

Correlation Between Mechanical Properties and Degradation Processes of Poly(methyl methacrylate-co-butyl acrylate) Films

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SYNOPSIS

Copolymer systems based on various molar ratios of methyl methacrylate (MMA)/butyl acrylate (BA) and different mass content of *N*-methylolacrylamide (NMA), as a cross-linking agent, were investigated. The influence of temperature, 150°C, under conditions similar to those used in the textile industry, and effect of ultraviolet (UV) irradiation were examined. The changes of mechanical properties were found to be connected with the cross-linking and/or degradation mechanisms. The effect of copolymer composition on the mechanical properties was established, especially during UV degradation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Properties of copolymer systems primarily depend on the ratio of individual sequences in copolymer chain, and by variations of the initial ratio of monomers in the feed, copolymers with a wide distribution of properties may be prepared, from stiff plastic to elastomeric materials.¹ In radical copolymerization the methyl methacrylate unit (M1) is a more active species than the butyl acrylate unit (M2) (i.e., $r_1 > r_2$), and in the whole composition range the copolymers produced is expected to contain more methyl methacrylate units.² The copolymer composition can be determined by various methods including spectroscopic methods.^{3,4}

By combining methyl methacrylate (MMA) units, which can be considered as hard sequences contributing stiffness, with appropriate acrylates as soft sequences,⁵⁻⁷ polymers with desired properties for specific purposes may be obtained.⁸ The combination of durability and versatility, and the ability to tailor molecules relatively easily for specific applications, have made acrylic and methacrylic esters prime candidates for numerous and diversified applications.⁸ Copolymers of MMA and butyl acrylate

(BA), with *N*-methylolacrylamide (NMA) as cross-linking agent, are utilized in the textile industry as auxiliary agents, which are consumed in large quantities for manufacturing, confectioning, and finishing of textiles. Textile auxiliaries are products that facilitate or, in fact, enable the manufacturing of semi-finished and finished textiles or impart to them certain mechanical and optical properties, such as durability and aesthetic appearance.⁸

In this article the influence of various structural parameters in cross-linked copolymers of MMA/BA, using various molar ratios, were investigated.

EXPERIMENTAL

Materials

Copolymers of MMA with BA having different ratios of comonomers were prepared by emulsion polymerization in a semiindustrial reactor using ammonium persulfate as initiator and NMA as a cross-linking agent. Copolymerization was performed at 50°C following the procedure described by Warson.⁸ The data in Table I represent the ratio of comonomers and cross-linking agent in monomer feed. The copolymerization reaction was stopped after monomers disappeared from the reaction mixture.

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Table I Ratio of Comonomers and Cross-Linking Agent in Feed

Sample	Monomer Ratio (Mass %)		Cross-Linking Agent, NMA (Mass %)
	MMA	BA	
A	60.00	35.00	5.00
B-1	56.54	43.46	0.00
B-2	55.30	43.70	1.00
B-3	54.00	41.50	4.50
B-4	50.60	44.60	4.80
B-5	50.00	44.11	5.89
C	40.70	54.80	4.50
D	30.00	66.00	4.00

Film Preparation

Films of investigated copolymers were prepared by drying the 48% aqueous emulsion at 40°C on glass plates to constant weight.

Aging of Samples

The films were exposed to hot air in an oven at 150°C from 3 to 60 min. The temperature was selected to be as used in common practice. These temperatures are used as cross-linking temperatures in bonding nonwoven fabrics in textile applications.

