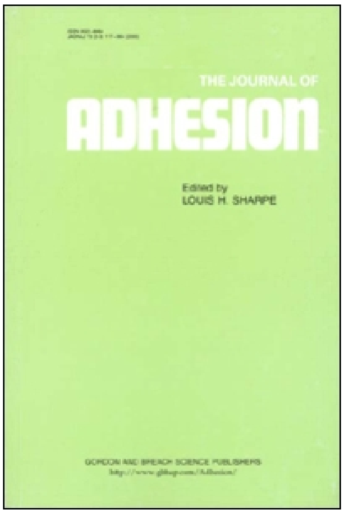

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Modification of Polychloroprene by Graft Copolymerization and its Application as an Adhesive

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Graft copolymerization of ethyl acrylate (EA) and methyl methacrylate (MMA) onto polychloroprene (PCP) were carried out in toluene using benzoyl peroxide (BPO) as an initiator. The polychloroprene-g-poly (ethyl acrylate) (PCP-g-P(EA)) and polychloroprene-g-poly (methyl methacrylate) (PCP-g-P(MMA)) were isolated from the homopolymers of poly(ethyl acrylate) (P(EA)) and poly (methyl methacrylate) (P(MMA)) by a selective solvent extraction technique using diisopropyl ether and acetic acid as solvents, respectively. The infrared (IR) spectra of PCP-g-P(EA) and PCP-g-P(MMA) showed an absorption band at 1730 cm^{-1}, a characteristic of the carbonyl band ($>\mathrm{C{=}O}$) of P(EA) or P(MMA) which is not present in PCP. The NMR spectrum of PCP-g-P(EA) copolymer showed the $-\mathrm{OCH}_2$ proton peak at 4.12 ppm, the methylene proton peak at 2.28 ppm and the methyl proton peak at 1.25 ppm. The NMR spectrum of PCP-g-P(MMA) copolymer shows the $\alpha-\mathrm{CH}_3$ proton at 0.95 ppm and $-\mathrm{OCH}_3$ proton at 3.5 ppm. The IR and NMR studies on the graft copolymer showed the occurrence of grafting. The mechanism of the grafting seems to be by chain transfer as evidenced by the decrease in chlorine content of the graft copolymers. These graft copolymers were blended with tackifier and filler for adhesive applications. The peel and shear strength of the above adhesives with respect to upper leather to sole leather were investigated.

Keywords: Graft copolymerization of P(EA) onto PCP; graft copolymerization of P(MMA) onto PCP; adhesives; peel strength; shear strength

INTRODUCTION

The discovery of new polymers is a rarity these days and many attempts are being made to modify the existing polymers either through blend formation[1–3] or by graft copolymerization[4–6]. By these processes, many new materials have been formed which differ completely in both physical and chemical properties from the parent materials[7–8]. PCP finds extensive applications as an adhesive [9] and as molded articles[10] and it is usually used by blending with other compounds. These processes have certain advantages as well as disadvantages. Few studies have been reported on the modification of PCP in the literature. This communication deals with the graft copolymerization of EA and MMA onto PCP using BPO as an initiator in solution medium. The probable mechanism for the graft copolymerization is discussed. Adhesive formulations were prepared by using these graft copolymers blended with tackifier and filler. Using these formulations, the peel strength and shear strength with respect to upper leather to sole leather were measured.

EXPERIMENTAL

Materials

PCP (Bayprene 321 supplied by Bayer, Germany) with 38% chlorine content was used.

The monomers EA and MMA (both from BDH Chemicals, England) were freed of inhibitors by washing successively with 5% aqueous sodium hydroxide, drying over anhydrous $CaCl_2$, distilling under vacuum and storing in a refrigerator at 4°C. This monomer was used throughout the experiments.

BPO (BDH chemicals, England) was recrystallized from chloroform-methanol mixture.

Toluene (S. D. Fine chemicals, India) and isopropyl ether (S. D. Fine Chemicals, India) were all reagent grade.

