

# Physical Sciences Section

Pak J Sci Ind Res 1998 41 (1) 1-5

## SYNTHESIS OF n-BUTYL ACRYLATE-CO-ETHYL ACRYLATE AND POLYBLENDS WITH CHLORINATED RUBBER (CR)

A Rasheed Khan\*, Kausar Ali Syed, Khalid Mehmood and A F K Ibrahimi

PCSIR Laboratories Complex, Off University Road, Karachi-75280, Pakistan

(Received 7 May 1995; accepted 26 July 1997)

Free radical copolymerisation of n-butyl acrylate (n-BA) and ethyl acrylate (EA) in methyl ethyl ketone (MEK) was accomplished at 60°C using BPO as initiator. It was observed that these monomers form copolymers in all monomeric ratios. Tensile properties and hardness were investigated for the polyblends prepared from chlorinated rubber and n-BA-Co-EA. It was further observed that crosslinking density is increased with increase in the concentration of chlorinated rubber. Increase in crosslinking density appeared in the form of more tensile strength. Plasticizer and copolymer made the polyblends more soft and flexible. It is concluded that these blends may serve as good film forming materials.

**Key words:** Polymer blends, Chlorinated rubber, Butyl acrylate, Ethyl acrylate.

### Introduction

A significant amount of literature refers to the blending technique for the modification of properties of acrylic polymers, copolymers and terpolymers (Keskkula 1967; Davies 1968; Bruins 1970; Goh and Lee 1990; Neo *et al* 1991). Due to some disadvantages like tackiness and difficulty in handling, these polymers cannot be used in the coating formulations particularly for leather. This disadvantage may be removed by blending acrylic polymers with chlorinated rubber (CR). These polyblends may serve as a good film forming materials (Davies 1968; Pitchumani *et al* 1982; Goh *et al* 1990; Neo *et al* 1991). In these modifications the role of plasticiser is very important. Plasticiser produces lower glass transition temperature ( $T_g$ ) and lower tensile strength for the principal polymers. This paper describes the copolymerization of n-butyl acrylate (n-BA) and ethyl acrylate (EA) and modification of the properties of copolymer with CR.

### Experimental

n-Butyl acrylate (Fluka) and ethyl acrylate (Merck) were purified before use. These monomers were first washed with sodium hydroxide to remove inhibitor and then with water three times, dried on calcium chloride and finally distilled. The middle fractions were used for copolymerisation. Methyl ethyl ketone (Merck) and xylene (laboratory reagent grade) were purified and distilled. Benzoyl peroxide was crystallized in chloroform twice. Chlorinated rubber (KOH value=0.899, iodine

value 0.24%) was purified by dissolving in MEK and precipitating by methanol.

**Procedure of copolymerisation.** Copolymerisation reactions were carried out in a four neck round bottom flask fitted with a stirrer funnel, condenser and thermometer and kept at 60°C for 5 h. The required amount of monomers and BPO as shown in Table 1, was added in the reaction flask already containing a fixed volume of MEK (46 ml). After required reaction time, the product was precipitated into water-methanol and dried to a constant weight. A highly tacky transparent material was obtained, which was found to be soluble in a number of organic solvents but insoluble in MEK. The IR spectra of the product were also recorded to ensure copolymer formation and the refractive index was measured on refractometer No.122894 of Zeiss Opton (Germany). The copolymer samples were also estimated for C and H.

**Preparation of blends.** Binary blends of CR and copolymer in weight ratios were prepared in xylene by constant stirring at 60°C. The resulting viscous solution was clear and homogeneous. Films (10cm x 15 cm) were casted in a die at room temperature from blend solution and solvent was allowed to evaporate slowly over a period of 2 days. The films were dried in vacuum to remove solvent and stored in desiccator.

**Measurements of hardness and tensile properties.** Tensile strength and elongation at break were measured on Instron Universal Testing Machine Model No.4031 as per ASTM-D-412 (ASTM Standards 1965). Hardness of films pre-

\*Author for correspondence

pared from the polyblends was also measured on Rubber Tester Model 1951.

