Synthesis of Terpolymer of Ethyl Acrylate (EA), n-Butyl Acrylate (n-BA) and Butyl Methacrylate (BMA) and Solution Blending with Chlorinated Rubber (CR)

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Free radical terpolymerization of ethylacrylate, n-butyl acrylate and butyl methacrylate has been carried out at 95°C using benzoyl peroxide as initiator. It has been observed that the three monomers polymerized simultaneously and form terpolymer in all monomeric ratios. EA enters in the growing polymer chain more rapidly than n-BA and BMA. The terpolymers of 24130-38575 molecular weight are obtained. All terpolymer samples are highly tacky transparent viscous material. The refractive index of terpolymer samples ranges 1.495-1.497. It may be used as tackifying agent in the preparation of adhesive. Besides, the blends of chlorinated rubber and terpolymer alongwith plasticizer may be used as a good film forming materials in the surface coating of leather.

Key words: Terpolymerization, Ethylacrylate, Chlorinated rubber, Flexible.

Introduction

Polyacrylates are important in surface coating formulations to meet various type of applications like leather finishing (Bruins 1970). The blends of polyacrylates and chlorinated rubber (CR) in the presence or absence of suitable plasticizer form soft flexible and tack free films on the surface of the leather. The treatment of such blends on the surface of leather give good finishing (Pitchuman *et al* 1982). In our earlier publications the blending of copolymer of n-butyl acrylate and ethyl acrylate and terpolymer of butyl acrylate, ethyl hexylacrylate and MMA with chlorinated rubber was reported (Khan *et al* 1998 and 1999). The tensile properties of such blends were discussed and reciepts were recommended. This paper deals with the synthesis of a terpolymer of ethyl acrylate, butyl methacrylate and n-butyl acrylate using benzoyl peroxide as catalyst and solution blending of this terpolymer with CR and study of their tensile properties.

Experimental

Materials. Chlorinated rubber (KOH value = 0.899, iodine value 0.24%) was purified by dissolving in MEK and precipitating by methanol. Ethyl acrylate (EA), n-butyl acrylate (n-BA) and butyl methacrylate (BMA) were purified before use. These monomers were washed with alkali to remove added inhibitor and then with water thrice, dried on $CaCl_2$ and finally

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distilled. Benzoyl peroxide (BP) was crystallised in chloroform. All organic solvents were distilled before use.

Procedure of polymerization. All reactions were carried out in sealed tubes. Required quantity of monomers as shown in Tables 1 and 2 were transferred to reaction tubes already containing BP. The tubes were then cooled and sealed at constriction. The sealed tubes were heated at 95°C in a water bath. After required reaction time, the tubes were cooled and broken open. The resulting viscous product was precipitated with aqueous methanol to remove unreacted monomers. It was then finally dried to remove methanol and water to a constant weight. A highly tacky transparent material was obtained which was found to be soluble in benzene, toluene, xylene, acetone, MEK, ethyl acetate, butyl acetate and partially in THF. The product swelled in isopropanol, methanol, ethanol, cyclohexane etc. Besides homopolymers of EA, BMA and n-BA were also prepared to compare different parameters like carbon, hydrogen refractive index and tensil properties of the blends with the product. The IR spectrum of the product was also recorded to establish terpolymer formation. The spectrum of the product showed absorption bands with maxima at 2980(s), 1740(s), 1450(m), 1370(w), 1260-1140(s), 1020(w), 840(w) cm^{-1}. The product samples were also analysed for carbon and hydrogen. The elemental analysis of the nine samples of the product are illustrated in the respective tables. They contain 63.3 to 65.25% carbon, 8.7 to 9.2% hydrogen and 25.55-28.0% oxygen (by difference). Homopolymer of

BA contains 59.9% carbon and 7.93% hydrogen and homopolymer of BMA estimates 56.15% carbon, 9.78% hydrogen whilst poly (n-BA) shows 65.5% carbon and 9.25% hydrogen. Refractive index was also measured on refractometer no.122894 of Zein Opton (Germany). The refractive index of product was measured at room temperature. The refractive index of the product samples ranges 1.495 to 1.497 (see Table 3) whereas poly (EA), poly (BMA) and poly (n-BA) give refractive index as 1.4940, 1.4974 and 1.4020 respectively. The viscosities of the dilute solutions of product samples were measured at 30°C using acetone as solvent. The following relations was used to calculate molecular weight (Fox *et al* 1962). This equation is valid to calculate molecular weight of polyacrylate solution in acetone:

$$[\eta] = 7.7 \times 10^{-5} \overline{M}_n^{0.7}$$

Where $[\eta]$ is the intrinsic viscosity of dilute solution of terpolymers obtained by ploting η_{sp}/C against C. Here η_{sp} is the specific viscosity and C is the concentration of dilute solutions of terpolymer prepared in acetone. The intrinsic viscosity of terpolymer was found to be in the range 0.09 - 0.125 dl g^{-1} and molecular weight ($\overline{M}_n$) was calculated to be 24130 - 38575. The detailed data are shown in Table 3.