Resin (*t*-butylphenol resin, Grade HR 6422, Hylak, Bakelite Hylam Ltd., India) and magnesium oxide (Laboratory reagent, Loba Chemicals, India) were used as such.

Grafting Procedure

PCP (100 gm) was dissolved in toluene (575 ml) by using a mechanical stirrer. The solution was transfered into a three necked flask, fitted with a condenser and a stirrer, which was immersed in a thermostatic water bath maintained at 70°C. A known quantity of monomer [EA (2.5×10^{-1} mol/l) or MMA (2.5×10^{-1} mol/l) and initiator (1.03×10^{-3} mol/l dissolved in 10 ml of toluene)] was added and stirred well (total volume 600 ml). A slow stream of nitrogen was passed throughout the experiment and the polymerization reaction was carried out for 6 hours. Then the three-necked flask was removed from the thermostatic water bath and the reaction was arrested using an ice-salt mixture.

Isolation of Graft Copolymer

A part of the solution was poured into an excess of methanol to precipitate the polymer. The polymer contains both the grafted and ungrafted backbone and unbound homopolymer. The unbound homopolymer was separated from the polymer mixture using a selective solvent extraction technique (72 hours). The unbound homopolymer P(EA) was extracted from the PCP-g-P(EA) using diisopropyl ether as a solvent. Acetic acid was used as a solvent to remove the unbound P(MMA) from the PCP-g-P(MMA) graft system.

Estimation of Chlorine

The estimation of chlorine in the PCP and the PCP graft copolymers was carried out using the procedure described in Ref. 11.

Preparation of Graft Copolymer for Adhesive Formulations (I)

The grafting of EA (2.5×10^{-1} mol/l) or MMA (2.5×10^{-1} mol/l) onto PCP (100 gm in 575 ml of toluene) was carried out for 6 hours at 70°C using BPO (1.03×10^{-3} mol/l) as an initiator in toluene (total volume 600 ml) as described in the grafting procedure.

Complex Preparation (II)

Magnesium oxide (5 gm) was placed in a container and 2 ml of water was added. Tackifier (*t*-butylphenol resin, 45 gm) dissolved in toluene

(100 ml) was added slowly and stirred well for 24 hours. This solution was filtered and used.

The graft copolymer (I) and the complex (II) were blended together using a Remi cutter type stirrer for 2 hours. This formulation (III) was used as an adhesive for testing the peel strength and shear strength for upper leather and sole leather.

PREPARATION OF ADHERENDS

Preparation of Upper Leather

The grain surface of the upper leather was roughened using a wire brush, so as to remove the grain layer completely to produce a raised surface of the stronger corium fibers[12]. The upper leathers used for adherends were 3 × 1 inches (7.6 × 2.5 cm) in size with a thickness of 1.2 – 1.3 mm.

Preparation of Sole Leather

The flesh side of the sole leather was roughened using a wire brush, so as to remove all horizontal or loose flesh fibers and to produce a raised surface of the stronger corium fibers. Adherends used for the testing were 3 × 1 inches (7.6 × 2.5 cm) in size with a thickness of 4.5 mm.

Methodology for the Application of Adhesive

The treated pieces of the materials were coated with the adhesive formulation (Tab. I) using a soft bristle brush with strokes in the same direction and without any "starved" surface on the adherends. After a 30-minute drying of the first coat, a second coat of adhesive was applied[13]. The coated surface of the two adherend strips were aligned face to face, carefully, without entrapping air, in the same direction for peel strength testing and in the opposite direction for shear testing. Then the materials were pressed together in a bonding press at a pressure of around 10–12 kg/cm^2 for 15 seconds at room temperature.

