C and another for the glassy copolymer at around 145°C. The T_g of the rubber phase is too high for many applications and should be lowered by decreasing the MAN content of the rubber copolymer.

The impact-modified copolymer is opaque to translucent, whereas the unmodified copolymer is transparent. The opaqueness is due, of course, to a difference in refractive index of the rubber phase and the glassy copolymer phase.

Substantial impact improvement of the copolymer could not be obtained by mixing rubber and copolymer latexes, melt blending of rubber and copolymer, or melt blending with ABS.

Processing characteristics of the AMS–MAN copolymer will be discussed in another article.[3]

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References

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