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Graft copolymerization of polychloroprene with methylmethacrylate and its application as a single component adhesive on difficult surfaces

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ABSTRACT

This investigation attempts to elucidate the graft copolymerization of methylmethacrylate (MMA) with polychloroprene (PCP) via the radical initiator, benzayl peroxide (BPO). The graft copolymer of PCP made free from the respective acrylic homopolymer (PMMA) and unreacted PCP by appropriate solvent extraction using acetic acid (AcOH) as a solvent. The IR & proton-NMR studies on the graft copolymer showed the occurrence of grafting. The IR-spectrum of the graft copolymer PCP-MMA showed an absorption band at $1730 cm^{-1}$ a characteristic of the carbonyl band of PMMA which is not present in PCP. The proton- NMR spectrum of the latter copolymer showed the α-methyl proton at 0.95ppm and OCH3 proton at 3.5ppm. The mechanism of the grafting seems to be by chain transfer to macromolecule as evidenced by the decrease in chlorine content of the graft copolymer. Thereafter the graft copolymer was blended with heat- reactive phenolic resin (tackifier), MgO, ZnO etc for adhesive applications. The peel & shear strengths of the above formulated contact adhesive were investigated.

KEYWORDS

Graft copolymerization;
Functionalization;
PCP;
Contact adhesive;
Peel strength;
Shear strength.

INTRODUCTION

The discovery of new polymers is a rarity nowadays many attempts are being made to modify the existing polymers either through blend formation[1-3] or by graft copolymerization[4-6]. By these two processes many new materials have been formed which differ completely in both physical & chemical properties from the parent materials[7,8].For example polychloroprene (PCP) finds extensive applications as an contact adhesive[9] and as a molded articles[10-14] Also it is usually used by blending with other compounds. These processes leave certain advantages as well as disadvantages. Few studies have been reported on the modification of PCP in the literature. Strictly speaking in our studies on this field we couldn't find any report on the modification of PCP in the literature especially through it is modify adhesion on unmodified surfaces. Grafting is a well known technique of improving chemical & physical properties of hydrophobic fibers such as polypropylene fibers (pp). Grafting it imparts desirable properties including dye ability, soil repellency and creation of active sites for covalent immobilization of bio-macromolecules[15-18]. The most widely used method for the functionalization of polyolefins & olefinic elastomers is to graft acrylic monomers[19-24]. Functionalized polyoefins such as pp samples with different percentage of grafted itaconic acid (IA) or its derivalives like monomethyl ester of IA (MMI) and dimethyl ester of IA (DMI), with similar molecular weights were used as compatibilizers in polyolefin-clay nanocomposits[25-29].Since the commercialization of pe & pp, the functionalization of polyolefins through grafting with polar acrylic monomers has been significantly interesting and technologically important research subject with mainfocus being on improving the adhesion and compatibility with other materials[30-51]. Functionalization of polyolefins through grafting of polar monomers has been the subject of intense research during recent years with the aim of introducing functional polar groups in to their non- polar olefinic chains. The resulting compounds have been used as a compatible polymer with blend of polyolefins with other polar polymers[52-54]. The R&D efforts towards development of chemical polymer blends of polyolefins and related polymers and copolymers such as linear low density polyethylenes (LLDPE) or very low density polyethylenes (VLDPE), ethylene propylene copolymer rubbers(EPR), elastomeric terpolymers from ethylene-propylene diene monomer (EPDM) system & ethylene vinyl acetate (EVA) copolymers through graft copolymerization could be affected[55-56].

EXPERIMENTAL

Materials and methods

PCP (Bayprene 321, 38% chlorine content was used), Zinc-Oxide, magnesium Oxide, chlorinated rubber (Pergot S-20), reactive phenolic resin (Sp 154- Schenctady); 2,6-Di-t-butyl-4-methylphenol (as an antioxidant-BHT) purchased from Bayer chemical company-Germany. The Monomer MMA (methyl methacrylate) purchased from BDH chemical company, England. It was purified from inhibitor by washing successively with 5% aqueous sodium hydroxide, drying over anhydrous $CaCl_2$, distilling under Vacuum & storring in a refrigerator at 4°C. BOP (Benzoyl peroxide) also from BDH Chemical company–England was recrystallized from chloroform- methanol mixture.

Aerosil-R-200 from Degussa-Germany; concentrate nitric acid, benzene, sodium carbonate, potassium carbonate, potassium thiocyanate and ferric chloride were purchased from Merck chemical company-Germany.

