

COPOLYMERIZATION OF METHYL METHACRYLATE (MMA) AND BUTYL ACRYLATE (BA) AND POLYBLENDS WITH CHLORINATED RUBBER (CR)

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Synthesis of MMA-Co-BA was accomplished at 60°C using benzoyl peroxide as initiator. It is observed that MMA and BA form copolymers in all monomeric ratios. Tensile properties and hardness were determined for the films prepared from the blends of chlorinated rubber and MMA-Co-BA. Tensile strength of the films increases as the amount of chlorinated rubber is increased. The increase in tensile strength might be due to intermolecular and intramolecular rearrangements of copolymer molecules with chlorinated rubber and an increase in the crosslinking density of the system. The rearrangement of copolymer molecules with chlorinated rubber also enhanced the elongation at break. The addition of copolymer and plasticizer make the films more soft and flexible.

Key words: Monomeric ratios, Tensile properties.

Introduction

Solution blending of butyl acrylate/ethylate copolymers (Khan *et al* 1998) and methyl methacrylate/butyl acrylate/ethyl hexyl acrylate terpolymer with chlorinated rubber have been reported earlier (Khan *et al* 1999). The main aim of those studies was to determine the tensile properties of the blends. It was concluded that the blends serve as good film forming materials and may be used in surface coating formulations for leather. The present paper deals with the synthesis of MMA-Co-BA using benzoyl peroxide as catalyst and MEK as a solvent. Solution blending of this copolymer with CR is being investigated.

Experimental

Materials. Butyl acrylate (Fluka), methyl methacrylate (E.Merck) were purified before use. These monomers were successively washed with 5% NaOH and distilled water to remove inhibitor and dried over anhydrous sodium sulfate. The monomers were thus distilled and middle fractions were collected. Solvents like MEK, toluene, xylene, DMF, DMSO, benzene, acetone, THF, ethyl acetate and alcohol were distilled before use. Benzoyl peroxide was recrystallized twice from chloroform-methanol solvent precipitant system. Chlorinated rubber (Cl 65%, KOH value 0.899, Iodine value 0.24%) was dissolved in MEK and by precipitating with methanol, chlorinated paraffine of commercial grade was used.

Procedure of copolymerization. All copolymerization reactions were carried out in flange flask fitted with stirrer, con-

denser, thermometer, funnel and nitrogen inlet and kept at 60°C for 3.5 hrs. The required quantity of BA and MMA as shown in Table 1 was transferred to the reaction flask already containing an equal quantity of MEK and benzoyl peroxide (1%). After the required reaction time, aqueous methanol (50%) was added to stop the reaction. A viscous material was obtained. It was then precipitated and washed to remove unreacted butyl acrylate and methyl methacrylate with water methanol mixture and dried to constant weight by keeping the product sample in a desiccator under vacuum. The product was found soluble in most of the organic solvents like benzene, toluene, xylene, acetone, ethyl acetate, chloroform, THF but insoluble in MEK. It swells in DMF, DMSO, silicone oil and alcohol. I.R.spectrum of the product was also recorded to identify the attachment of butyl acrylate and MMA molecules by the appearance of characteristics absorption bands. The copolymer samples were estimated for C and H.

Table 1
Copolymerization of butyl acrylate (BA) and methyl methacrylate (MMA) using benzoyl peroxide as initiator at 60°C for 3.5 hr.

MMA mole	BA mole	Yield %	Elemental analysis %			[η] dl/g	Mn
			C	H	O		
0.188	0.5612	65.5	62.40	7.9	29.7	0.17	59855
0.376	0.4209	74.0	61.99	8.1	29.91	0.18	64945
0.564	0.2806	84.7	61.94	8.4	29.64	0.21	80945
0.752	0.1403	90.2	61.00	8.2	30.8	0.24	97955

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Preparation of polyblends for casting films. Blends of chlorinated rubber and copolymer samples in xylene were prepared at 60°C according to the ratios depicted in Table 2 and 3. Films (10x15 cm²) of the polyblends were cast at room temperature. Solvent was evaporated slowly over a period of 2 days and the films were dried by keeping in a vacuum desiccator.

Measurements of tensile properties and hardness. Tensile strength and elongation at break were measured on an Instron Universal Testing Machine Model No.4031 as per ASTM-D/412. (ASTM 1965). Hardness of the films were measured on rubber tester model 1951.

Results and Discussion

Table 1 illustrates the results of copolymerization of MMA and BA in MEK using benzoyl peroxide as initiator at 60°C. Tables 2-5, include the data regarding tensile properties of polyblends prepared from the binary mixture of chlorinated rubber (CR) and product samples in different ratios.

