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Grafting of sodium carboxymethylcellulose (CMC) with glycidyl methacrylate and development of UV curable coatings from CMC-*g*-GMA induced by cationic photoinitiators

Ong Hui Lin, R.N. Kumar*, H.D. Rozman, Mohd. Azemi Mohd. Noor

School of Industrial Technology, Universiti Sains Malaysia, 11800 Pulau Pinang, Malaysia

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Abstract

With a view to developing UV curable surface coatings from renewable raw materials, carboxy methyl cellulose (CMC), one of the well-known cellulose derivatives, was subjected to a grafting reaction to introduce photoreactive epoxide groups onto the cellulose chain. Glycidyl methacrylate (GMA) was chosen and grafted onto the sodium carboxymethyl cellulose (SCMC) polymer chain using ceric ammonium nitrate (CAN) as initiator in a homogenous reaction system. Acrylate groups were involved in the grafting reaction while the glycidyl groups remained as pendant groups for a subsequent reaction induced by cationic photoinitiators and UV light. The percentage of grafting was found to increase with the increase of GMA monomer concentration within the range studied. FTIR spectra analysis provided evidence of grafting and a mechanism for the grafting reaction has been suggested. CMC was found to become hydrophobic on account of grafting and to account for such a transformation a spherical core–shell configuration has been proposed for the grafted polymer. CMC-*g*-GMA in cycloaliphatic diepoxied (CAE) system was found to exhibit pseudoplastic behaviour with a hysteresis suggestive of thixotropicity, a property favourable to surface coatings. The cure behaviour and mechanical properties of the cured films were studied and these results are reported in this paper

Keywords: CMC-*g*-GMA; Photoinitiator; Grafting

1. Introduction

Radiation curable coating systems are increasingly being chosen as an environmentally favourable alternative to traditional solvent-based finishing systems. These systems possess low levels of emission of volatile organic compounds(VOC).

Radiation curing is now being increasingly used in various sectors of applications, mainly in the coating industry, graphic arts, and microelectronics, replacing conventional solvent-based coatings, inks and adhesives. They have other advantages such as fast cure speed, room temperature operation, high-quality end products, less rejection rates, less-energy consumption and requirement of less floor space.

The formulations for the UV curable systems consist of:

1. Oligomers
2. Reactive diluents
3. Photoinitiators
4. Surface active agents, pigments, etc.

Cellulose and starch can be considered to be valuable substrates for effecting suitable modification by introducing the appropriate telechelic groups to make it UV curable. They are both important renewable resources and lend themselves to be converted into products which can serve as alternate raw materials for the UV curable coating systems. Extensive potential therefore exists for employing cellulose and starch in surface coating applications by suitable chemical modification. Cellulose derivatives have not so been used extensively as good overall substitutes for synthetic polymeric materials which are primarily produced from petrochemical raw materials.

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* Corresponding author. Fax: +60 04 657 3678.
E-mail address: rnkumar@usm.my (R.N. Kumar).

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In this study cellulose derivatives which can undergo cross-linking on exposure to UV radiation were prepared.

The principle of such a development is to introduce pendant reactive groups into cellulose to produce derivatives which can undergo cross-linking when exposed to UV radiation. Thus some of the hydroxyl groups present in starch and cellulose molecules can be substituted by reactive acrylic or epoxy groups which have the potential to undergo photopolymerization either induced by free radical or cationic photoinitiators.

These derivatives so obtained when incorporated in the surface coating formulations can produce hard, scratch-resistant and solvent-resistant film following irradiation by UV light. Both conventional chemical reactions through functional groups as well as free radical grafting reactions can be employed for the purpose. The present work employs carboxymethyl cellulose as a substrate for the grafting reaction.

Sodium carboxymethylcellulose (CMC), also known as cellulose gum, is anionic, water-soluble cellulose ether, available in a wide range of substitution (Majewicz & Podlas, 1966). The CMC structure is based on the β-(1→4)-D-glucopyranose polymer of cellulose. Different preparations may have different degrees of substitution, but it is generally in the range 0.6–0.95 carboxymethyl groups per monomer units (Chaplin, 2002).

CMC molecules are somewhat shorter, on average, than native cellulose with uneven derivatization giving areas of high and low substitution. This substitution is mostly 2-O and 6-O-linked, followed in order importance by 2,6-di-O- then 3-O-, 3,6-di-O- lastly 2,3,6,-tri-O-linked. CMC molecules are mostly extended (rod-like) at low concentrations but at higher concentrations the molecules overlap and coil up and then, at high concentrations, entangle to become a thermo-reversible gel. Increasing ionic strength and reducing pH both decrease the viscosity as they causes the polymer to become more coiled (Chaplin, 2002).

CMC is soluble in hot and cold water. The introduction of the –CH_2–COOH groups into the cellulose molecule results in two opposing effects:

(a) Opening up of the cellulose structure thereby enhancing the diffusion and adsorption of both the monomer (GMA) and the initiator. This in turn would increase the graft yield.
(b) Blocking some of the hydroxyl groups along the cellulose chains.

Effect (a) leads to increase in the graft yield whereas the effect (b) would decrease. With methyl methacrylate and acrylic acid, effect (a) has been reported to outweigh the effect (b). Glycidyl metharylate monomer employed in the present work is also expected to behave similarly.

The choice of GMA as the monomer for grafting is due to its dual functionality. When the acrylic groups are involved in the grafting on to the cellulose molecule, the pendant glycidyl groups can serve as photo-reactive groups and can undergo co-polymerization with cycloaliphatic diepoxides to form interpenetrating polymer network.

Cerium(IV) ion, as ceric ammonium nitrate (CAN) has been employed as the initiator for the grafting reaction. CAN is capable of producing free radicals on the cellulose backbone at room temperature. Cerium(IV) ions are versatile reagents for oxidation of numerous functional groups in organic synthesis, as well as in transition metal chemistry. Ceric ions, as redox system for initiating vinyl polymerization, are reactive both by themselves as well as in association with organic substrates functioning as reducing agents.

2. Materials and methods

2.1. Sodium carboxymethyl cellulose (CMC)

Sodium carboxymethyl cellulose used for the graft copolymerization was supplied by Fluka Chemie. It was used without further treatment. Sodium carboxymethyl cellulose (Fig. 1) is a white powder with a degree of substitution of 0.6–0.95 and the viscosity of 4% dry substance in water is 20–50 mPa s.

2.2. Glycidyl methacrylate (GMA)

Glycidyl methacyclate (GMA) of 97% purity with 0.005% hydroquinone (Fig. 2) was obtained from Fluka

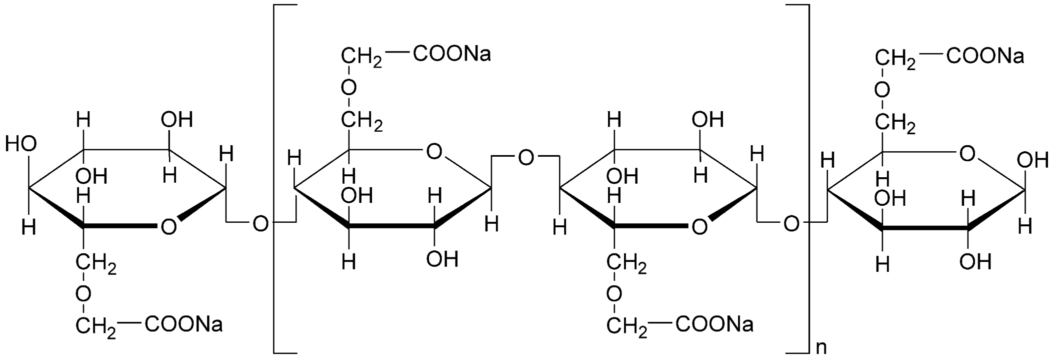


Fig. 1. Sodium carboxymethyl cellulose molecule structure.