Grafting principle

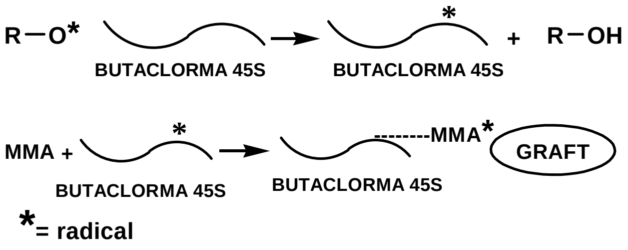
The technique involves a reaction between polychloroprene rubber and methyl methacrylate monomer in solution to obtain a polychloroprene-methyl methacrylate grafted copolymer. It is necessary to avoid oxygen contact.

Initiation

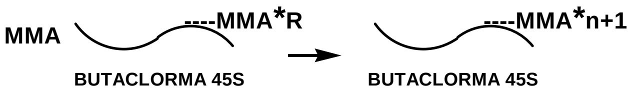
The initiator (an organic peroxide) is decomposed by temperature and gives two free radicals:

$$R--O--O--R \xrightarrow{t°C} 2R--o*$$

The transfer of a free radical on the PCP chain is the starting point of the growth of a MMA graft:

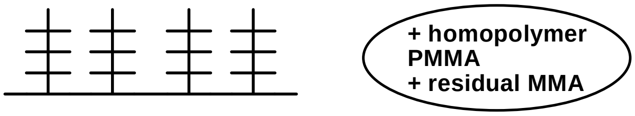


Propagation (Graft growth)



Termination

Stop of the propagation reaction by destruction of the free radicals with a phenolic antioxidant, the result of grafting reaction is a mixture of:



Polychloroprene-MMA grafted copolymer

Grafting formulation

Ingrediedients

TABLE 1 : Butaclor MA45S methylmethacrylate

Ingredients	Parts	%
Butaclor ma45 S	100	13.48
Methyl methacrylate	60	8.09
Toluene	493	66.5
Ethylmethyl ketone	87	11.7
Benzoyl peroxide (bpo)	0.5	0.0674
2, 6-di-tert-buthyl-4-methylphenol(bht)	1	0.135

Conditions

Temperature: 90°C ; Pressure : 1atm.

Equipment

The grafting reaction can be conducted in a reaction vessel equipped with a heating and cooling jacket, in order to heat the solution for starting the reaction; and to cool down for control the temperature. In addition, the reactor has to be tight enough to avoid solvent loss and keep the reacting mass far from air. The agitation speed must be enough to obtain a homogeneous reactive mass and a good heat exchanging.

Grafting procedure

PCP(100gm) was dissolved in toluene (493ml) using a mechanical stirrer. The solution thus obtained was transferred into a laboratory reactor (a cylindrical vessel with a glass jacket for heating & cooling duties with capacity of 3 liters), fitted with a condenser & a mechanical stirrer in a thermostatic water-bath maintained at 90°C and standard pressures. The grafting reaction was carried out in the cylindrical glass reactor by taking a known quantity of methyl methacrylate (60ml, 2.5×10^{-1} mol/l) and an appropriate initiator (0.5gm, 1.0×10^{-3} mol/l dissolved in 10 ml of toluene. A slow stream of an inert atmosphere of nitrogen was passed throughout the reaction. The grafting polymerization reaction was carried out for 6 hours. Thereafter the propagation reaction was arrested by destruction of the free-radical with BHT, a phenolic antioxidant (1gm). The reaction vessel was removed from the thermostatic water-bath and the reaction was arrested using an ice-salt mixture. The resuit of the grafting reaction is a mixture of PMMA, PCP and the functionalized polychloroprene.

Grafting control

Solid content of the solution increases regularly during the reaction; it is related to the conversion of MMA at any time (T) of the reaction, the conversion of MMA may be calculated from the following equation.

$$\mathbf{Conv.rate\% = \frac{MA45Swt}{MAA\ wt.} \times \frac{solid\ content\ at\ time\ T - initial\ solid\ content}{Initial\ solid\ content}}$$

Initial solid content: after adding BPO, the optimal conversion rate of MMA is about 30%. It is far better to make a double check using a chromatographic method.