The product samples were identified to be copolymers of BA and MMA with the help of elemental analysis, solubility, I.R.spectral studies, molecular weight. The composition of the product was determined for C and H. The four samples of the product contain 61-62.4% C, 7.9-8.4% H and 29.64-30.8% O (by difference) whereas prepared sample of poly (MMA) contains C, H and O respectively as 59.9%, 7.98% and 32.1%. Similarly the estimation of prepared sample of poly (BA) gives C, H and O as 65.5%, 9.2% and 25.0% respectively. The variation in composition infers that both monomers have participated in the reaction to form a new product. Solubility of the product samples in different organic solvents may help in the identification and confirms the participation of both monomers in the copolymerization.

Table 2

Tensile properties, hardness of the films prepared from the blends of chlorinated rubber (CR) and

copolymer $\left(\frac{\text{MMA}}{\text{BA}} = \frac{0.188}{0.5612} \text{ mole}\right)$

CR wt %	Copolymer wt %	Plasticizer wt %	Tensile strength MPa	Eloagation at break %	Hardness shore-A
100	0.0	-	7.485	0.5	75
100	0.0	1.0	6.400	1.5	75
60	4.0	-	33.0	9.5	76
60	40	1.0	25.5	16.0	60
55	45	-	33.0	10.5	76
55	45	1.0	29.0	18.5	75
50	50	-	31.7	15.0	75
50	50	1.0	21.0	21.0	68

The product is found to be soluble in most of the organic solvents like benzene, toluene, xylene, ethyl acetate, acetone, chloroform, THF, methylene chloride and butyl acetate but insoluble in MEK. In general, the acrylates when free of crosslinking are soluble in chloroform, ethyl acetate, toluene, acetic acid and related solvents whereas poly (MMA) and other acrylates slowly dissolve in acetone. These observations support the evidences of elemental analysis. I.R. spectral studies have also been carried out. In the spectrum of the product the absorption bands with maxima at 3250 (s) 2800 (w), 1600 (w), 1450(m), 1300(m), 1150(s), 980 (cm)⁻¹ are characteristics of C-C bands. The 1720 cm⁻¹ (s) absorption is a characteristic stretching vibration. The evidence is

Table 3

Tensile properties, hardness of the film prepared from the blends of chlorinated rubber (CR) and

copolymer $\left(\frac{\text{MMA}}{\text{BA}} = \frac{0.376}{0.4209} \text{ mole}\right)$

CR wt %	Copolymer wt %	Plasticizer wt %	Tensile strength MPa	Eloagation at break %	Hardness shore-A
100	-	-	7.485	0.5	75
100	-	1.0	6.240	1.5	75
60	40	-	33.0	28.5	77
60	40	1.0	27.5	34.5	75
55	45	-	30.0	27.5	76
55	45	1.0	30.5	36.0	75
50	50	-	31.7	28.5	75
50	50	1.0	30.0	39.9	75
55	45	-	29.0	29.0	70
55	45	1.0	27.0	39.6	70

Table 4

Tensile properties, hardness of the film prepared from the blends of chlorinated rubber (CR) and

copolymer $\left(\frac{\text{MMA}}{\text{BA}} = \frac{0.5640}{0.2806} \text{ mole}\right)$

CR wt %	Copolymer wt %	Plasticizer wt %	Tensile strength MPa	Eloagation at break %	Hardness shore-A
100	-	-	7.485	0.5	75
100	-	1.0	6.40	1.5	75
60	40	-	38.6	7.6	75
60	40	1.0	28.6	9.8	75
55	45	-	27.0	10.0	75
55	45	1.0	22.0	13.7	72
50	50	-	26.0	10.5	70
50	50	1.0	28.0	15.0	70
45	55	-	31.4	12.0	70
45	55	1.0	28.0	16.5	72

sufficient to confirm the coupling of the growing polymer chains of poly (BA) and poly (MMA) to form MMA-co-BA, an alternating copolymer.

In Fig 1 yield (%) is plotted against MMA (%) in feed which indicates that in the binary mixture of MMA and BA, the rate of formation of copolymers increases with increasing concentration of MMA and shows that both monomers participate in the reaction and form copolymers at all monomeric ratios.

The measurement of viscosity of dilute solutions is the most commonly used method for determining the molecular weight. Mn of the copolymer sample were calculated from the intrinsic viscosity $[\eta]$ -- molecular weight relationship (Fox *et al* 1962).