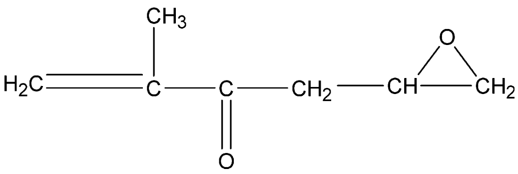


Fig. 2. Glycidyl methacrylate chemical structure.

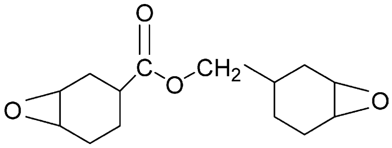


Fig. 3. Cycloaliphatic diepoxide formula structure.

Chemie AG. GMA obtained is of a high purity, dual functionality monomer and contains both acrylic and epoxy groups, ideally suited for coating and resin applications. The most important feature of GMA monomer is its versatility—the benefit is that the formulator or polymer manufacturer can tailor an end product to meet a wide variety of demanding specifications.

2.3. Ceric ammonium nitrate (CAN)

CAN was obtained from Fluka Chemie AG.

2.4. Oligomer (cycloaliphatic diepoxide)

Oligomer, which is used in this work, is cycloaliphatic diepoxide (ERL-4221) (Fig. 3) from Union Carbide. It is also known as 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexene carboxylate. Cycloaliphatic diepoxide has been used as a binder with photoinitiator in cationic UV radiation cured coating. It is capable of furnishing clear, shining, and highly rigid coating when cured with onium salt photoinitiator.

2.5. Photoinitiator

Triarylsulphonium hexafluorophosphate (CYRACURE® UVI-6990) (Fig. 4) photoinitiator was obtained from Union Carbide Corp. Triarylsulphonium salts have complex metal halide precursor anions photoinitiator for cationic polymerization. Sulfonium salts are photoactive (Crivello & Lam, 1979).

3. Methodology

3.1. Graft copolymerization CMC with GMA

A definite amount of CMC (4.0 g) was dissolved with stirring and warming in distilled water (200 ml). When all CMC was dissolved to form a clear solution, it was poured into a 500 ml 2 neck round bottomed flask fitted with magnetic stirrer. Inert gas (N_2) was bubbled through at room temperature. After 30 min, 0.68 g CAN dissolved in 2 ml of distilled water was added followed (after approximately 10 min) by addition of GMA monomer in the range from 1 to 4 g. Graft copolymerization was conducted at room temperature for 3 h. The resulting product (pH 4) was centrifuged for 10 min using a laboratory centrifuge [model MLW, type T51.1; swing-out rotor (8×15 ml A)] with speed 2750 rpm and relative centrifugal force of 1125*g*.

A yellowish white graft copolymer product was then washed with acetone, centrifuged, and air-dried. Polyglycidyl methacrylate (PGMA) homopolymer was removed by soxhlet extraction with tetrahydrofuran (THF) for 2 h.

3.2. Mechanism of grafting reaction

The mechanism of grafting reaction is illustrated in Fig. 5.

3.3. Confirmation of graft copolymer formation

3.3.1. Acid hydrolysis

Like all carbohydrate glycosides, cellulose is susceptible to acidic hydrolysis. The degree of susceptibility varies according to the region, amorphous or crystalline, concentration, type of acid and temperature.

CMC graft copolymer was determined by the weight loss during the course of acid hydrolysis. 40.5 ml of HCl (SG = 1.191 g/ml), which is 37.8% w/w, was diluted in 1 l distilled water to prepare a 0.5 N solution. A slurry of 3 g of sample graft copolymer in 270 ml of 0.5 N HCI was then refluxed for 3 h. PGMA was separated from hydrolyzed CMC by filtration. After drying to a constant weight, the graft percentage was determined.

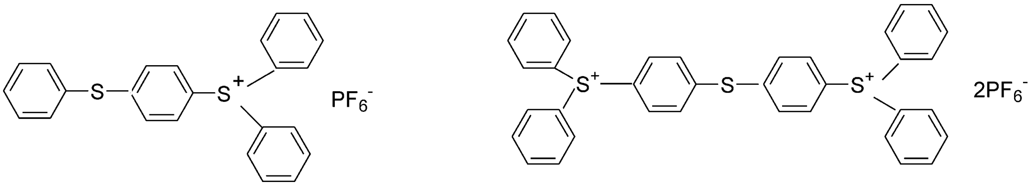


Fig. 4. Combination of triacrylsulfonium hexafluorophosphate salt molecule structure.

$$\text{Grafting percentage (\%)} = \frac{\text{Weight of PGMA}}{\text{Weight of graft copolymer}}100$$

$$= \frac{\text{Weight after acid hydrolysis}}{\text{Weight before acid hydrolysis}}100$$

The hydrolysis process takes place as shown in Fig. 6.

3.3.2. Infrared spectroscopy (FTIR)

The spectra of sodium carboxymethyl cellulose and CMC graft GMA copolymer were recorded on a Perkin–Elmer Fourier transform infrared spectrophotometer, using the potassium bromide (KBr) disk sampling technique. The scanning of the FTIR spectrophotometer was carried out from 4000 to 400 cm^{-1}.

3.4. Rheological properties

The viscosity of the CMC and CMC-*g*-GMA in the cycloaliphatic diepoxy system was determined using the rotor viscometer type Haake PK 100 Rotor Visco RV at room temperature. CMC was added in the oligomer cycloaliphatic diepoxide at different percentages: 10, 15, 20, 25 and 30% in the five small glass bottles. The solutions were stirred until homogenous and viscosity was determined under a shear rate 50 cm^{-1}. Ten values were obtained from which the means were calculated.