TABLE I Adhesive formulation of PCP grafted with EA/MMA and control

S. NO.	*Contents*	*Formulation (weight in gm)*		
		I	*II*	*III*
1.	Polychloroprene	100	100	100
2.	Tackifier	45	45	45
3.	MgO	5	5	5
4.	EA	15	–	–
5.	MMA	–	15	–
6.	Solvents (to adjust the solid content to 20%)			

Peel Strength and Shear Strength Testing

Peel strength and shear strength testing in a dry condition and a wet condition (immersing the sample for 6 hours in distilled water) was carried out at 20 ± 2°C at 65% RH in an Universal tensile testing machine (Instron Model No. 2500).

RESULTS AND DISCUSSION

Characterisation of Graft Copolymers

Infra Red (IR)

PCP, PCP-g-P(EA) and PCP-g-P(MMA) were dissolved in toluene. These solutions were poured onto a mercury bed separately and allowed to dry to produce films. The IR spectra of the films were recorded using a Nicolet 20 DXB instrument (Fig. 1). The isolated graft copolymer showed an absorption band at 1730 cm^{-1}, a characteristic of the $>C{=}O$ of P(EA) or P(MMA) which is not present in the backbone polymer (PCP), indicating that the P(EA) or P(MMA) grafted onto the PCP.

Nuclear Magnetic Resonance (NMR)

The NMR spectra of PCP, PCP-g-P(EA) and PCP-g-P(MMA) dissolved in deuterated chloroform, recorded using Perkin-Elmer R 32 instrument, are shown in Figure 2. The graft copolymer of PCP-g-P(EA)

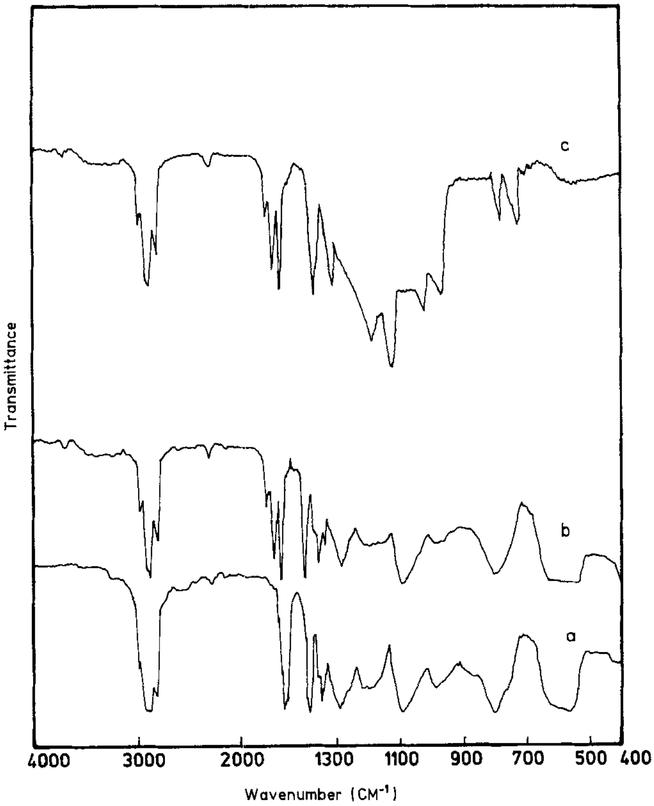


FIGURE 1 IR spectra of a. PCP; b. PCP-g-P(EA); c. PCP-g-P(MMA).

shows the —OCH_2 proton at 4.12 ppm, the methylene protons at 2.28 ppm and the methyl proton at 1.25 ppm. The PCP-g-P(MMA) shows the α-methyl proton at 0.95 ppm and the —OCH_3 proton at 3.5 ppm. The presence of these signals in the isolated graft copolymer also support the evidence of P(EA) or P(MMA) grafted onto PCP.