Copolymer films were irradiated for various times in air at 15 cm distance and 60°C with a UV lamp (Desaga Multi Purpose Equipment) for $\lambda = 254/366$ nm. Characteristics of UV lamp: the light-in-

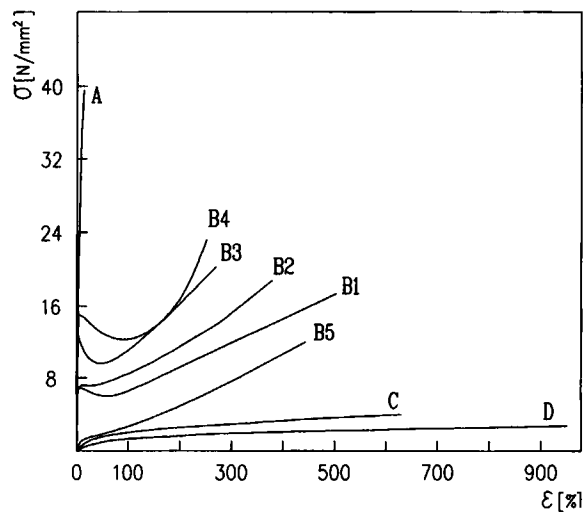
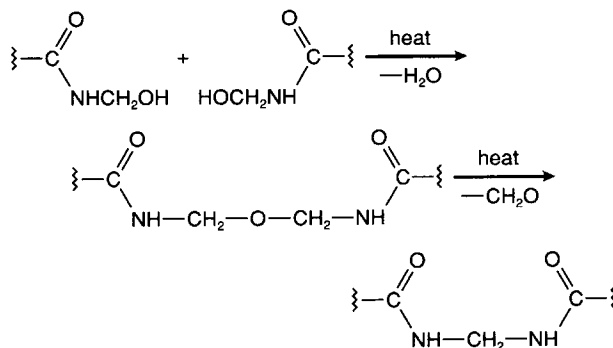


Figure 1 Tensile properties of various MMA-BA-NMA systems (see Table I).



Scheme 1

tensity flux at the film surface measured with a low-pressure mercury vapor lamp was $2.6 \cdot 10^{-1} \text{ J/m}^2\text{s}$.

Characterization of Samples

Mechanical properties of films were determined on a Zwick universal testing machine 1445 at 20°C and 60% relative humidity. The resulting stress-strain curves and characteristic strength values were obtained in accordance with DIN 53 445. Infrared (IR) spectra were recorded on a Perkin-Elmer spectrophotometer model 257.

RESULTS AND DISCUSSION

The mechanical properties of the investigated copolymer systems show that the shapes of the stress-

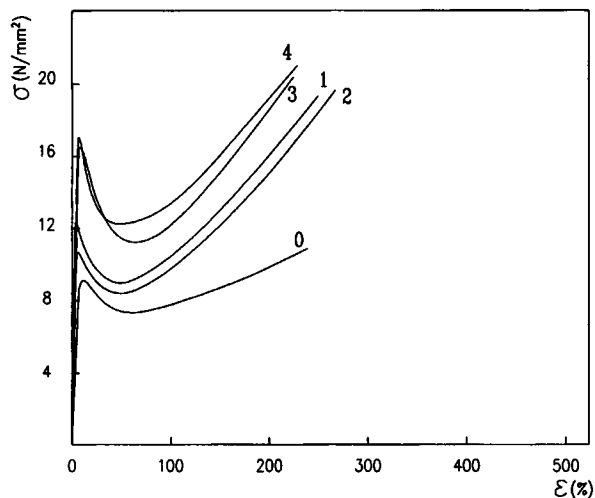


Figure 2 The influence of thermooxidative heating (150°C) on stress-strain curves of thermoplastic sample B3 (0) before; after: (1) 3 min; (2) 15 min; (3) 30 min, and (4) 60 min.

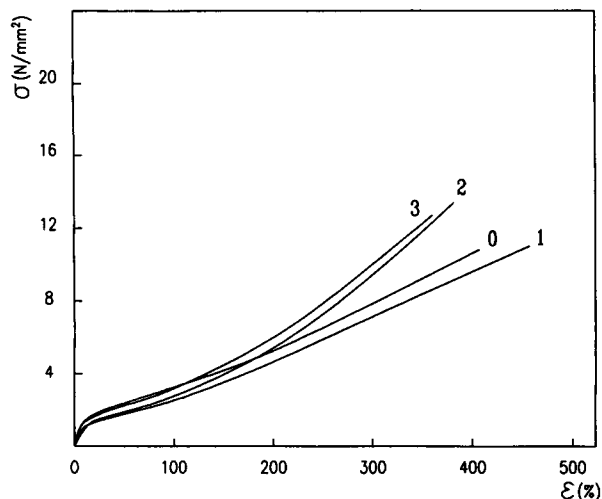


Figure 3 Changes in tensile properties of elastomeric sample B5 (0) before and after thermooxidative treatment for: (1) 3 min; (2) 15 min; and (3) 60 min.