Table5

Tensile properties, Hardness of the film prepared from the blends of chlorinated rubber (CR) and copolymer ($\frac{\text{MMA}}{\text{BA}} = \frac{0.752}{0.140}$ mole)

CR wt %	Copolymer wt%	Plasticizer wt %	Tensile strength	Eloagation at break	Hardness shore-A
100	-	-	7.485	0.5	75
100	-	1.0	6.140	1.50	75
60	40	-	28.50	13.7	70
60	40	1.0	26.2	21.4	65
55	45	-	24.0	15.0	70
55	45	1.0	20.0	50.0	65
50	50	1.0	20.0	116.0	65
50	50	1.0	17.0	118.0	60
45	55	-	13.0	246.0	60
45	55	1.0	11.0	250.0	55

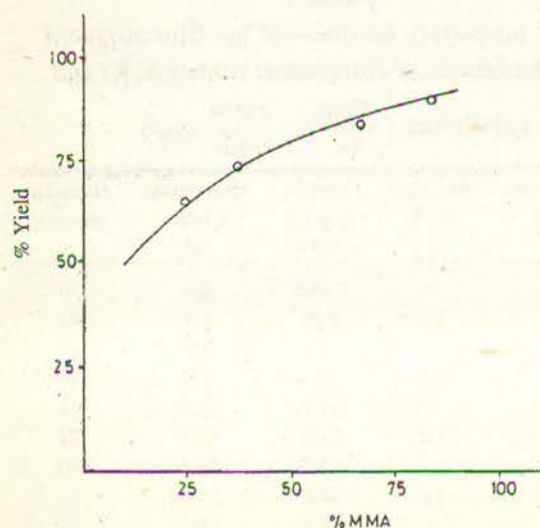


Fig 1. A plot % yield vs % MMA in feed.

$$[\eta] = 7.7 \times 10^{-5} \text{Mn}^{0.7}$$

The intrinsic viscosity of dilute solutions of the product samples prepared in acetone was determined by plotting η_{sp}/C vs C where η_{sp} is the specific viscosity and C is the concentration of dilute solution expressed in percentage. Viscosity was measured at 30°C. The intrinsic viscosity of the copolymer samples was found to be in the range 0.17-0.24 dl/g and the molecular weight was calculated to be 59855 - 97955.

Polyacrylates are generally used in surface coating formulations to meet various types of applications. Specially they are used in coating formulation for leather finishing. Polyacrylates yield films but possess some disadvantages like tackiness and difficulties in handling. To overcome this drawback, blends of polyacrylates with CR were prepared at 60°C according to ratios shown in Tables 2-5. Films of these blends in the presence and absence of chlorinated paraffin (as plasticizer) were cast. Films cast for 100% CR were found to be brittle or rigid. Addition of plasticizer decreased the rigidity of the films. Tables 2-5 explain tensile properties and hardness of the films prepared from the blends of copolymer and CR. Tensile strength of the films prepared from 100% CR was measured as 7.5 MPa whereas elongation at break was found to be as 0.5%. The addition of chlorinated paraffins decreased the tensile strength upto 6.4 MPa whereas the addition of copolymers of different compositions enhanced the tensile strength of the films giving results in the ranges 31.7-33.0 MPa for 0.188/0.5612 mole (MMA/BA), 29.0-33.0 MPa for 0.376/0.4209 mole (MMA/BA), 31.4-38.6 MPa for 0.564/0.2806 mole (MMA/BA) and 13.0/28.5 mole (MMA/BA). It shows that tensile strength gets increased with increasing concentration of CR in blends. The increase in tensile strength might be due to intermolecular and intramolecular rearrangement of copolymer molecules with chlorinated rubber and an increase in the cross-linking density of the system. Similar observations were made in the blend of polyurethane-polyacrylate (MMA/MA) copolymer (Encyclopedia 1970; Frisch *et al* 1974; Khan 1998) and chlorinated rubber- polyacrylate copolymer (Pitchumani *et al* 1982). Due to cross-linking, swelling properties of such polyblends get developed. The rearrangement of copolymer molecules with CR also enhanced the elongation at break. Furthermore, copolymer monomer units also affect the tensile properties as indicated by the tensile properties of blends prepared with copolymer samples of different monomeric ratios (Tables 2-5). In an earlier paper (Khan *et al* 1999) tensile strength of polyblends based on 40% terpolymer sample (BA-MMA-ethylhexylacrylate) and 60% CR in the presence or absence of plasticizer has been

reported respectively as 36.9 or 31.5 MPa whereas the copolymer under discussion at these ratios shows tensile strength in the presence or absence of plasticizer as 27.5 or 33.0 MPa respectively (Table-3). In another paper (Fox *et al* 1962) the polyblends based on 40% copolymer (BA-Co-EA) and 60% CR in the presence and absence of chlorinated paraffin gives tensile strength respectively as 19.4 and 23.8. It means that the nature of copolymer or terpolymer influence the strength of films. Besides tensile strength and elongation at break, the addition of plasticizer and copolymer/terpolymer also affects the hardness of the films prepared with CR. The hardness gets decreased from 75 to 60. According to these results, it is evident that the addition of plasticizer and copolymer makes the films soft and flexible.

In brief, the blends of copolymer MMA-Co-BA and CR alongwith chlorinated paraffin are able to form films free of tackiness and may be used in leather finishing.

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