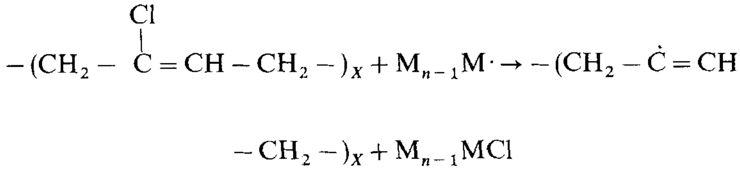
Mechanism of Grafting

The percentages of chlorine in the PCP, PCP-g-P(EA) and PCP-g-P(MMA) were found to be 38, 32 and 31%, respectively, indicating that there is a 6 and 7% reduction in the chlorine content of the

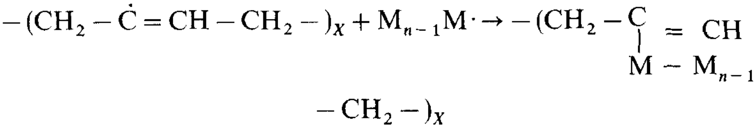
FIGURE 2 1_H NMR spectra of a. PCP; b. PCP-g-P(EA); c. PCP-g-P(MMA).

PCP-g-P(EA) and PCP-g-P(MMA) as a result of graft copolymer formation. Under similar experimental conditions, PCP was found to be stable and the estimated chlorine content remained 38%. Hence, the direct elimination of chlorine creating a radical site is eliminated as a possibility in the PCP backbone polymer. Alternatively, the elimination of chlorine by a chain transfer reaction and, thereby, creating a radical site in the PCP is a possibility[11] and the probable mechanism of graft copolymerization in the present study is given below:

$$I\cdot + nM \rightarrow (M)_{n-1}M\cdot$$



$$-(CH_2-\overset{\overset{\large Cl}{|}}{C}=CH-CH_2-)_X + M_{n-1}M\cdot \rightarrow -(CH_2-\dot{C}=CH-CH_2-)_X + M_{n-1}MCl$$



$$-(CH_2-\dot{C}=CH-CH_2-)_X + M_{n-1}M\cdot \rightarrow -(CH_2-\underset{\underset{\large M-M_{n-1}}{|}}{C}=CH-CH_2-)_X$$

In Table I, the adhesive formulations of PCP grafted with EA and MMA and the control without grafting of acrylic monomers are given. All these adhesives have a free flowing property with a viscosity in the range of 2800–3000 cps. The peel strength of the different adhesive formulations for bonding upper leather to leather sole in wet and dry conditions are given in Table II. Table II shows that the adhesive prepared with the MMA grafted onto PCP has peel strengths of 5.21 kg/cm and 3.48 kg/cm under dry and wet conditions, respectively. We observed 100% of surface failure of the sole leather in dry and wet

TABLE II Peel strength of leather-to-leather joints using the formulation of PCP grafted with EA, MMA and the control

		Peel strength kg/cm				
Formulations	*Dry*	*Nature of failure*	*Wet*	*Nature of failure*	*Dry*	*aging Nature of failure*
I PCP-g-P(EA)	4.57	20% SSL 80% C	2.74	50% SSL 50% C	2.88	70% SSL 30% C
II PCP-g-P(MMA)	5.21	100% SSL	3.48	100% SSL	4.10	100% SSL
III CONTROL	4.71	50% SSL 50% SUL	2.50	100% NC	2.80	100% C

C : Cohesive failure of adhesive within the layer, but not at the interface.
SSL: Surface of Sole leather.
SUL: Surface of upper leather.