Preparation of polyblends. The polyblends of terpolymer and CR in weight ratios were prepared in xylene as given elsewhere (Khan *et al* 1998) by constant stirring at 60°C. A clear viscous homogeneous solution was obtained. Films (30 cm x 20 cm) were cast in a die at room temperature and dried by keeping in vacuum desiccator.

Measurement of tensile parameters and hardness. Hardness of the films prepared from polyblends were measured on rubber tester model 1951. Tensile strength and elongation at break were measured on Instron Universal Testing Machine Model no.4031 as per (ASTMD-412 1965). All data are shown in the respective Table 4.

Results and Discussion

Tables 1-2 illustrate the results obtained by bulk free radical terpolymerization of ethyl acrylate (EA), butyl methylacrylate (BMA) and n-butyl acrylate (n-BA) using BP as initiator at 95°C for 8 h whereas Table 3 includes some physical parameters like intrinsic viscosity, molecular weight, refractive index etc. of terpolymer.

Estimation of product for elemental analysis solubility, refractive index, IR spectral studies, intrinsic viscosity establish the product to be a terpolymer. The nine samples of the product contained 63.3 to 65.25% carbon, 8.7 to 9.2% hydrogen and 25.55 - 28.0% oxygen. The percent of oxygen was obtained by difference. The prepared samples of poly (EA), poly (BMA)

and poly (n-BA) contained 59.9% carbon and 7.93% hydrogen, 56.15% carbon and 9.78% hydrogen and 65.5% carbon and 9.25% hydrogen respectively. The variation in percentage of carbon and hydrogen showed the coupling of growing polymer chains of EA, BMA and n-BA to each other and form a new product. Aromatic and chlorinated hydrocarbons (benzene, chloroform), esters (butyl acetates), 80/20 toluene/methyl alcohol mixture gave low viscosity solution of polyacrylates. The poly (acrylates) when free of crosslinking dissolve in chloroform, ethyl acetate, toluene, acetic acid and related solvents whereas poly (MMA) and other acrylates slowly disperse in acetone. The product samples were soluble in acetone, benzene, toluene, xylene, ethyl acetate, butyl acetate but insoluble in chloroform (CC1$_4$), petroleum, methylene chloride, acetic acid. It swelled in isopropanol, methanol, ethanol, cyclohexane etc. IR spectral studies were also carried out which supported the results of elemental analysis and solubility. It was observed that the spectra of the polymer were much simpler than monomer itself. This was due to the fact that the degree of freedom of vibration was restricted in the polymer, copolymer and terpolymer. However, the general patterns of the spectra of polymer and monomers remained the same. The spectra of terpolymer as a rule should show the addition on commutative behaviour of its monomers. The spectra of the product showed lesser bands than the spectra

Table 1
Bulk terpolymerization of ethyl acrylate (EA), n-butyl acrylate (n-BA) and butyl methacrylate (BMA) using benzoyl peroxide (1%) as initiator at 95°C for 8h

S.no.	EA m.moles	n-BA m.moles	BMA m.moles	Conversion g	Elemental analysis %C	%H	%O
1.	20.0000	15.6250	42.2535	9.3	62.25	9.20	25.55
2.	25.0000	19.5312	35.2112	8.6	64.70	9.11	26.19
3.	30.0000	23.4375	28.1690	8.3	64.50	9.06	26.44
4.	30.0000	31.25000	21.1267	7.9	64.07	8.7	28.00
5.	160.0000	140.6250	49.2957	36.9	63.30	8.7	28.00

Table 2
Effect of benzoyl peroxide on the bulk terpolymerization of ethyl acrylate (25.0 m.moles) n-butyl acrylate (19.5312 m.moles) and butyl methacrylate (35.2112 m.moles) at 95°C for 8h

