

## ***Synthesis of Chlorinated Acrylate Ester and Incorporation Effect on Thermal and Mechanical Properties of Prevulcanised Natural Rubber Latex***

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*Chlorinated acrylate ester has been synthesised from chloroacetic acid, ethylene glycol, and acrylic acid. The yield from the reaction was incorporated into prevulcanised natural rubber latex system. The effect of the CAE on PV latex system was investigated by varying the percentage of CAE at 3%, 5%, 10% and 15% (wt/wt). The sheets of modified latex was prepared and cured. Fourier transform infrared (FTIR) spectra has proven the presence of C-Cl bond and formation of ester linkage in the CAE. The thermal property of cured samples was examined. The tensile strength decreased as the ester percentage was increased.*

**Keywords:** Natural rubber latex; chlorinated acrylate ester; esterification

Chlorinated rubber and rubber hydrochloride have been known for many years in the field of adhesives. Chlorinated rubber has been commercially prepared by direct chlorination of thin sheets or by chlorination of rubber in solution<sup>1</sup>. This study attempted to develop chlorinated rubber by introducing chlorinated acrylate ester (CAE) in the rubber crosslink system.

The benefits of chlorination in the rubber industry are improvement of adhesion, cheap, and easy to apply<sup>2</sup>. Chlorinated rubber films are impermeable to water, highly resistant to most aqueous reagents (including acids and alkalis), and mainly used as corrosion resistant

coatings<sup>3</sup>. It was reported that the chlorination has improved the durability and ageing resistance of the joints and the treated surfaces remained reactive with the adhesive for at least three month after surface preparation. Besides, chlorine treated rubbers have long been prominent in the field of adhesives and were proven suitable for bonding various types of rubbers<sup>4</sup>.

Plasma chlorination has been found to increase the peel strength of styrene butadiene rubber (SBR)<sup>5</sup>. Chlorination of vulcanised SBR with trichloroisocyanuric acid (TCIA) has been used as an adhesion activator to improve adhesion between surfaces<sup>6</sup>. The

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actual chlorinating species was performed by the reaction of TCIA with the organic solvents (ketone and ester), which produce the chlorination in the *trans* C=C bonds of butadiene creating chlorinated hydrocarbon and other C-Cl moieties<sup>2</sup>.

In this study, CAE was produced by esterification process. The CAE was introduced to the PV latex before being casted and cured under room temperature. The characterisation of CAE and its effect on tensile strength, glass transition temperature and decomposition temperature of the cured modified rubber were studied.

## EXPERIMENTAL

### Materials

Chloroacetic acid ( $94.49 \text{ g mol}^{-1}$ , 99%) and acrylic acid ( $72.06 \text{ g mol}^{-1}$ , 99%) were purchased from Merck Schnuchardt. Ethylene glycol ( $62.07 \text{ g mol}^{-1}$ , 99.5%) and ammonia solution ( $17.03 \text{ g mol}^{-1}$ , 28%) were supplied by Friendemann Schmidt. Hydroquinone ( $110.11 \text{ g mol}^{-1}$ , 99.5%) from Sigma Aldrich was used as an inhibitor. p-toluenesulphonic acid (p-TSA) ( $156.20 \text{ g mol}^{-1}$ ) as a catalyst was purchased from Fine-Chem Ltd. and cyclohexane ( $84.16 \text{ g mol}^{-1}$ , 99.5%) as water carrying agent (azeotrope) was purchased from Merck KGaA. Prevulcanised latex (PV latex) was supplied by synthomer with 60.5% total solid content and 0.68% ammonia content.

### Esterification Reaction of CAE

The esterification reaction was done by mixing chloroacetic acid, ethylene glycol and acrylic acid in the present of p-TSA, cyclohexane and hydroquinone. The reaction was done in a 5-neck round-vessel under temperature of 80-120°C with continuously stirred.