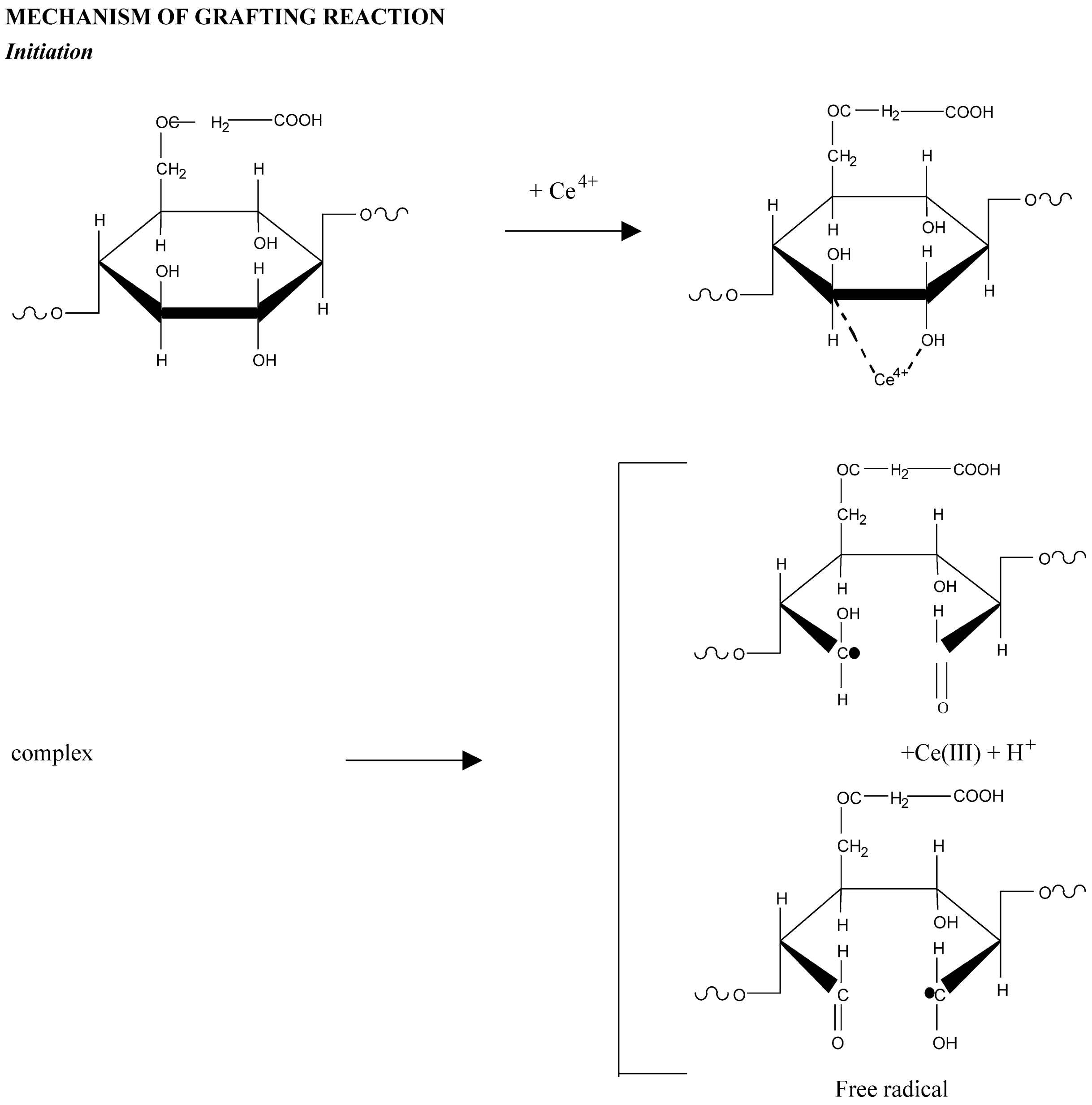
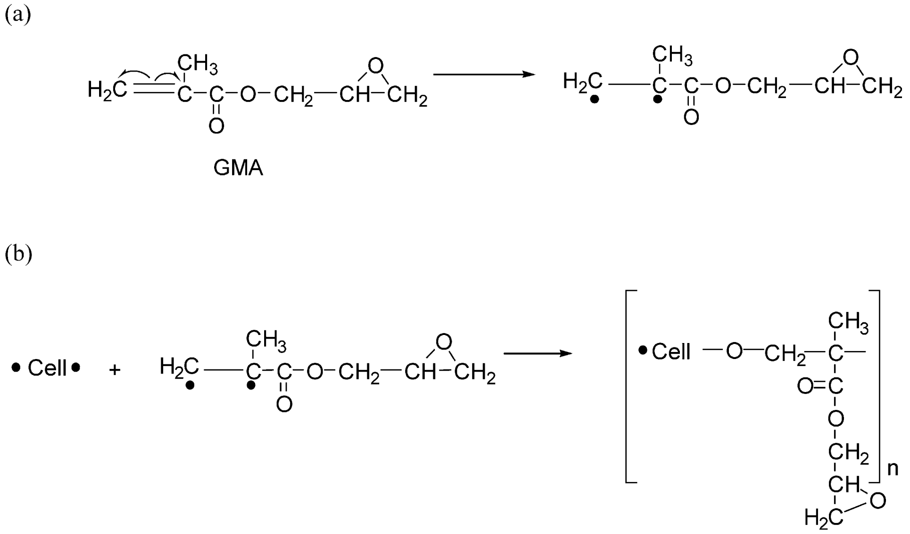


Fig. 5. Graft copolymerization reaction of GMA onto carboxymethyl cellulose (CMC).

Propagation



Termination

$$(P\,[CMC - GMA])_m\bullet + (P\,[CMC - GMA])_n\bullet \longrightarrow (P\,[CMC - GMA])_{m+n}$$

Fig. 5 (*continued*)

The above procedure above was repeated for the copolymer CMC-*g*-GMA. After that, viscosity determination of CMC (20%) and CMC-*g*-GMA (20%) in the cycloaliphatic diepoxide system was carried out using different shear rate: $D = 40$, 50, 60, 70, 80, 90 and 100 s^{-1}.

3.5. Preparation of UV curable coating formulations

The coatings were made according to the formulations given in Table 1.

CMC-*g*-GMA which had 66% of grafting was powdered by using a hammer mill to disintegrate the agglomerated particles and reduce the size. Particles were then ground in a mortar and pestle followed by sieving to get fine and uniform particle size fractions. The powdered CMC-*g*-GMA was mixed with CAE. Further grinding was performed using the mortar and pestle to produce the homogenous mixture. Photoinitiator was added subsequently into the mixture. The mixture was then coated on glass plate and aluminum substrate by using hand coater and wire wound roller coater. The surface of substrate must be very clean before the mixture was coated on it. So, every surface of the substrate was washed with detergent and wiped with acetone using white cotton fabric (Table 2).

3.6. UV curing

Coated samples were cured using UV/V machine with medium pressure (1–2 atm) UV lamp at 10 m/min for five passes. The cured films were further post-cured at 120 °C for

$$\text{Grafting percentage (\%)} = \frac{\text{Weight of PGMA}}{\text{Weight of graft copolymer}} \times 100 = \frac{\text{Weight after acid hydrolysis}}{\text{Weight before acid hydrolysis}} \times 100$$

The hydrolysis process takes place according to the following chemical equation:

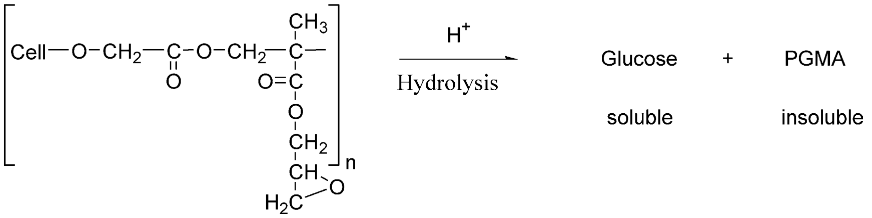


Fig. 6. Reaction of grafted carboxymethyl cellulose in acid hydrolysis.

Table 1
Coating formulations with pure ACE and those based on CMC, CMC-*g*-GMA in ACE

Sample	CMC (%)	CMC-*g*-GMA (%)	Photoinitiator (%)
A	–	–	3
B	20	–	3
C	–	20	3

30 min in an oven. Samples were conditioned in a desiccator at room temperature for at least 24 h before determination of the coating properties.