S.no.	Benzoyl peroxide %	Conversion g	Elemental analysis %C	%H	%O
6.	0.5	8.6	64.80	9.10	26.10
7.	1.0	8.8	64.70	9.11	26.19
8.	1.50	9.2	64.64	9.08	26.28
9.	2.0	9.6	64.60	9.10	26.74

of poly (EA), poly (BMA) and poly (n-BA). In the spectrum of the product, the absorption bands with maxima at 2980, 1450, 1370, 1260, 1140, 1020, 840 cm^{-1} wave number are characteristics C-C bands whereas, absorption bands at 1740 cm^{-1} were number showed characteristics stretching vibration. These evidences confirmed the addition of EA monomer unit in the growing polymer chains of BMA and n-BA and that the product was certainly a terpolymer.

The refractive index of prepared sample of poly (EA), poly (BMA) and poly (n-BA) was measured at room temperature as 1.4940; 1.4974 and 1.4020 respectively. The product samples showed refractive index as 1.495 to 1.4977. This difference in the values of refractive index though very little provided further reasons to believe that the product was a terpolymer.

Due to some experimental problems involved in estimation of functional groups of the monomers like-COOC (CH$_2$)$_3$, CH$_3$-COO (CH$_2$)$_3$ CH$_3$ and - COOC$_2$H$_5$, the quantitative treatment of terpolymer equation was quite complex. It involved nine propagation reactions, six termination reactions and six monomers reactivity ratios. In our earlier publications for free radical terpolymerization of vinyl monomers, the probable composition of terpolymer sample was suggested to be calculated on the basis of yield and elemental analysis (Khan and Yousufzai 1989; Khan and Tehzeeb 1990; Khan *et al* 1993; Khan *et al* 1994). Similarly the probable composition of terpolymer samples were determined and plotted in Fig. 1. These plots indicated that the rate of propogation of growing polymer chains of EA, BMA and n-BA increased with increase in

Fig 1. Plot showing rate of propagation (conversion) of growing polymer chains of EA, BMA and n-BA.

concentration in the feed and these three monomers were polymerized simultaneously. At the early stage of reaction these three monomers generated initiating free radicals. Unreacted monomers and growing polymer chains of each monomer caused mutual termination of growing polymer chains monomer and hence formed terpolymer. The product so obtained were the mixture of homopolymer (comparatively very little) and terpolymer.

The molecular weight of terpolymer sample was calculated by using intrinsic viscosity molecular weight relation given in experimental part. Viscosity was measured at 30°C. The intrinsic viscosity of terpolymers samples was found to be in the range 0.99 - 0.125 dl g^{-1} and molecular weight was calculated to be 24130 - 38575. Keeping in view the elemental analysis and probable composition of monomer molecules in terpolymer (Fig 1), the degree of polymerization ($\overline{P}_n$) of n-BA, BMA and EA (probable number of monomer units in terpolymers chains, Table 3) have been determined. These results indicated the major participation of ethyl acrylate monomer units (Pn = 49 - 120) in the formation of terpolymer in a bigger range as compared with n-BA (Pn = 37 - 105) and BMA (Pn = 36 - 106). At a feed of 140.625 moles n-BA, 49.2957 m.moles BMA and 160.0 m.moles EA, an alternating terpolymer of the following type may be obtained.

$$\sim (EA)_{115} - (BMA)_{36} - (BA)_{105} \sim$$

Hence on the basis of elemental analysis, yield, spectral studies, this may be concluded that these three monomers form polymer chains more rapidly than n-BA and BMA (Fig 1). The order of reactivity may be as

