

# Studies on Graft Copolymerization of Cyclohexyl Methacrylate onto Chloroprene Rubber

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**ABSTRACT:** Graft copolymerization of cyclohexyl methacrylate (CMA) onto chloroprene rubber (CR) was carried out in toluene using benzoyl peroxide as an initiator. The graft copolymer was isolated from the gross polymer by extracting it with a butanone solution. Infrared (IR) spectra of the graft copolymer showed the occurrence of grafting. Optimization of various parameters of the grafting, namely, time, temperature, and initiator concentrations, was performed. The mechanical adhesive properties of the graft copolymer, CR-*g*-CMA, were measured and compared with those of the graft copolymer of methyl methacrylate (MMA) onto CR, CR-*g*-MMA. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1733–1737, 1997

**Key words:** graft copolymerization; cyclohexyl methacrylate; chloroprene rubber; adhesive

## INTRODUCTION

Chloroprene rubber (CR) has been used as an important material for adhesives for a long time. Chemical modification can be devised to give rubber more desirable properties. The grafting copolymerization of the acrylate monomer onto CR has been reported.<sup>1,2</sup> For example, grafting copolymerization of methyl methacrylate (MMA) onto CR has been intensively studied and the graft copolymer CR-*g*-MMA is now a commercial product.<sup>3,4</sup>

A cyclohexyl methacrylate (CMA) monomer with a stronger electron-attracting ester group was more reactive than was MMA.<sup>5</sup> The graft copolymer of CMA onto CR can be expected to have better mechanical adhesive properties. An attempt was made to modify the CR by graft copolymerization with the CMA monomer using benzoyl peroxide as an initiator in toluene. The graft product was isolated by extracting and characterized by infrared spectra. The effects of different conditions of the experiment on conversion, the ratio

of the graft, and grafting efficiency were studied. The measured results of the mechanical adhesive properties for the copolymers indicated that the graft copolymer of CMA onto CR, CR-*g*-CMA, has better mechanical adhesive properties than those of CR-*g*-MMA.

## EXPERIMENTAL

### Materials

Chloroprene rubber (CR), type A-90, was purchased from Japan and the face of the rubber was cleaned with acetone and dried before use. The cyclohexyl methacrylate (CMA) monomer was prepared by ester interchange between cyclohexanol and MMA in the presence of *p*-toluene sulfonic acid. The crude CMA was washed, dried, and distilled three times under reduced pressure; bp 80°C/10 mmHg. The monomer was characterized by gas chromatography, IR (Fig. 1), and refractometry  $n_D^{20} = 1.4578$ . The initiator, benzoyl peroxide (BPO) was purified by repeated recrystalli-

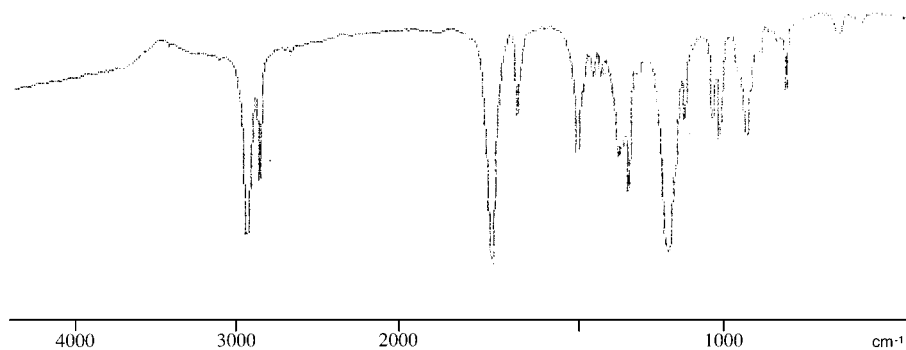


Figure 1 IR spectrum of CMA.

zation from chloroform. The solvents used were all of reagent grade.

### Graft Copolymerization

CR was dissolved in toluene by stirring at room temperature. The flask containing known quantities of CR, CMA, BPO, and toluene was immersed in a thermostatic water bath and a slow stream of nitrogen was passed throughout the experiment. Graft copolymerization was thermally carried out. After the required reaction time, hydroquinone (HQ) was added immediately; then, the copolymer solution was removed from the water bath and cooled to room temperature. The basic formulation and variable conditions of copolymerization are shown in Tables I and II, respectively.