Water produced as by product was removed during reaction in order to prevent reverse reaction and maximise the reaction conversion. The acid value of the solution was measured every 1 h until the constant value was obtained. The yield was extracted with diethyl ether in a separating funnel. Then it was washed using distilled water followed by 0.1 M sodium carbonate to remove acid residue. The neutral mixture was added with sodium sulphate and filtered to remove water remains. Diethyl ether and cyclohexane was removed by rotorvap distillation process.

### Preparation of Rubber Samples

The CAE obtained was treated with ammonia solution to reach the pH of PV latex. Then the solution was added into PV latex for 3%, 5%, 10%, and 15% (wt/wt) and stirred slowly until a homogenous mixture was formed. The mixture was poured into mould and allowed to dry at room temperature before being cured at 80°C for 1 hour.

TABLE 1. FORMULATION OF SAMPLES

Sample	Percentage of chlorinated ester to PV latex (wt/wt)
PV	0
PV-3	3%
PV-5	5%
PV-10	10%
PV-15	15%

### Fourier transform infrared (FTIR) characterisation

Infrared (IR) spectra for CAE and its precursors were recorded using FTIR instrument Thermo Scientific Model Nicolet 6700 in the range of  $500 - 4000 \text{ cm}^{-1}$  with 16 times of scanning.

### Thermal Properties Characterisation of Cured PV+CAE

Thermogravimetric analysis (TGA) was performed with TGA 7 by Perkin Elmer to investigate the thermal degradation of the cured rubber. The temperature range used was from 30°C to 600°C, heating rate of 10°C/min, and nitrogen purging of 20 mL/min.

Glass transition temperature,  $T_g$  of cured sample films were characterised using DuPont DSC 7 by Perkin Elmer. Sample was weighed and crimped in the aluminium pan. The cured sample was then heated at 10 K/min heating rate from -80°C to 150°C with nitrogen purging of 50 mL/min.

### Tensile Test

Tensile strength measurement was done according to American Standard Testing Method D412 using Tensile Instron Shimadzu with speed of 500 mm/min.

## RESULTS AND DISCUSSIONS

### Esterification Reaction of Chlorinated Acrylate Ester (CAE)

The synthesis of CAE involved chloroacetic acid, ethylene glycol, and acrylic acid in two stages of reaction. Chloroacetic acid and ethylene glycol reacted at initial stage to form an ester<sup>2</sup>. This reaction was characterised by acid number which represented the amount of acid functionality in chloroacetic acid. After 8 h of reaction, acid value decreased from 413.67 to 46.21 (*Figure 2*). This showed that 89% of the carboxylic acid group in the compound has been converted to ester and ready for the next stage. During the second stage, the reaction was continued with the addition of acrylic acid into the system (*Figure 1*). The addition of

acrylic acid raised up the acid value to 304.12 due to the increasing of H<sup>+</sup> in the system. After 32 h of reaction, acid value had reached a constant value of 45.11 indicating that the reaction was completed.

### Fourier Transforms Infrared Spectroscopy (FTIR) Analysis for CAE

The FTIR spectra in *Figure 3* show four different spectra for CAE and its precursors. Broad peak at 3200-3400 cm<sup>-1</sup> for the precursors indicated the presence of hydroxyl group (OH). In the spectrum of the CAE, the peak of hydroxyl group observed at around 3200 cm<sup>-1</sup> in the spectra of ethylene glycol, chloroacetic acid, and acrylic acid disappeared<sup>10,11</sup>. It indicates that most of the hydroxyl groups had been converted to ester. This was verified by the reduction of acid value during reaction. The peaks at 1073 cm<sup>-1</sup>, 1036 cm<sup>-1</sup> and 965 cm<sup>-1</sup> were attributed to the C-O-C bonds of the chlorinated ester. The absorption peak for C-Cl stretching at ~698 cm<sup>-1</sup> and multiple Cl substitutions at 781 cm<sup>-1</sup> was also observed<sup>12,13</sup>.