3.7. Determination of coating properties

3.7.1. Water absorption

The films (10 cm×4 cm×60 μm) together with aluminum plate were weighed accurately and immersed in distilled water for 10 h. The films were wiped using tissue paper and weighted again. Percentage of water absorption was determined using the equation below:

$$\text{Water absorption}\ (\%) = \frac{\text{Weight after immersion} - \text{weight before immersion}}{\text{Weight before immersion}} 100$$

3.7.2. Pendulum hardness (DIN 53157)

The films that were coated uniformly on glass plates were employed for the pendulum hardness testing using Erichsen Pendulum Hardness Test Instrument, Model 299/300. In this test, a pendulum makes contact with a coated panel through two steel balls. As the pendulum swings back and forth through a small angle, movement of the balls required some deformation of the coating near the surface. The instrument is equipped with an automatic counter and acoustic signal. The digital value on the counter indicates the number of oscillations executed by the pendulum in changing the angle from 6 to 3°.

3.7.3. Mandrel flexibility (ASTM D552 93b)

The films were coated uniformly on aluminum plates and the flexibility of the coated film was determined by performing the mandrel flexibility test. The test equipment consists of cylindrical steel rods with 14 different diameters in millimeters and a means for firmly supporting them during the test. The testing procedures adopted was as follows:

(a) The test panel was placed over a mandrel with the uncoated side in contact with the mandrel surface and with at least 50 mm overhang on other side.
(b) The panel was bent approximately around the mandrel.
(c) The panel was removed and examined immediately for any cracks visible to the unaided eye.
(d) If the cracking had not occurred, the procedure was repeated using successively smaller diameter mandrels until failure eventually occurred or until smallest diameter mandrel had been ultimately used.

The elongation of the coating was calculated according to the following equation:

$$E = e_1 + tc_1$$

where:

E, total elongation (%),
e_1, elongation from Table 3 (%)
t, thickness, mill, and
c_1, correction factor (for film thickness exceed 1 mill) from Table 3.

For this research t is 2.4 mills because the film thickness is 60 μm.

3.7.4. Gel content

Gel content of the coating was determined by Soxhlet extraction using hot toluene as solvent. The cured film together with aluminum plate was weighed and placed in a cellulose extraction thimble in the Soxhlet's extractor. Four sets of Soxhlet's extractor have been used. The solvent extraction was carried out with 250 ml toluene for 2 h.

After that, the samples were taken out followed by vacuum dried and re-weighed until it approached a constant weight.

Gel content of the coating was calculated according to the following equation:

$$\text{Gel content}\ (\%) = \frac{\text{Weight after extraction}}{\text{Weight before extraction}} 100$$

Table 2
Different substrates for testing

Testing	Substrate	Types of coater	Coating thickness (μm)	Substrate dimension
Pendulum hardness	Glass plate	Hand coater	60	10 cm× 15 cm×0.5 cm
Mandrel flexibility	Aluminum	Roller coater	60	4 cm×10 cm× 0.05 cm

Table 3
Relationship between the mandrel diameter and the elongation

Mandrel diameter (mm)	Elongation, e_1 (%)	Correction factor, c_1
12	7.15	0.41
5	17.70	0.91
4	22.29	1.52
3	30.02	1.45
2	45.66	2.11

4. Results and discussion

Fig. 6 shows the grafting mechanism of GMA monomer onto CMC in a manner similar to the one proposed by Charles et al. for other vinyl monomers. Accordingly cerium salt (Ce^{IV}) functioned as a powerful oxidizing agent while cellulose itself acted as a reducing component in the redox system. The active centers are directly produced on the cellulose backbone and no charge transfer mechanism is necessary to initiate cellulose graft copolymer formation (Hebeish & Guthrie, 1981). Cerium (IV) ions in acidic solution form chelates with the hydroxyl groups on carbons C-2 and C-3 of the anhydroglucose unit of CMC. Transfer of electrons from CMC to Ce(IV) gives Ce(III) which dissociates from the chelate. The anhydroglucose ring is scissioned between carbons C-2 and C-3 and a short-living radical is formed. In the presence of monomer GMA, grafting reactions are initiated to produce copolymer with the glycidyl pendent group.

The presence of two functional groups, hydroxyl and carboxyl, in carboxymethylated cellulose affords attractive sites for further chemical modifications, such as grafting. Because the presence of bulky groups, such as $-CH_2COOH$ in the cellulose may open up the cellulose structure, thereby increasing the diffusion of the initiator and the monomer in the cellulose. In other words, during swelling of PCMC in the reaction medium, there is a breakdown of many hydrogen bonds in the amorphous region of the cellulose and the chain molecules are then able to move apart. Hence, there will be a better tendency for the molecules of monomer and initiator to approach the crystalline region better than when the reaction is performed on unmodified cellulose.

Introduction of $-CH_2COOH$ groups into cellulose molecule results in two opposing effects: (a) opening up the cellulose structure, thereby enhancing diffusion and adsorption of both monomer and the initiator, and (b) blocking some of the hydroxyl groups along the cellulose chains. Effect (a) leads to an increase in the graft yields, whereas effect (b) gives rise to a decrease. Which of the two effects predominates would be the factor controlling graft yields.

4.1. Confirmation of graft copolymerization

The FT-IR spectra of the raw sodium carboxymethyl cellulose and the CMC-*g*-GMA of different degrees of grafting (% GMA/100 g CMC) are shown in Figs. 7–11. The CMC-*g*-GMA exhibited the following characteristic absorption bands: (a) absorption bands of epoxy groups at 900–909 cm^{-1} due to the terminal oxiranes groups derived from GMA; (b) absorption band at 1730–1736 cm^{-1} attributed to the stretching of C=O group which was the introduction of ester carbonyl group of the grafted glycidyl methacrylate (Kumar, Woo, & Abubakar, 1999); (c) absorption bands at 3400–3600 cm^{-1} due to –OH stretching frequency of anhydroglucose units (AGU) (Athawale & Lele, 1999). It was proved that on increasing the GMA monomer concentration, the absorption peak of terminal epoxy groups became sharper and intense. The appearances of new peaks in the spectrum of CMC-*g*-GMA gave supporting evidence for the grafted product and suggest that GMA had been successfully grafted onto CMC.