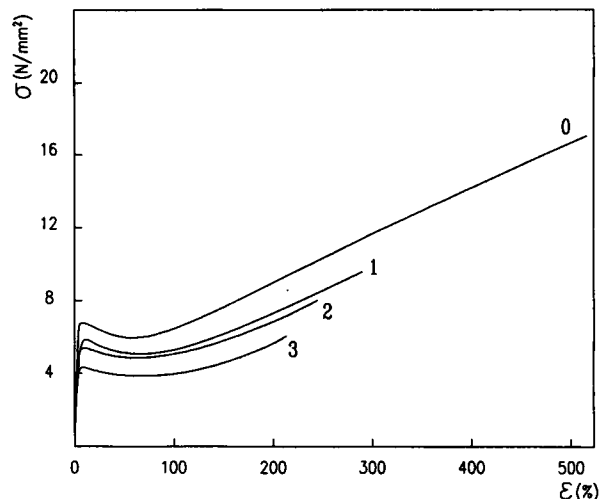


Figure 5 Changes in elongation of MMA-BA-NMA system B1 (Table I) (0) before and after ultraviolet treatment: (1) 7 h; (2) 15 h; and (3) 20 h.

strain curves depend strongly on the MMA/BA ratios (Fig. 1). Samples with higher content of soft BA sequences behave as elastomeric materials and readily undergo deformation and exhibit large elongations under small applied stresses (samples C and D in Fig. 1).

The influence of the cross-linking agent NMA was also considered. Samples with similar compositions (B1 and B2 in Fig. 1) showed that a small amount of cross-linking agent increases strength and lowers the elongation because of the formed cross-linked structure. This was even more pronounced

in sample B3 prepared with higher amount of NMP. The difference between samples B4 and B5 is significant because it points to the optimal amount of cross-linking agent and shows the transition from thermoplastic to elastomeric behavior. The cross-linking process in the first stage of the reaction with NMA leads to the formation of ether linkages and in the second stage to methylene amine linkages (Scheme 1).⁹⁻¹¹

The aim of such investigations was also to define the structure-mechanical properties relationship with optimal hard/soft ratio at a given level of cross-

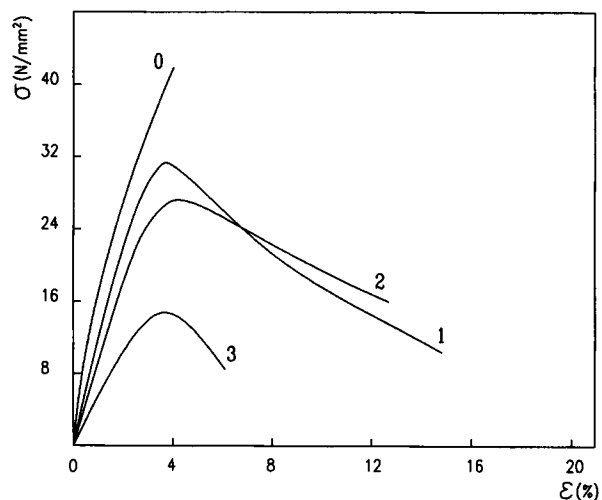


Figure 4 Changes in tensile properties due to photooxidative degradation of acrylate system A (Table I) (0) before and after: (1) 5 h; (2) 15 h; and (3) 20 h.