### Characterisation of Cured PV+CAE

*FTIR Analysis for Cured PV+CAE.* FTIR spectra of control and modified samples showed evidence of modification of cured PV latex system as compared to the control sample (*Figure 4*). The appearance of OH stretching at ~3394 cm<sup>-1</sup> showed that the ester was introduced onto the rubber system. The peak was broader on the cured PV+CAE than the cured PV, showing the increasing amount of O-H bond (hydroxyl group). The appearance of peak at 1731 cm<sup>-1</sup> assigned the existence of C=O (carbonyl) in the PV+CEA system<sup>14</sup>. The substitution of Cl in the system was assigned by the peak at ~756 cm<sup>-1</sup> absorption bands of C-Cl stretching<sup>13</sup>. The

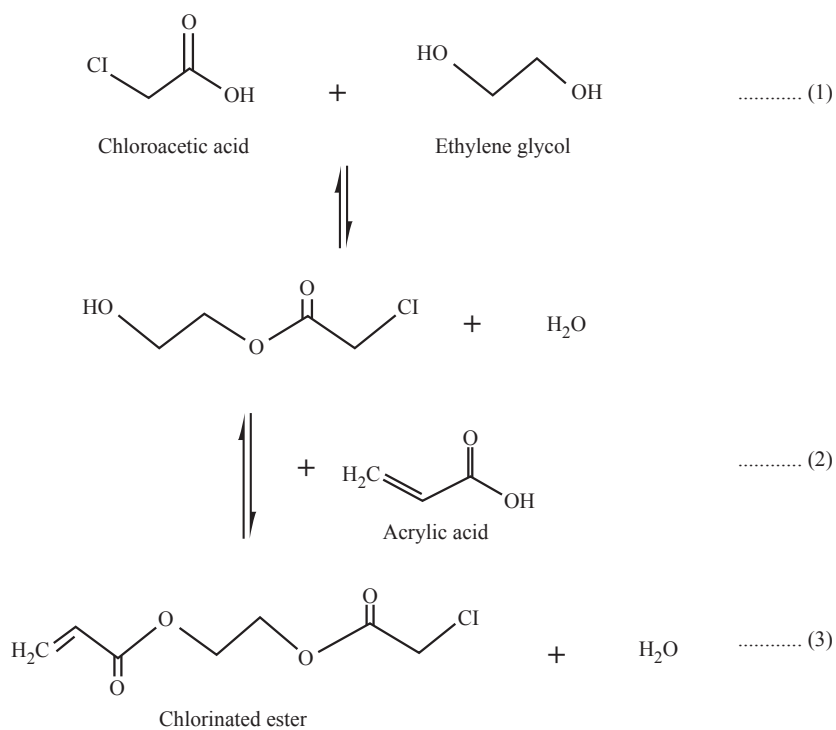


Figure 1. Schematic reaction mechanism of preparation of CAE<sup>7-9</sup>.

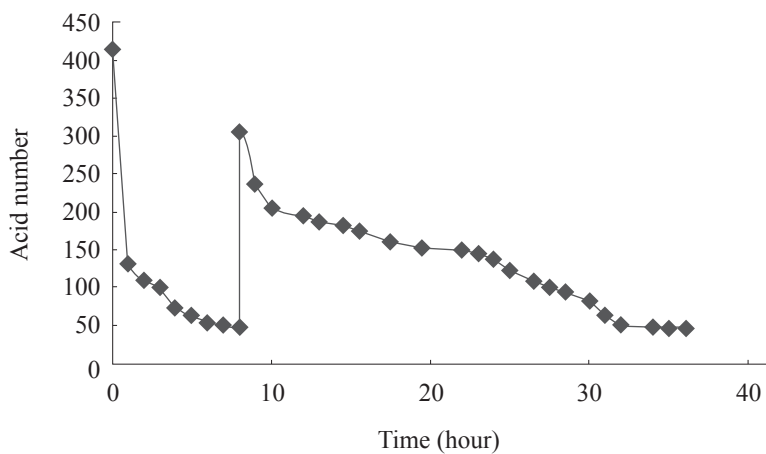


Figure 2. Acid number versus reaction time for CAE.