$$EA > BMA > n\text{-}BA$$

All terpolymer samples were highly tacky transparent viscous material. The best solvents for terpolymer were acetone, xylene, benzene tolune etc. These polymers may be used as an adhesive but according to the survey of the literature and our experience these terpolymers may be used in leather finishing after removing the drawbacks associated with them. These drawbacks are tackiness and difficulty in handling. Due to these drawbacks terpolymer samples cannot be used as such in the coating formulations particularly for leather. This disadvantage may be removed by blending terpolymer with chlorinated rubber (CR). These polyblends may serve as a good film forming material. For this purpose binary blends of CR and terpolymer (sample no.5) in weight ratio using xylene as a solvent were prepared at 60°C according to the ratios shown in Table 4. Films (30 cm x 20 cm x 1.5 mm) of these blends were cast at room temperature. Tensile strength and elongation at break were measured on Instron Universal Testing Machine. The results are summarized in Table 4. Hardness of these films
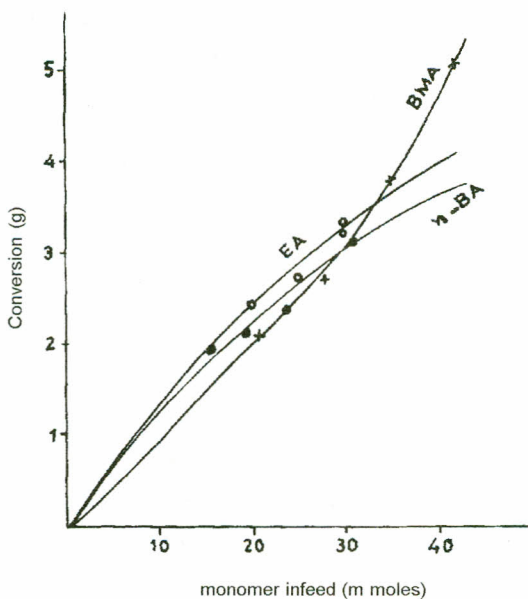
Table 3

Some physical parameters of terpolymer samples of ethyl acrylate, n-butyl acrylate and butyl methacrylate

S.no.	Intrinsic viscosity $[\eta]$ dl g^{-1}	$\overline{Mn}$	Probable number of monomer units in terpolymer		(Pn)	Colour	Appearance	Consistancy	Refractive index
			EA	n-BA	BMA				
1.	0.0.90	24130	49	37	102	Transparent	Viscous	Highly tacky	1.4970
2	0.100	28045	72	54	98	//	//	//	1.4970
3.	0.110	32140	99	75	89	//	//	//	1.4950
4.	0.125	38575	120	90	106	//	//	//	1.4960
5.	0.105	30070	115	105	36	//	//	//	1.4950

Table 4

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

S.no.	CR wt%	Terpolymer wt%	Plasticizer kgwt%	Tensile strength kgf cm^{-2}	Elongation %	Hardness (shor-D)
1.	70	30	-	205	13	68
2.	70	30	1.0	88	243	50
3.	40	60	-	128	18.5	68
4.	40	60	1.0	68	26.0	66
5.	30	70	-	105	21.0	68
6.	30	70	1.0	54	27.0	70
7.	100	-	-	75	0.5	75
8.	100	-	1.0	61	1.3	75

*A mixture of EA (160 m.moles), n-BA (140.625 m.moles) and BMA (49.295 m.moles) using 1% BP at 95°C were polymerized $\overline{Mn}$ = 30070.

were determined on Rubber Tester Model 1951. The films casted from 100% CR was found to be brittle or rigid. The films of terpolymer of EA, MBA & n-BA were highly tacky, flexible and difficult in handling due to which it was not possible to measure their tensile strength and elongation at break. The tensile strength and percentage elongation of pure CR films were measured. Tensile strength and elongation at break of the films prepared from 100% CR was found respectively to be as 75.0 kgf cm^{-2} and 0.5%. The addition of plasticizer (chlorinated paraffin CP) lowered the tensile strength upto 61.0 kgf cm^{-2} whereas, it enhanced the elongation at break upto 1.3%. The results shown in Table 4 further indicated that addition of terpolymer in chlorinated rubber enhanced the tensile strength of the films in the ranges 105-205 kgf cm^{-2} and the elongation in the ranges 13-21%. The % composition of the blends also affect on tensile properties as shown in Table 4. The enhancement of tensile properties was due to intermolecular or intramolecular rearrangements or linkages of terpolymer molecule with CR units and an increase of crosslink density of the system (Khan et al 1995). The molecular rearrangements of CR and terpolymer also ehnanced the elongation at break.Furthermore, the addition of chlorinated paraffine (CP) in the blend reduced the tensile strength and

increased the elongation at break. It might be due to penetration of chlorinated parraffine molecule between the polymer chains in blends which allowed the polymer to be more flexible. The addition of terpolymers and platicizer also affects shore D hardness of the films prepared with CR. In all the blends the amount of added plasticizer was 1% by weight of the total blend. The hardness reduces from 75 to 50. It shows that terpolymer and CP make the film soft and flexible. Hence the blend of CR and terpolymer alongwith plasticizer may be used as a good film forming materials in surface coating of leather.

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