4.1.1. Acid hydrolysis

In order to separate the grafted polymer, the CMC-*g*-GMA copolymer was subjected to acid hydrolysis (Lee Han, 2002). A clear solution, which contained the carbohydrate component were obtained on refluxing the graft copolymer

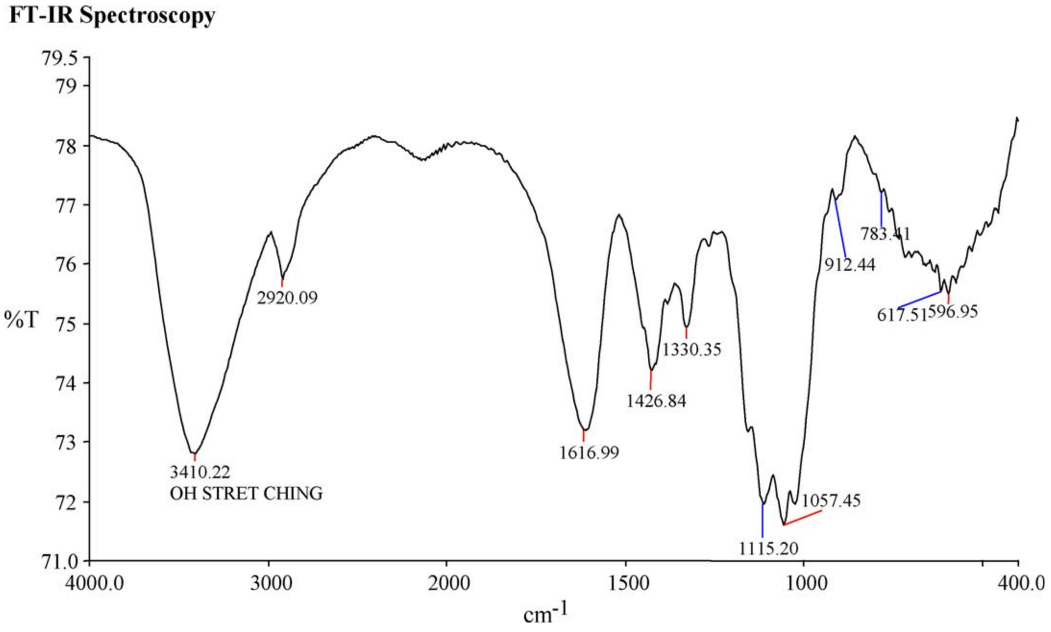


Fig. 7. FTIR spectra of sodium carboxymethyl cellulose (CMC).

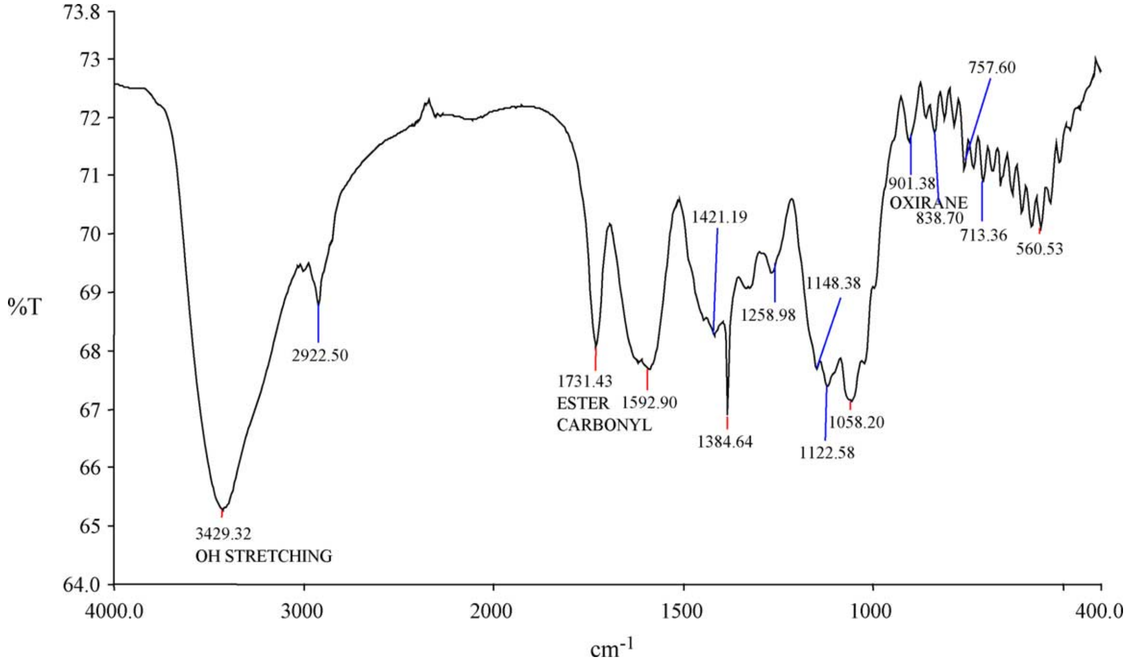


Fig. 8. FTIR spectra for CMC-*g*-GMA (1.00 g GMA/0.02% concentration of CMC solution).

in 0.5 N HCI for 3 h. After refluxing, the grafted polymer was filtered, dried and weighed. The weight of graft copolymer was substituted in the following equation to calculate the percentage of grafting at different concentrations of GMA monomer employed

$$\text{Grafting (\%)} = (\text{weight of PGMA} \div \text{weight of graft polymer})100$$

4.1.2. Effect of GMA monomer concentration

Fig. 12 shows the plot of percentage of grafting vs GMA monomer concentration.

It is clear that an increase of the monomer concentration increases the percentage of grafting within the range of study. The percentage of grafting increases almost linearly from 28.66% at 1 g GMA/0.02% concentration of CMC solution to 66.12% at monomer concentration of 4 g GMA/0.02% concentration of CMC solution.

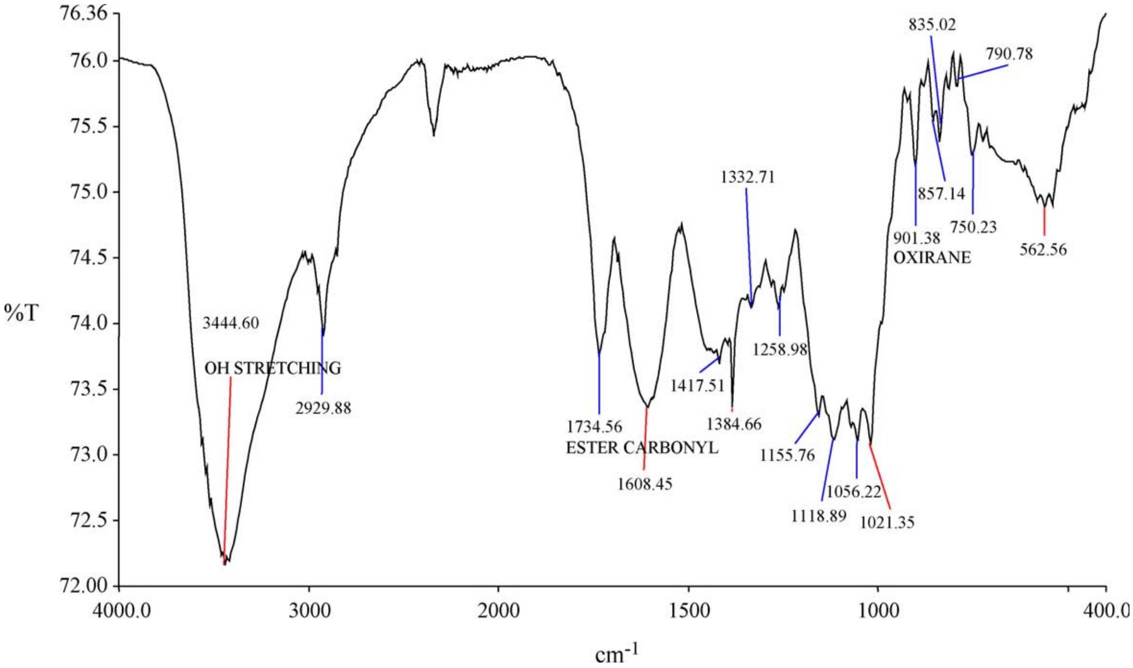


Fig. 9. FTIR spectra for CMC-*g*-GMA (2.00 g GMA/0.02% concentration of CMC solution).