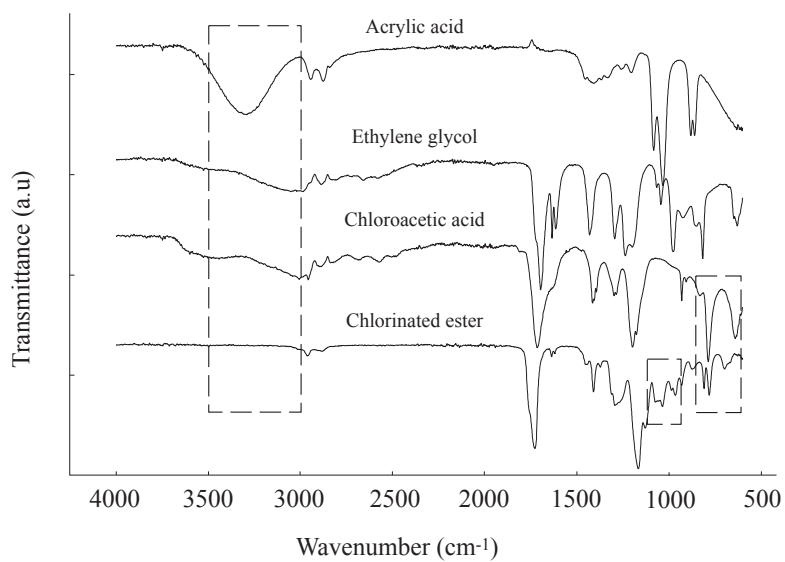


Figure 3. FTIR spectra of chlorinated acrylate ester and its precursors.

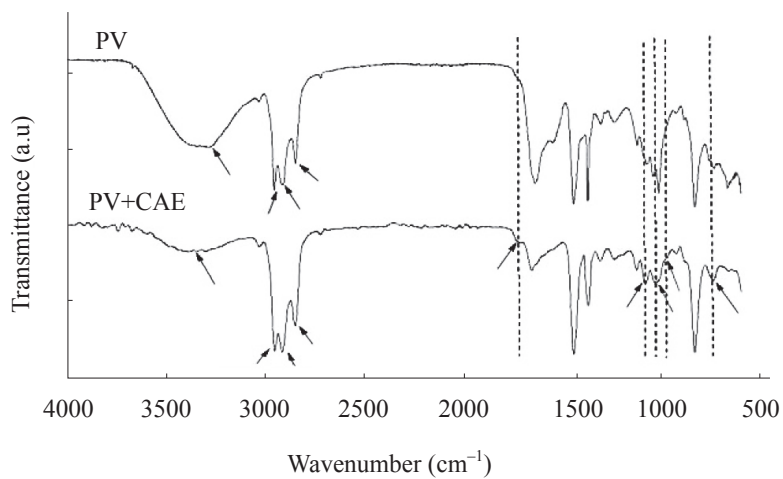


Figure 4. FTIR spectra of cured samples.

peaks at  $1187$ ,  $1070\text{ cm}^{-1}$ , and  $1038\text{ cm}^{-1}$  were attributed to the C-O-C bonds (ether). The increasing in amount of hydroxyl group, the appearance of carbonyl group, ether group and chlorine group in PV+CAE indicate that the CAE was incorporated into the system. The characteristic peak at approximately  $2700$ - $2900\text{ cm}^{-1}$  represented C-H stretching of  $-\text{CH}_3$  group and  $-\text{CH}_2$  group in aliphatic compound, corresponded to polyisoprene<sup>13</sup>.

*Thermal Properties of Cured PV+CAE: Thermal Gravimetric Analysis (TGA).* The TGA thermograms of cured samples are shown in *Figure 5*. The thermograms of samples showed a one-step drop in weight which indicated one degradation stage. This shows that the system consists of one component where CAE was mixed homogenously in the system. The degradation was observed within  $301$ - $322^\circ\text{C}$  (*Table 2*) which corresponded to the decomposition of rubber hydrocarbon<sup>13</sup>.

### Differential Scanning Calorimetry (DSC)

DSC instrument was utilised to determine the glass transition temperature of the samples. The glass transition temperatures of the cured PV and PV+CAE are shown in *Table 3*. The incorporation does not affect the transition temperature of PV. It demonstrated that the CAE present did not change the molecular structure of the PV.