### Separation of Polymers

Five grams of the copolymer solution was poured into 50 mL of methanol. The precipitate produced was separated and dried for 24 h at room temperature and at 50°C under a vacuum until a constant weight of a gross polymer was obtained. From the weight of the gross polymer, the total solid content of the copolymer solution can be obtained by conversion. The gross polymer obtained consists of ungrafted polychloroprene, unbound CMA homo-

polymer, and the grafted copolymer, CR-*g*-CMA. The homopolymer poly(cyclohexyl methacrylate) (PCMA) was separated from the rest of the polymer by extracting the gross polymer in a solution mixture of butanone and methanol (2 : 1) for 48 h by the Soxhlet extraction method. The remaining polymer was dried for 24 h at room temperature and at 50°C under a vacuum for 2 h and then weighed. The weight was taken as ungrafted polychloroprene and polychloroprene-*g*-PCMA (CR-*g*-CMA). The experiments on the optimal extractive time from 36 to 72 h was carried out. The results indicated that after 48 h the extractive quantity remained constant. From the above results, the amount of the graft copolymer was calculated.

The conversion of the CMA monomer was calculated as follows:

Percent conversion (pc%)

$$= \frac{\text{wt total solid} - \text{wt CR added}}{\text{wt CMA monomer added}} \times 100$$

The grafting ratio (GR) was calculated as follows:

Percent grafting ratio (GR%)

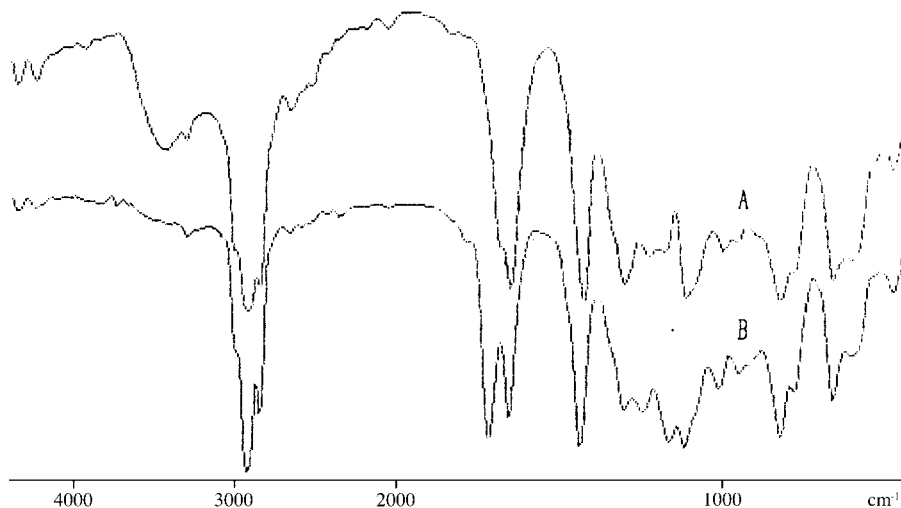
$$= \frac{\text{wt grafted poly(CMA)}}{\text{wt CR backbone polymer}} \times 100$$

Table I Basic Formulation

Constituents	Weight
CR A-90	100
CMA	80
BPO	1
Toluene	680
HQ	2

Table II Conditions of Various Experiments

Conditions	Variables
Reaction time	3, 4, 5, 6 (h)
Reaction temperature	50, 60, 70, 85 (°C)
BPO amount	0.3, 0.6, 1.0, 1.5 (by wt)



**Figure 2** IR spectrum of (A) polychloroprene rubber and (B) the CR-*g*-CMA copolymer.

The grafting efficiency (GE) was calculated as follows:

Percent grafting efficiency (GE%)

$$= \frac{\text{wt grafted poly(CMA)}}{\text{wt grafted poly(CMA)} + \text{wt of homopoly(CMA)}} \times 100$$

#### Graft Copolymerization of MMA onto CR

To make a comparison between CR-*g*-CMA and CR-*g*-MMA in grafting conditions and mechanical adhesive properties, a graft copolymerization of MMA onto CR was carried out under otherwise equal conditions. It was found that under the condition of the optimal temperature of 70°C for the grafting of CMA the conversion of MMA is low and the optimal temperature for grafting of MMA is 85°C. The graft copolymer was isolated by extracting the gross polymer in acetone for 48 h.

## RESULTS AND DISCUSSION

### Characterization of the Graft Copolymer

#### Infrared Spectra

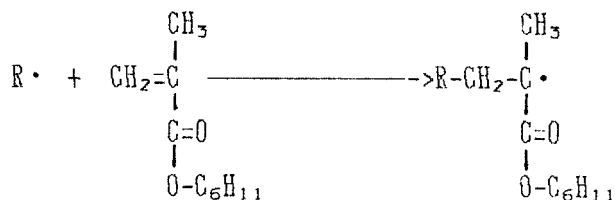
Figure 2 shows the IR spectra of ungrafted CR and the graft copolymer. The characteristic

band of C=O at 1722 cm<sup>-1</sup> from the grafted copolymer fraction indicates the presence of acrylate chains.