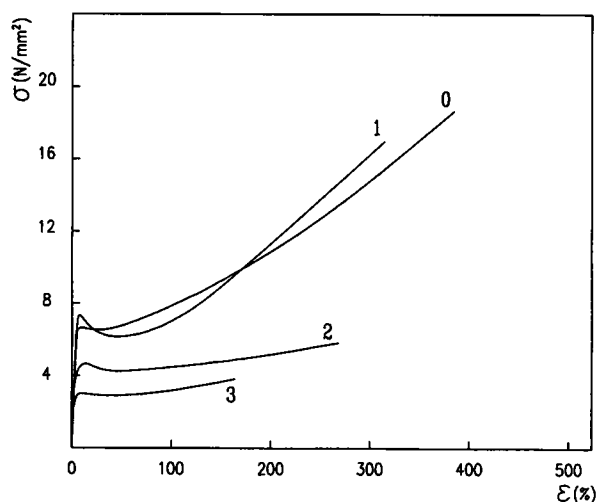


Figure 6 Tensile properties of thermoplastic system B2 (Table I) (0) before and after UV treatment: (1) 5 h; (2) 15 h; (3) 24 h.

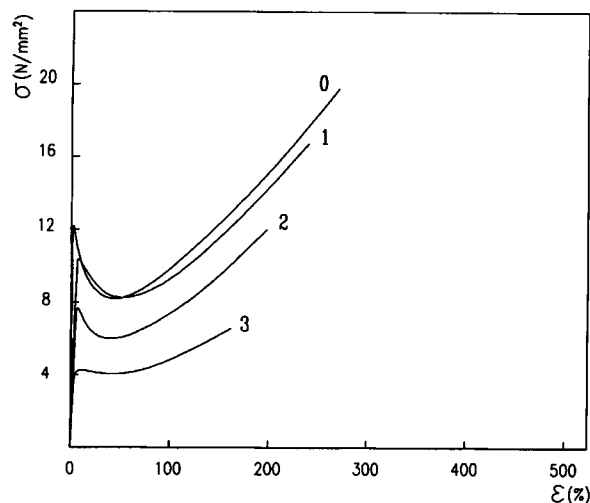


Figure 7 Change in tensile properties due to the photooxidative degradation of sample B3 (Table I) (0) before and after: (1) 5 h; (2) 10 h; and (3) 20 h.

linking for special applications^{8,9} considering also the degradation conditions.

The results in Figures 2 and 3 show the increase in strength and decrease of elasticity with increasing time of exposure at 150°C, as a consequence of enhanced cross-linking processes. The changes with heat were pronounced in samples with a high amount of cross-linking agent (Fig. 3). Heat treatment at 150°C is a common curing process in the industry and no degradation phenomena were expected. In the IR spectra of investigated samples the structural changes after heat treatment were not visible.

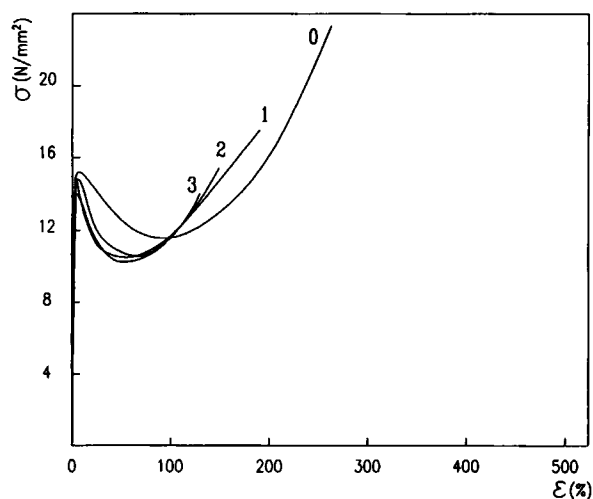


Figure 8 Change in tensile properties due to the influence of ultraviolet irradiation (0) before and after: (1) 10 h; (2) 15 h; (3) 24 h on MMA-BA-NMA system B4 (Table I).