## Results and Discussion

Table-1 includes data regarding the copolymerisation of n-BA and EA in MEK using BPO (1%) as initiator at 60°C for 5 h. The copolymers prepared in different monomeric ratios were characterized by elemental analysis, solubility, refractive index and IR spectral studies. Five samples of the product contain 61.09 - 63.2% C and 8.2 - 8.7% H (Table 1). The prepared samples of poly (n-BA) and poly (EA) contain 65.4% C and 9.25% H and 59.9% C and 7.95% H respectively. This variation in percentages of C and H shows the attachment of growing polymer chains of poly (n-BA) and poly (EA) to each other. It is evidential of the formation of copolymer. Solubility plays a significant role in the identification and ensuring the participation of both n-BA and EA in the copolymerisation. The product is soluble in acetone, benzene, toluene, xylene, chloroform, ethyl acetate, butylacetate, THF and DMF but insoluble in MEK. The refractive index of poly (n-BA), poly (EA) and the product was recorded. The refractive index of

poly (n-BA) and poly (EA) was 1.4920 and 1.494 respectively whereas that of the product was 1.4824 - 1.4980. This difference in the value of refractive index, though little, provides further evidence that the product is a copolymer. The IR spectra of the product also support that the product is a copolymer. In spectrum of the product, the absorption bands with maxima at above 2950 (s), 1450(m), 1260 (m), 1136 (m), 952 (w)  $\text{cm}^{-1}$  are characteristics of C-C bands. The 1725  $\text{cm}^{-1}$  band is characteristic of the C-C stretching vibration. Hence all the evidences confirm the coupling of the growing polymer chains of poly (n-BA) and poly (EA) to form a copolymer.

The data shown in Table 1 indicates that the rate of formation of copolymers increased with an increase in the monomeric ratio of ethyl acrylate in the binary mixture of monomers. The conversion was maximum at a high feed value of ethyl acrylate. Copolymer samples were white, transparent, soft and highly tacky substances at room temperature.

Binary blends of these copolymers with CR in weight ratios were prepared with a view to achieve suitable blend composition. For this purpose, films of these blends in the presence or absence of plasticiser (chlorinated paraffin) were casted. The

**Table 1**  
Copolymerization of n-butyl acrylate (n-BA) and ethyl acrylate (EA) in the presence of methyl ethyl ketone (MEK) using benzoyl peroxide (1%) as catalyst at 60°C for 5 h

S.No.	n-BA g	EA g	Yield g	Elemental C (%)	H (%)	Analysis O (%)	Colour	Appearance	Consistency	refractive Index
1.	9.0	37.0	43.7	61.09	8.28	30.71	White	Soft	Highly tacky	1.4850
2.	13.5	32.5	43.0	61.60	8.38	30.02	"	"	"	1.4860
3.	18.0	28.0	41.4	62.06	8.45	29.49	"	"	"	1.4860
4.	22.5	23.5	40.5	62.63	8.65	28.72	"	"	"	1.4840
5.	27.0	19.0	38.6	63.2	8.7	28.10	"	"	"	1.4824

**Table 2**  
Tensile properties, hardness of the films prepared from the blends of chlorinated rubber (CR) and n-BA/EA (19.5/80.5) copolymer

S.No.	CR wt %	Copolymer wt %	Plasticizer wt %	Tensile strength MPa	Elongation %	Shore A hardness
1.	70	30	-	33.668	18.7	70
2.	70	30	1.0	22.131	45.0	65
3.	60	40	-	16.432	124.3	67
4.	60	40	1.0	15.940	144.3	65
5.	50	50	-	13.812	242.0	65
6.	50	50	1.0	11.400	269.0	60
7.	100	-	-	7.485	0.5	75
8.	100	-	1.0	6.140	1.3	75

amount of CR in the binary blends varied within the range of 50-70% to conserve the main characteristics of the films. The films casted from CR (100%) was found to be brittle or rigid. Addition of plasticiser decreased the rigidity of the films. The films of copolymer of n-BA and EA were highly tacky, flexible and difficult in handling due to which it was not possible to measure their tensile properties.

Tables 2-6 describe tensile properties and hardness of the films prepared from the blends of copolymers and CR. Tensile strength of the films prepared from 100% CR was found to be 7.485 MPa and elongation at break was measured as 0.5%. The addition of chlorinated paraffin lowered the tensile strength upto 6.140 MPa but enhanced the elongation at break upto 1.3%. Data shown in Tables 2-6 indicate that the addition of copolymer enhanced tensile strength of the films in the ranges 11.4 - 33.6 MPa, 13.8 MPa, 17.1-38.4 MPa, 15.7-35.5 MPa, 13.7-35.1 MPa and the elongation in the ranges 18.7-269%, 20.5-280%, 7.3-235%, 7.7-293% and 7.5-377% for the co-