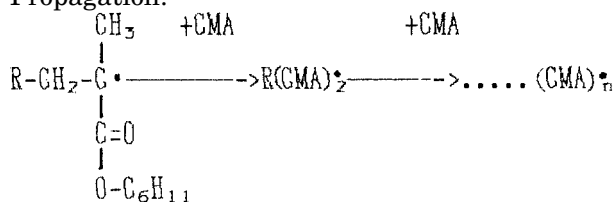
#### Mechanism of Grafting

The following mechanism is proposed to explain the graft copolymerization of CMA onto CR by the free-radical method:

Initiation:



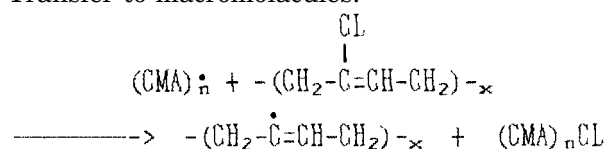
Propagation:



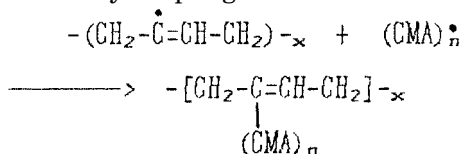
**Table III** Mechanical Adhesive Properties of the Graft Copolymer

Copolymer	GR%	GE%	Shear Strength (kg/cm <sup>2</sup> )	Peel Strength (kg/m)
CR- <i>g</i> -CMA	44.3	68.0	8.4	2.92
CR- <i>g</i> -MMA	48.2	71.6	4.0	2.56

Transfer to macromolecules:



Termination by coupling:



### Mechanical Adhesive Properties

One of the most effective applications for the graft copolymer is to use it as an adhesive. The graft copolymer need not be separate from the solution and the procedure is quite simple. The shear strength for the bonding steel plate (type O8F) and the peel strength for bonding plasticized poly-(vinyl chloride) were measured. The results are shown in Table III.

From Table III, it is seen that when the graft copolymer is applied to the adhesion, the graft copolymer of CMA onto CR is superior to that of MMA in mechanical adhesive properties, particularly for bonding metal.

### Effect of Variables on Graft

#### Effect of Reaction Time

The copolymerization was carried out in toluene solution at 70°C with a constant concentration of CR, CMA, BPO, and HQ for 3, 4, 5, and 6 h. The effect of the reaction time on the grafting conditions are shown in Table IV.

It is observed from Table IV that with increase

**Table IV Effect of Reaction Time**

Time (h)	PC(%)	GR(%)	GE(%)	Shear Strength (kg/cm <sup>2</sup> )
3	40.0	9.4	29.5	4.8
4	62.3	22.6	45.4	7.0
5	81.5	44.3	68.0	8.4
6	81.7	44.8	68.5	8.4

Grafting temperature 70°C; by wt: CR 100, CMA 80, BPO 1, HQ 2, Toluene 680.

**Table V Effect of Reaction Temperature on Grafting**

Temp (°C)	PC(%)	GR(%)	GE(%)
50	31.9	8.0	31.2
60	51.1	20.2	49.4
70	81.5	44.3	68.0
85	82.6	36.5	55.2

Reaction time 5 h; by wt: CR 100, CMA 80, BPO 1, HQ 2, toluene 680.

in reaction time the percent conversion of the CMA monomer, grafting ratio, grafting efficiency, and shear strength have a regular increase up to 5 h. After 5 h, the grafting conditions varied slightly.

#### Effect of Reaction Temperature

The graft copolymerization was carried out at four different temperatures over the range 50–85°C, for 5 h, keeping the amount of all reagents constant, as shown in Table V.

As can be seen, the percent conversion of the CMA monomer, grafting ratio, and grafting efficiency increased with increase in temperature up to 70°C. A further increase in temperature decreases the grafting ratio and grafting efficiency. This may be due to the formation of more homopolymer. In fact, the deeper brown of the copolymer solution was observed at the higher temperature.

#### Effect of the Initiator BPO

Benzoyl peroxide (BPO) as an initiator was used in the grafting reaction of CMA onto CR. In the present investigation, the amount of initiator added into the system was from 0.3 to 1.5 (relative

**Table VI Effect of Initiator Concentration**

BPO (wt)	PC(%)	GR(%)	GE(%)
0.3	34.1	10.5	38.5
0.6	42.0	20.8	61.9
1.0	81.5	44.3	68.0
1.5	75.8	40.5	66.8

Reaction temp: 70°C; time 5 h; by wt: CR 100, CMA 80, HQ 2, toluene 680.

to CR 100, by wt). The variation of the BPO concentration has a profound effect on the grafting conditions, as seen in Table VI.

From Table VI, it is seen that when the amount of BPO is smaller than 1.0, with increase in initiator concentration, the percent conversion of CMA, grafting ratio, and grafting efficiency increase. But further increase in the amount of the initiator decreases grafting conditions.

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