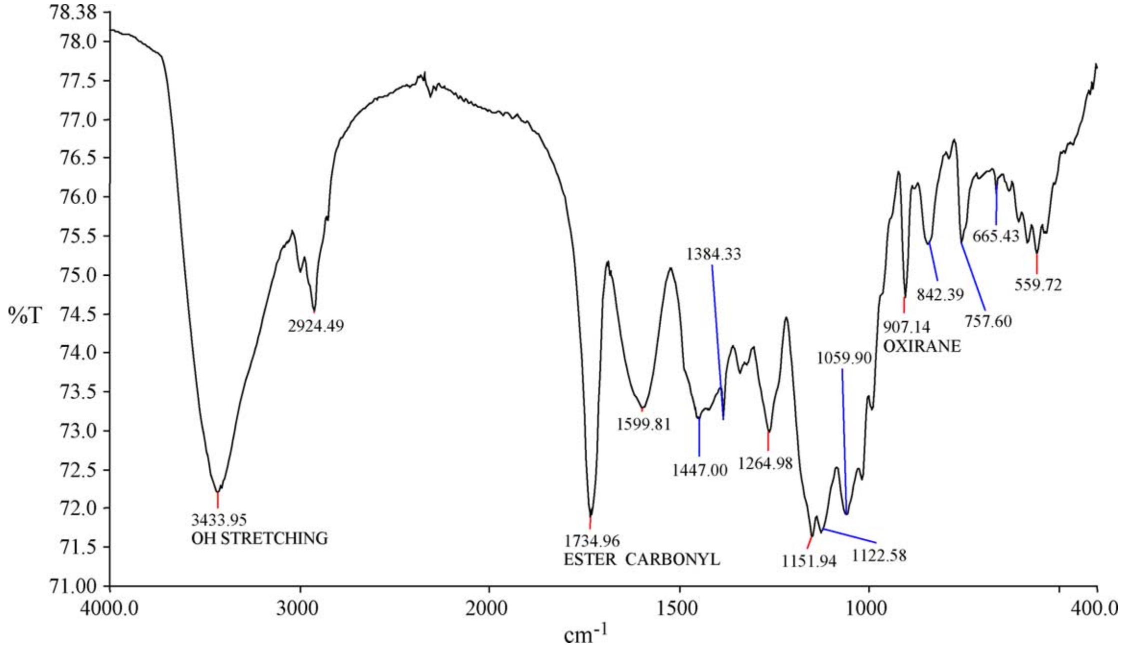


Fig. 10. FTIR spectra for CMC-*g*-GMA (3.00 g GMA/0.02% concentration of CMC solution).

At higher concentration of GMA, the gel effect brought about by the solubility of poly (glycidyl methacrylate) in its own monomer seems to be more pronounced. As a result, termination of growing grafted chain radicals by coupling is hindered, while the swelling of PCMC is enhanced. The ultimate effect of this is to increase grafting (Hebeish & Guthrie, 1981). An observation of the work worthy of significance is that films of good durability or biodegradability can be produced by an appropriate change of GMA concentration.

4.2. Rheological properties

Rheological behaviour of the coating systems incorporating the CMC-*g*-GMA in the in the CAE was studied and compared with the CAE–unmodified CMC. These studies were intended both to ascertain the efficacy of the modification as well as the determination of the maximum amount of the grafted polymer that can be incorporated in the coating formulations to obtain coating systems of practical viscosity for easy application onto the substrates.

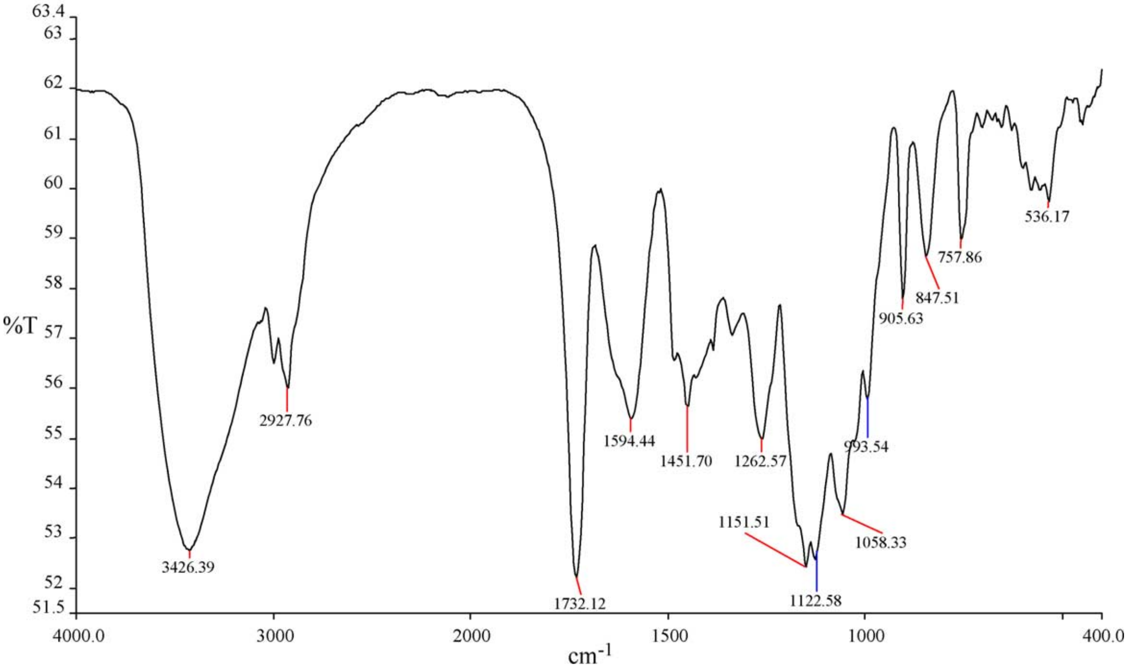


Fig. 11. FTIR spectra for CMC-*g*-GMA (4.00 g GMA/0.02% concentration of CMC solution).

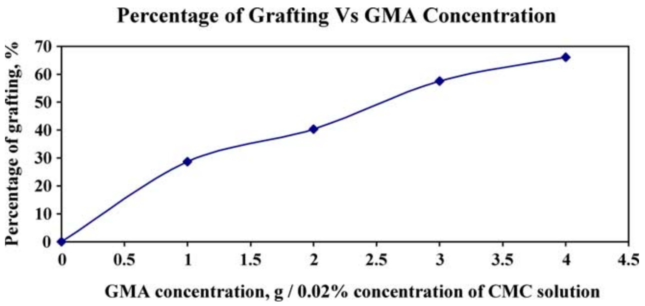


Fig. 12. Graph percentage of grafting vs GMA concentration.

The plots of viscosity vs percentage of unmodified and modified CMC in CAE system are shown in Fig. 13. Increasing the percentage both modified and unmodified CMC in CAE system increases viscosity when the shear rate was kept constant at 50 s^{-1} at room temperature. However, the viscosity of (CMC-*g*-GMA)–CAE system is lower than the CMC–CAE system. Similar trend can be observed at other shear rates also (Fig. 14). These results prove the efficacy of incorporating the grafted CMC in the coating formulations. Hence higher percentages of the grafted material can be incorporated in the CAE without significantly increasing the viscosity thereby reducing the cost of coating.