polymer of different compositions. In Fig. 1, the tensile strength is plotted against percentage of chlorinated rubber in the blends. It shows that the tensile strength increased with increasing concentrations of CR in the blends. This may be due to increase in the crosslink density of the system caused by intermolecular or intramolecular linkages of copolymer molecules with CR units. It may also be due to homogenous blending and thermoplasticity of the blend in nature. Similar things happened in the blend of polyurethane-polyacrylate (MMA-MA) copolymer (Frisch *et al* 1974; Encyclopedia 1970) and chlorinated rubber polyacrylate (BMA-EA) copolymer (Pitchumani *et al* 1982). But the polyblends of BMA-Co-EA and CR show different tensile strength and elongation at break. For example at a ratio 53.3/46.7 (CR/Copolymer) in the absence of plasticizer, the polyblends show tensile strength and elongation at break respectively as 11.98-22.8 MPa and 3.0-7.0%. On the other hand, the polyblends of CR and n-BA-Co-EA at a ratio 50/50 (CR/copolymer) show tensile strength

Table 3

Tensile properties, hardness of the films prepared from the blends of Chlorinated Rubber (CR) and n-BA/EA (29.3/70.7) copolymer

S.No.	CR wt %	Copolymer wt %	Plasticizer wt %	Tensiler strength MPa	Elongation %	Shore A hardness
1.	70	30	-	30.950	20.5	70-67
2.	70	30	1.0	29.969	25.2	65
3.	60	40	-	23.485	101.8	67
4.	60	40	1.0	17.535	121.9	65
5.	50	50	-	15.648	227.4	67
6.	50	50	1.0	13.832	280.8	65
7.	100	-	-	7.485	0.5	75
8.	100	-	1.0	6.140	1.3	75

Table 4

Tensile properties, hardness of the films prepared from the blends of Chlorinated Rubber (CR) and n-BA/EA (39.3/60.7) copolymer

S.No.	CR wt %	Copolymer wt %	Plasticizer wt %	Tensile strength MPa	Elongation %	Shore A hardness
1.	70	30	-	38.406	7.28	70
2.	70	30	1.0	33.756	10.50	68
3.	60	40	-	32.824	36.2	68
4.	60	40	1.0	22.170	144.4	68
5.	50	50	-	17.501	237.0	65
6.	50	50	1.0	17.108	235.0	60-65
7.	100	-	-	7.485	0.5	75
8.	100	-	1.0	6.141	1.3	75

as 227-343 MPa and elongation at break as 13.8-17.5%. The values of polyblends related to BA-Co-EA are on higher side. Chlorinated rubber used in the formation of blends show KOH value as 0.899 and iodine value 0.24% (very low unsaturation). Both copolymers BMA-Co-EA and n-BA-BA-Co-EA are different in physicochemical nature. Butyl methyl acrylate  $H_2C=C(CH_3)CO_2(CO_2)_3 CH_3$  contains methyl group on the vinyl side chain of BMA resulting in the increase of negative charge which alters its chemical activity (Yousufzai et al 1985; Encyclopedia 1970). On the other hand butyl acrylate  $H_2C=CHCO_2(CH_2)_3CH_3$  contains H on the vinyl side chain which makes BA less reactive towards EA. In other words reactivity of BMA is greater than BA towards EA. This influences the crosslink density of the system caused by intermolecular or intramolecular linkages of copolymer molecules and CR units and hence the tensile properties. Moreover tensile strength increases with increased n-BA content in the copolymer whereas percentage of elongation decreases with the increasing amount of n-BA in the copolymer. It shows that

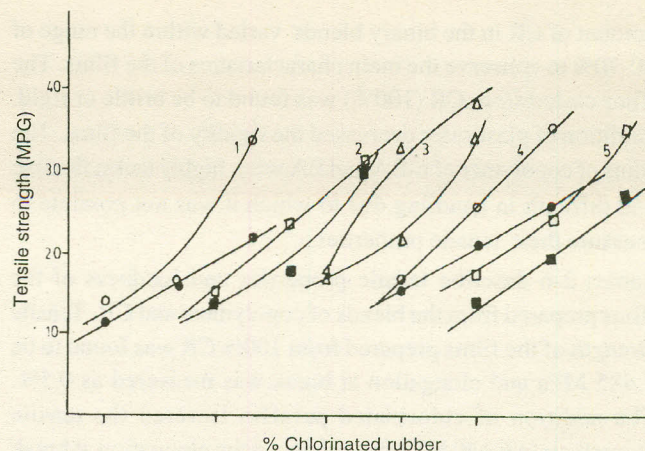


Fig.1.Effect of concentration of CR on tensile strength of polyblends prepared from chlorinated rubber and poly (n-BA-co-EA). Hollow points show polyblends without plasticizer and solid points relate to polyblends with plasticiser. Number shows the composition of copolymer, (1) BA/EA=19.5/80.5, (2) BA/EA=29.3/70.7, (3) BA/EA=29.3/70.7 (4) BA/EA=48.9/51.1, (5) BA/EA=58.7/41.3. Each line starts from 50% to 70% along X-axis.