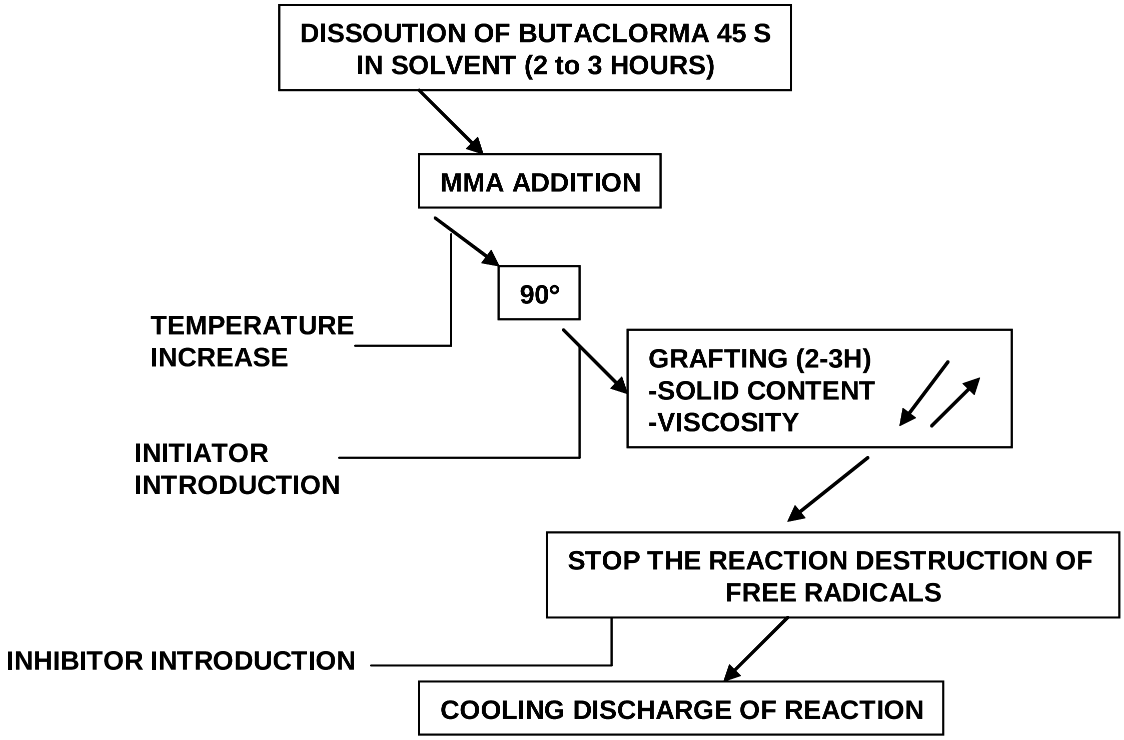
Estimation of Chlorine

A weighed quantity of polychloroprene was taken in a porcelain crucible and swollen with benzene. 6g of mixture containing 2 parts sodium nitrate. 1 part sodium carbonate, and 1 part potassium carbonate were added and mixed with the swollen polychloroprene. The benzene was evaporated at 100°C; 4g of sodium carbonate was placed on top of mixture in the crucible and the latter was covered with porcelain cover. The crucible was then heated, first over a low flame, gradually increasing to a full flame. After 3 hrs heating, the material was allowed to cool and subsequently transferred to a beaker first warm distilled water and, then 13ml of concentrated nitric acid was added on a steam bath to dissolve all the materials. To a solution, diluted to about 150ml, was added an excess of standard silver nitrate solution. The precipitated silver chloride was filtered off and washed with silver nitrate, and then finally with distilled water. The filtrate and washing were combined and titrated with standard thiocyanate solution. The filtrate from the precipitated chloride was treated with 5ml of the ferric solution and the excess silver determined by addition of the thiocyanate until a permanent reddish-brown colour was produced and the amount of chloride was estimated using standard procedure[22].

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 unbonds homopolymer. The unbonded homopolymer was separated from the polymer mixture using a selective solvent extraction technique (72 hrs). The unbounded

GRAFTING PROCESS



homo polymer (MMA) was extracted from PCP-g-p (MMA) using acetic acid as an extracting solvent.

Preparation of adhesive for 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 fibers[23]. The upper leathers used for adherents were 3×1 inches $_{(7.6\times2.5cm)}$ in size with a thickness of 1.2-1.3mm.

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 raise surface of the stronger corium fibers. Adherents used for the testing were 3×l inches$_{(7.6\times2.5cm)}$ in size with a thickness of 4.5mm.

Methodology for the aplication of adhesive

The treated pieces of the materials were coated with the adhesive formulation using a soft bristle brush with strokes in the same direction and without any “traved” surface on the adherends. After 30 minutes drying of first coat, a second coat of adhesive was applied[24]. 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 10-12kg/cm^2 for 15 seconds at room temperature.

Peel strength and shear strength testing

Peel strength and shear strength testing in a dry and wet conditions (immersing the sample for 6 hours in distilled water). The test carried out at 20±2°C at 65% RH in an universal tensile testing machine (Instron Model wo.2500).