The results of Fig. 14 further shows that the CMC–CAE and (CMC-*g*-GMA)–CAE systems exhibit non-Newtonian behaviour because their viscosities decrease with change in shear rate, i.e. pseudoplastic behaviour. This could be due to two causes: (1) The long chain molecules tend to orient themselves in the direction of flow; as the force increased, the resistance to flow (viscosity) is decreased. (2) Disruption of entanglement may be another reason for the observed behaviour. Another interesting phenomenon is the hysteresis as shown in Fig. 14 Many coatings exhibit this kind of behaviour, but with time dependency. There is a pronounced delay in viscosity increase after force has been removed. This behaviour of pseudoplasticity with this hysteresis namely thixotropy is shown in Fig. 14. Obviously the long-chain polymers have a considerable amount of interaction and tend to develop a three-dimensional structure exhibiting thixotropy. The solution develops some gel strength and if sufficient force (shear stress) is exerted the structure tends to break and the apparent viscosity reduces. It may also be noticed that the viscosity of the formulation containing the CMC-*g*-GMA is much lower than that containing CMC. This reduction is due to the steric stability conferred on the CMC by the grafted GMA which prevents particle agglomeration by coalescence.

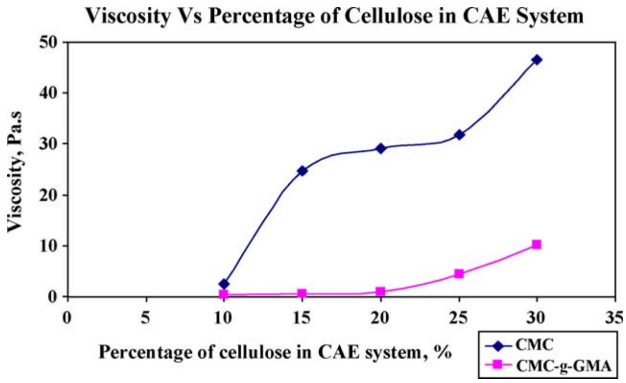


Fig. 13. Graph viscosity vs percentage of cellulose in CAE system with shear rate 50 s^{-1} at 26 °C.

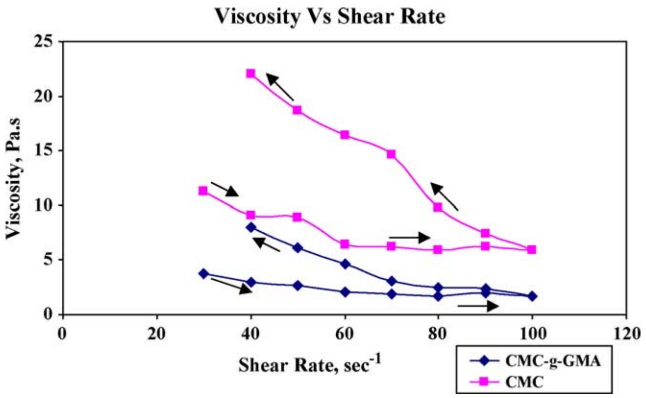


Fig. 14. Graph viscosity vs shear rate of cellulose in CAE system at 26 °C.

Table 4
Properties of cured film

Sample	Pendulum hardness	Mandrel flexibility	Gel content (%)	Water absorption (%)
A	106	17.58	99.61	1.70
B	90	33.51	97.85	38.18
C	35	50.73	96.33	0.86

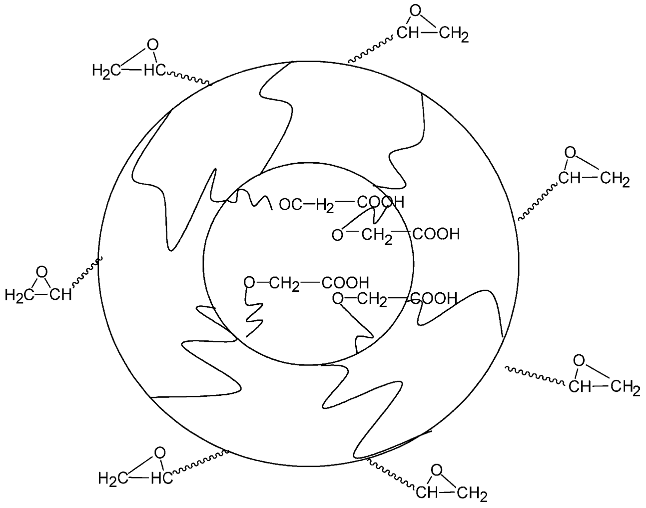


Fig. 15. Depiction of spherical shell structure of CMC-*g*-GMA.