Table 5

Tensile properties, hardness of the films prepared from the blends of Chlorinated Rubber (CR) and n-BA/EA (48.9/51.1) copolymer

S.No.	CR wt %	Copolymer wt %	Plasticizer wt %	Tensiler strength MPa	Elongation %	Shore A hardness
1.	70	30	-	35.473	7.7	70
2.	70	30	1.0	26.261	36.8	68
3.	60	40	-	25.947	74.9	66
4.	60	40	1.0	21.150	132.2	65
5.	50	50	-	17.295	281.0	65
6.	50	50	1.0	15.696	293.0	60-65
7.	100	-	-	7.485	0.5	75
8.	100	-	1.0	6.141	1.3	75

Table 6

Tensile properties, hardness of the films prepared from the blends of Chlorinated Rubber (CR) and n-BA/EA (58.7/41.3) copolymer

S.No.	CR wt %	Copolymer wt %	Plasticizer wt %	Tensile strength MPa	Elongation %	Shore A hardness
1.	70	30	-	35.149	7.5	70
2.	70	30	1.0	26.820	31.8	65
3.	60	40	-	23.828	41.5	66
4.	60	40	1.0	19.364	162.5	65
5.	50	50	-	17.402	343.0	65
6.	50	50	1.0	13.763	377.0	60-65
7.	100	-	-	7.485	0.5	75
8.	100	-	1.0	6.141	1.3	75

more n-BA content does not produce flexibility in the films.

The effect of plasticiser, viz chlorinated paraffin was also investigated. From the results shown in Tables 2 - 6, the addition of chlorinated paraffin in the blend reduced the tensile strength and increased the elongation at break in all the system. A little amount of chlorinated paraffin makes the film flexible. Plasticiser molecules penetrate between the polymer chains, thus reducing their mutual attraction and allowing the polymer to be more flexible.

Hardness of the films prepared from different compositions of blends were measured. The films prepared in the absence or presence of plasticiser from 100% CR give Shore-A hardness 75. The addition of copolymer as well as that of plasticiser in the blend, decreased Shore-A hardness upto 60. It shows that copolymer and plasticiser produce softness and flexibility in the film.

### References

- ASTM 1965 Method of Tensile Testing D1708 Part 27 and 412D. American Society for Testing Materials Philadelphia U.S.A.
- Bruins P F 1970 *Polyblends and Composites*. Wiley Interscience, New York.
- Davies D L 1968 *Technology of Paints, Varnishes and Lacquers*. Martens C E ed., Reinhold Book Corporation New York, 1968.
- Frisch K C, Klempner D, Antczak T, Frisch H L 1974, Stress-strain properties of polyurethane - polyacrylate interpenetrating polymer networks. *J Appl Polym Sci* **18** 1683.
- Goh S H, Lee S Y 1990 Miscible binary blends of poly  $\alpha$ -methyl styrene-Co-acrylonitrile with poly Chloromethyl methacrylate and poly methoxymethyl methacrylate. *Polymer Commun* **31** (12) 463.
- Keskkula H 1967 *Polymer Modification of Rubber and Plastics*. Wiley Interscience, New York.
- Neo M K, Lee S Y, Goh S H 1991 Miscibility of poly 2-chloroethyl methacrylate with poly styrene-CO-AN and poly p-methyl styrene-CO-AN. *Eur Polym J* **27** (8) 831-836.
- Pitchumani S, Rami R C, Rajadurai S, Joseph K T, Santappa M 1982 Tensile properties of blends of copolymers of n-Butyl methacrylate with ethyl acrylate and chlorinated rubber. *Eur Polymer J* **18** 949-952.
- Van Oss J F 1973, *Chemical Technology*. Barnes & Noble Books, New York Vol IV. pp 630.
- (a) *Encyclopedia of Polymer Science and Technology* 1970. John Wiley and Sons Inc. New York Vol 13.
- (b) Yousufzai A H K, Khan A Rasheed, Akhtar Tehzeeb 1985, Free radical copolymerization of MMA with  $\alpha$ -pinene. *Pak J Sci Ind Res* **28** (2) 135.