RESULT AND DISCUSSION

Characterization of graft copolymers

Infrared (IR) spectra

PCP, PCP-g-P(MMA) and PCP-g-P(EA) were dissolved in toluene. These solutions were poured onto

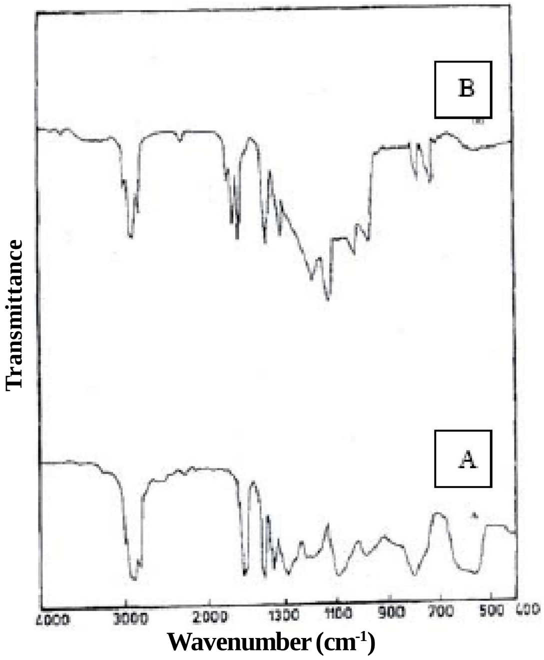


Figure 1 : IR spectra of A-PCP, B-PCP-g-P(MMA)

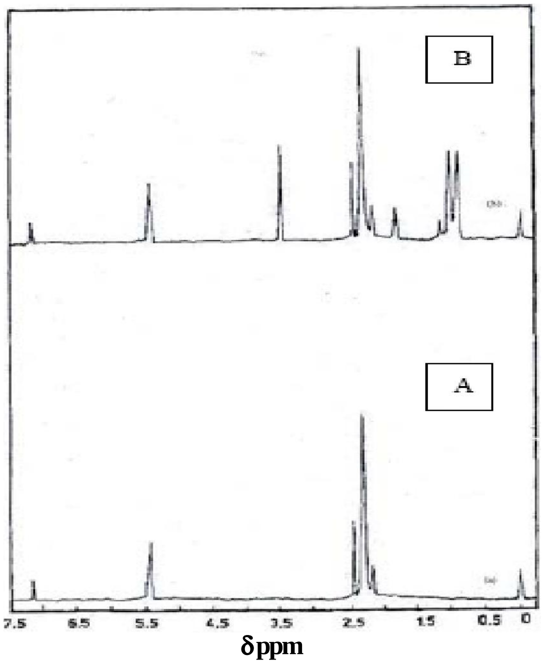


Figure 2 : ^{1}H NMR spectra (A) PCP; (B) PCP-g-P(MMA)

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. The isolated graft copolymer showed an absorption band at 1730cm^{-1} (Figure 1), a characteristic of the ester carbonyl stretching vibration.

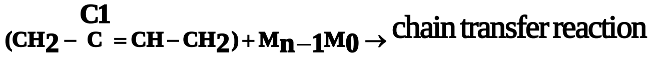
Nuclear magnetic resonance (H-NMR)

The proton NMR spectra of PCP & PCP-g-P(MMA) dissolved in deuterated chloroform, recording using Perkin-Elmer R-32 instrument, are shown in figure 2. The PCP –g-P(MMA) shows the α- methyl proton peak at 0.95ppm and the OCH_3 proton at 3.5ppm. The presence of these signals in the isolated graft copolymer also support the evidence of p(MMA) grafted on PCP.

Alternatively, the elimination of chlorine by chain transfer reaction causes creating a free radical site in the PCP. This is a possibility[22] and the probable mechanism of graft copolymerization in the present study given blow:

$RooR \rightarrow 2R° \leftrightarrow sI°$ Initiator decomposition

$I° + nM \rightarrow (M)_{n-1}M°$... homopolymer intiation



$(CH_2-\overset{C1}{C}=CH-CH_2)+M_{n-1}M_0 \rightarrow$ **chain transfer reaction**

$(CH_2-C^{*}=CH-CH_2)+M_{n-1}M-C1$

$(CH_2-C^{*}=CH-CH_2)+M_{n-1}M_0 \rightarrow$ **Graft propagation**

$(CH_2-C=CH-CH_2)M-M_{n-1}$

In TABLE 2 the general purpose contact adhesive formulation of PCP grafted MMA and the control (without grafting of acrylic monomers) is given.

Adhesive characteristics

Brookfield viscosity: around 2000 maps; Solid content: Adhesive I: 22.8%; Adhesive II 20.2%; Rubber Content (Rubber/Rubber +Solvent):16%

In TABLE 3 two formulas for solvent based leather shoes adhesive manufacturing are represented.