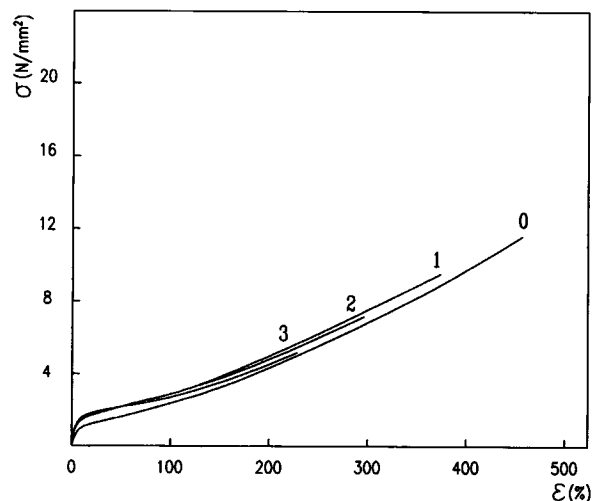


Figure 9 Stability of system B5 (Table I) under ultraviolet irradiation (0) before and after: (1) 5 h; (2) 19 h; and (3) 25 h (stress-strain).

The conclusion could be drawn that the B5 samples (Fig. 3), in comparison with the B3 samples (Fig. 2), under the influence of heat showed less changes because of the stabilizing influence of the cross-linked structure.

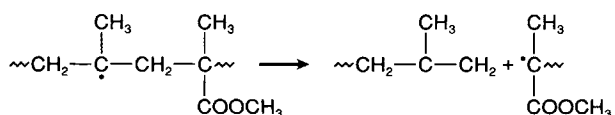
After UV irradiation of the various copolymer systems it was evident that at a longer time of exposure there were both decreases in strength and elongation of the samples (Figs. 4–9). The expected changes in the material structure can be accounted for by the degradation mechanisms of polyacrylate (PA) and polymethacrylate (PMMA) under UV irradiation.^{7,12}

Higher content of the MMA sequences in the copolymer systems causes preferential depolymerization (Scheme 2).^{7,12}

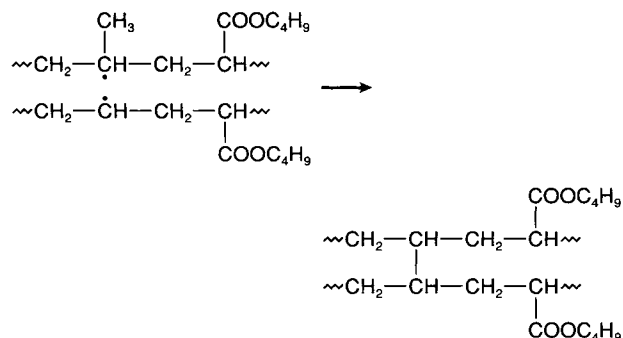
Butyl acrylate sequences in copolymer systems may be responsible for additional cross-linking via free radical combination (Scheme 3).^{7,12}

During UV degradation, PMMA molecular mass decreases,⁶ whereas PA become insoluble.^{6,7,13} Higher content of BA sequences in copolymer systems without cross-linking agent (Fig. 5) lowers the degradation processes because of possible concurrent reactions of the combination.

In the copolymer systems with similar initial ratios of MMA and BA units, the higher ratio of NMA



Scheme 2



Scheme 3

cross-linking agent, along with the mentioned stabilized effect of BA sequences, contribute more to the system stability (Figs. 6–9). The results also show that the reduced UV degradation relates to the higher content of MMA because of the stabilizing effect of the cross-linked structure.

CONCLUSIONS

The mechanical behavior under degradative conditions of the investigated systems indicates that the chemical composition of these copolymer systems has a specific influence on their properties in 6 thermooxidative and/or photooxidative degradation. It is concluded that a higher content of MMA units can lead to preferential depolymerization; the opposite effect was observed when BA content increases. A cross-linking agent should be used for the MMA/BA systems as a stabilizing component and leads to better retention of the mechanical properties. The spectroscopic investigation showed no substantial changes in IR spectra after thermal and UV degradation of the samples. The observed changes in mechanical properties found, that is, reduction of yield point, strength, and elongation, and

increase in brittleness, may be attributed to the presence of various ratios of constitutive sequences and cross-linked structures before and after degradation.

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