TABLE III Shear strength of the leather-to-leather joints for the three adhesive formulations

	Shear strength kg/cm²					
Formulations	*Dry*	*Nature of failure*	*Wet*	*Nature of failure*	*Dry*	*Nature of failure*
I PCP-g-P(EA)	17.1	100% SUL	15.1	100% SUL	14.8	100% SUL
II PCP-g-P(MMA)	18.1	100% SUL	14.5	100% SSL	15.3	100% SSL
III CONTROL	17.5	100% SUL	13.8	100% SSL	14.3	100% SUL

SSL: Surface of sole leather SUL: Surface of upper leather.

conditions. The PCP-g-P(EA) adhesive has peel strengths of 4.57 and 2.74 kg/cm in dry and wet conditions, respectively. The nature of these failure was 20% surface of sole leather and 80% cohesive failure of the adhesive in the dry condition and, in the wet condition, 50% surface of sole leather and 50% cohesive failure of the adhesive films. The adhesive formulation prepared from polychloroprene (control) has peel strengths of 4.71 kg/cm and 2.50 kg/cm in dry and wet conditions, respectively. The nature of the failures were 50% surface of the sole leather and 50% surface of the upper leather in the dry condition, and 100% cohesive failure of the adhesive films in the wet condition (Tab. II). Further, it is interesting to note that on aging, the adhesive prepared with the PCP grafted with MMA has better peel strength than that of the other two adhesives, namely, PCP-g-P(EA) and the control, since the grafting efficiency for the PCP-g-P(MMA) system (58%) is higher than that of the PCP-g-P(EA) system[14] (48%).

The shear strengths of the leather-to-leather joints for the adhesive formulations are given in Table III. The Table shows that the adhesive prepared using PCP-g-P(MMA) gives higher shear strength joints than those of the other two adhesives. Further, the results given in Table II show that the peel strengths of leather-to-leather joints made with this adhesive are also higher than those made with the other two adhesives.

CONCLUSION

Grafting of ethyl acrylate and methyl methacrylate onto polychloroprene was carried out using free radical initiators and the chain transfer mechanism was proposed. The graft copolymers were extracted from the grafting mixture by using a selective solvent extraction technique. The graft copolymers were characterised by IR and NMR. These graft copolymers were used as adhesives for upper leather to sole leather after blending with magnesium oxide and tackifier. The adhesive formulation prepared using the PCP-g-P(MMA) system has higher peel strength and shear strength than that of either the PCP-g-P(EA) system or the control.

References

[1] Olabisi, O., Roberson, L. M. and Shaw, M. T., *Polymer-polymer Misibility* (Academic Press, New York, 1979), Sec. 2, Chap. 7.
[2] Paul, D. R. and Newman, S., *Polymer Blends* (Academic Press, New York, 1978), Vol. 1, Chap. 6, pp. 244.
[3] Bhowmick, A. K., Chiba, T. and Inoue, T., *J. Appl. Polym. Sci.* **50**, 2055 (1993).
[4] Ceresa, R. J., *Block and Graft Copolymerization* (John Wiley and Sons, New York, 1976), Vol. 1 & 2.
[5] Severine, F., Pegorao, M. and Di La Laride, *Angew. Macromolecular Chemie* **190**, 177 (1991).
[6] Jannasch, P. and Wessler, B., *J. Polym. Sci. Chem. Ed.* **A33**, 1465 (1995).
[7] Elangovan, V. J. and Saccubai, S., *J. Appl. Polym. Sci.* **44**, 2179 (1992).
[8] Philips, R. B., Quere, J., Giurcy, G. and Stannet, V. T., *Tappi* **55**, 858 (1972).
[9] Dupont De Nemours, E. I. & Co. "Chloroprene solutions suitable for contact adhesives", *U. S. Patent 4, 136, 671*, May 29, 1979.
[10] Koch, S., *Manual for the rubber industry* (Farbenfabriken Bayer AG, Lerekusen, Germany, 1972), p. 11.
[11] Srinivasan, K. S. V., Radhakrishnan, N. and Kuttralam Pillai, M., *J. Appl. Polym. Sci.* **37**, 1551 (1989).
[12] Satra adhesives test method-AM 2 (1972).
[13] Indian Standard Specification for permanent rubber based adhesive for footwear industry (1968) IS: 4663.
[14] Periyakaruppan, Pr., Dissertation, M.Tech. Footwear and Engineering, Anna University, Madras, India (Jan. 1994).