TABLE 2. INITIAL DECOMPOSITION TEMPERATURE AND MAXIMUM DECOMPOSITION TEMPERATURES OF SAMPLES

Sample	Degradation Temperature, $T_{\text{max}}$ ( $^\circ\text{C}$ )
PV	316
PV-3	322
PV-5	322
PV-10	317
PV-15	301

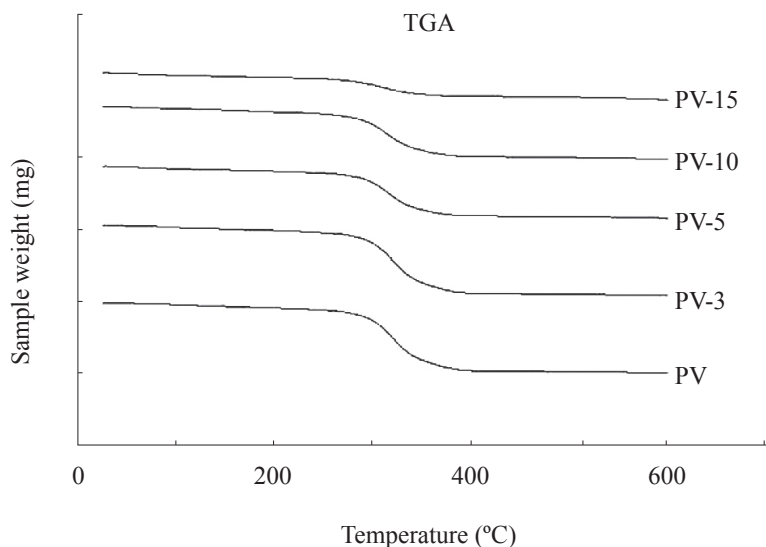


Figure 5. TGA thermogram of cured samples.

TABLE 3. GLASS TRANSITION TEMPERATURE OF EACH SAMPLE

Sample	Glass transition temperature, $T_g$ (°C)
PV	-60.9
PV-3	-60.7
PV-5	-60.9
PV-10	-60.9
PV-15	-61.0

### Tensile Strength

Tensile test was done to determine the effect of the incorporation of CAE in prevulcanised latex system on the strength of the cured samples (*Figure 6*). It can be seen that the tensile strength values of the PV+CAE system were significantly lower than those of the PV system. Tensile strength is the maximum tensile stress reached during stretching. The

tensile strength of the samples decreased as the amount of CAE in rubber increased. In the cured rubber system, covalent crosslinking and intermolecular forces (van der Waals forces) hold the long polymer chains in place<sup>15</sup>. The polymer chains were regularly arranged and may undergo strain crystallisation. As a result, natural rubber has the highest tensile strength of 21 MPa. The tensile strength of the rubber decreased with the addition of CAE. The presence of CAE affects the diffusion of molecules between the latex particles during film formation. The molecules cannot close pack each other due to the presence of CAE in the system.

The elongation at break and modulus were relative to the tensile strength of the samples. As the tensile strength decrease with the increase of chlorinated ester in the sample, the elongation at breaks and modulus also decrease (*Figures 7 and 8*).