Adhesive characteristics

Brookfield viscosity: around 2000 maps; Solid content: Adhesive No. I: 22.8%; Adhesive No. II: 21.3%; Rubber Content (Rubber/Rubber + Solvent): 15.8%.

Operating process

The operating process for both formulations of TABLE 2 & 3 is as the same. Put the solvent into the mixing vessel, add the oxides, the resin and silica into the mixture, and let to mix and dissolve during 30 minutes. Then incorporate the chips of PCP and the chlorinated rubber, wait until the viscosity remains stable, or the solid content reaches its theoretical value. All these adhesives have a free flowing properly 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

TABLE 2 : Adhesive formulation of PCP grafted with MMA and control (ungrafted)

No.	Content	Formulation (weight in gm)	
		I	II
1	Polycholoperne	100	100
2	Tackifier	45	45
3	Mgo	5	5
4	PCP-g-p(MMA)	15	-
5	Solvent to adjust the solid content to 20%		

TABLE 4 : Peel strength of the leather-to-leather joints using the formulation of PCP grafted with MMA and the control (ungrafted)

Formulation	Peel strength kg/ cm					
	Dry	Nature of failure	Wet	Nature of failure	Dry	Aging nature of failure
I-PCP-g-p(MMA)	5.21	100%SSL	3.48	100%SSL	4.10	100%SSL
II-Control	4.71	50%SUL 50%SSL	2.50	100%NC	2.80	100%C

SSL: Surface of sole leather; SUL: Surface of upper leathers, C: Cohesive failure of adhesive within the layer but not at all the interface

conditions are given in TABLE 4. This TABLE shows that the adhesive prepared with the MMA grafted onto PCP has peel strengths of 5.21kg/cm and 3.48kg/cm under dry and wet conditions respectively. We observed 100% of surface failure of the sole leather in dry and wet conditions. In dry condition the nature of these failure was 20% surface of sole leather & 80% cohesive failure of the adhesive In the wet condition, 50% for surface of sole leather and 50% cohesive failure of the adhesive films. The contact adhesive formulation prepared from polychloroprene has peel strength of 4.71kg/cm and 2.50kg/cm in dry and wet condition respectively. The nature of the failures were 50% surface sole leather and 50% surface of the upper leather in dry condition, and 100% cohesive failure of the adhesive film in the wet condition (TABLE 4).

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 other adhesive, namely, the control, since the grafting efficiency for the PCP-g-p(MMA) system (48%) is higher than of the PCP system[24]. The shear strengths of the leather-to-leather joints for the adhesive formulations are given in TABLE 5 The TABLE shows that the adhesive prepared using PCP-g-p(MMA) gives higher sheer strength joints than those of the other two adhesives.

TABLE 3 : Adhesive for leather shoes manufacturing and thermoplastic rubber (solvent based, heat resistant)

Ingredients	Adhesive I	Adhesive II
Polychloroprene	100	100
Reactive phenolic Resin	45	65
Silica(Aerosil-Rzoo)	2	2
Magnesium Oxide	5	5
Antioxidant(BHT)	1	1
PCP-g-p(MMA)	15	-
Active Zinc Oxide	1	1
Chlorinated rubber	10	10

Solvent system:(100%=total solvent quantity) Toluene 34%, Hexane 33%, Ethyl acetate15%

TABLE 5 : Shear strength of the leather- to-leather joints for the two adhesive formulations

Formula	Shear strength kg/ square cm					
	Dry	Nature of failure	Wet	Nature of faillure	Dry	Aging nature of failure
I-PCP-g-p(MMA)	18.1	100%SUL	14.5	100%SSL	15.3	100%SSL
II -Control	17.5	100% SUL	13.8	100% SSL	14.3	100%SUL

SSL: Surface of sole leather; SUL: Surface of upper leathers

Further, the results given in TABLE 4 shows that the peel strengths of leather-to-leather joints made with these adhesive are also higher than those made with other two adhesives.

CONCLUSION

Grafting of ethylacryl to methylmethacrylate onto polychloroprene was carried out using free radical initiators & the chain transfer mechanism was proposed. The graft copolymers were extravted from the grafting mixture by using a selective solvent extraction technique. The graft copolymers were characterized by IR and ^{1}H NMR. These graft copolymers were used as adhesion of upper leather to sole leather after blending with Mgo and tackifier and also as an alternative for two component systems in which polyisocyanates are used as hardener. The adhesive formulation prepared using the PCP-g-p(MMA) system has higher peel strength and shear strength than that of the control.

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