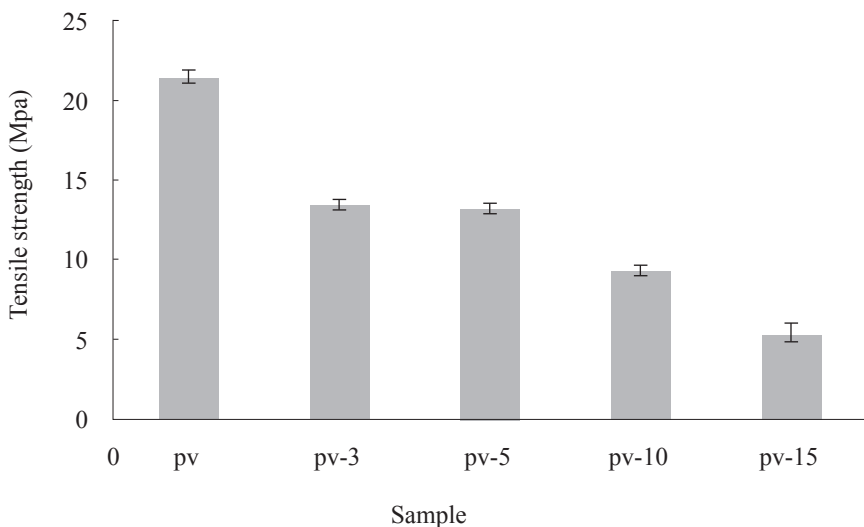


Figure 6. Tensiles strength of the test pieces.

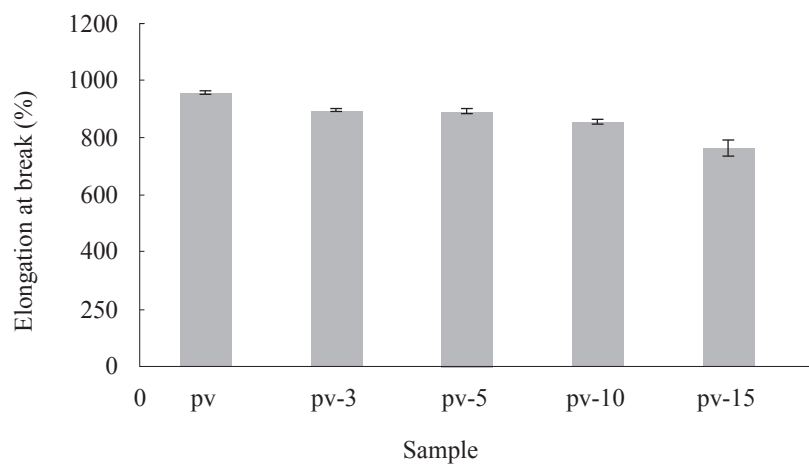


Figure 7. Elongation at break of the test pieces.

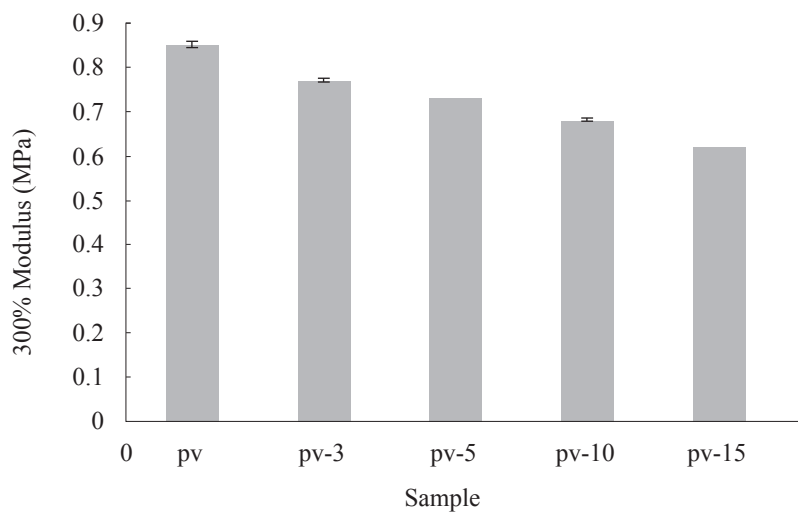


Figure 8. Modulus 300 of the test pieces.



## CONCLUSION

CAE was successfully produced and incorporated in PV natural rubber latex. The reduction of acid number value to the minimum constant value showed that the esterification reaction was accomplished. FTIR analysis revealed the presence of O–H, C=O, C–O–C and C–Cl in the cured PV+CAE. Thermal characterisation of the samples demonstrated that the degradation was within 301–322°C with glass transition temperature between -60.7°C to -61.0°C. The tensile test showed that tensile strength of cured rubber decreased as the amount of CAE increased.

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