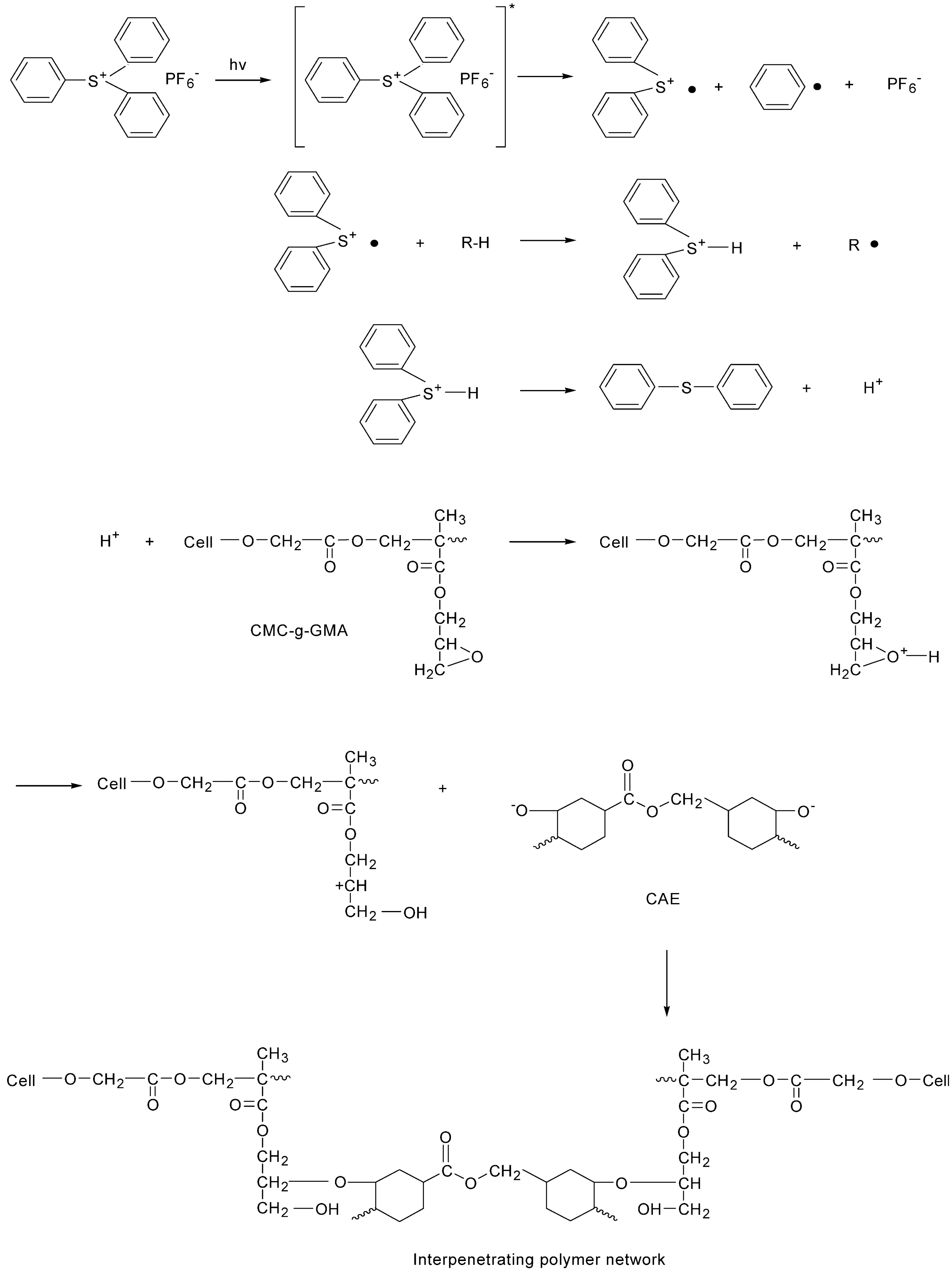


Fig. 16. Probable structure of the interpenetrating polymer network derived from the hybrid system after the cationic UV cured using triarylsulphonium salt photoinitiator.

Thixotropy exhibited in the CMC-*g*-GMA system is useful in coating systems since they become dripless. The coating begins as a moderately viscous material that stays on the brush but it quickly drops in viscosity under the shear stress of brushing force facilitating easy and smooth application. A return to higher viscosity, when shearing action stops, prevents dropping and sagging (Wicks, Jones, & Peter Pappas, 1999).

4.3. Properties of the UV cured films

4.3.1. Water absorption

The result of water absorption as displayed in Table 4 shows that addition of raw CMC in the coating formulation increased the water absorption from 1.70 to 38.18%. But, with the grafting of CMC with GMA initiated by ceric ammonium nitrate the cured film has a very low absorption of 0.86%, a value even less than that of CAE. It appears that the following phenomena are probable:

(1) An interpenetrating polymer network of grafted CMC-*g*-GMA with CAE as shown in Fig. 16.
(2) A cross-linking reaction between unreacted hydroxyl groups with the epoxide groups by CAE by a chain transfer process as shown in Fig. 17.

The reduction of the water absorption is due to the presence of glycidyl groups in the form of a protective shell around the CMC particle (Fig. 15). Thus there is a formation of a reactive and hydrophobic shell on the surface. This protective layer reduces the intermolecular hydrogen bonding thereby reducing the affinity to water. After grafting CMC with GMA, the CMC-*g*-GMA becomes hydrophobic and it does not absorb and swell in water.

The spherical core–shell configuration as described above promotes good adhesion between CMC particle and the matrix resin by the formation of an interpenetrating polymer network through the reaction between unreacted hydroxyl groups of the CMC with the epoxide groups by CAE by a chain transfer process as shown in Fig. 17.

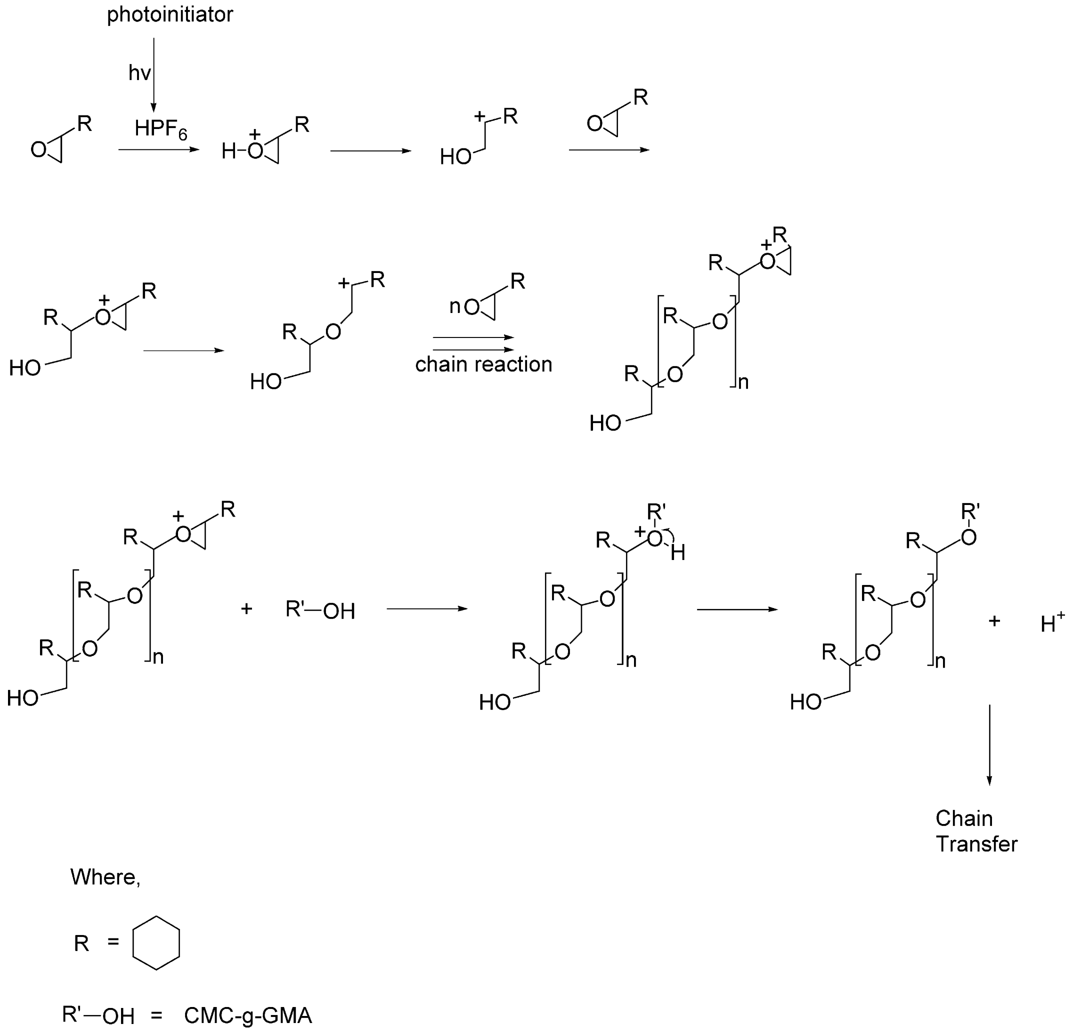


Fig. 17. Cross-linking reaction between unreacted hydroxyl groups with the epoxide groups in CAE by a chain transfer process.

4.3.2. Pendulum hardness

The results are displayed in Table 4. Pendulum hardness decreased from 106 to 90 on adding of sodium carboxymethyl cellulose into the coating formulation. It also showed the same result, by adding the CMC-*g*-GMA into the coating formulation pendulum hardness decreased to 35. CMC-*g*-GMA, which added into the coating formulation, showed the lowest reading of pendulum hardness. While achieving increased flexibility, it is generally inevitable that there is a trade off in film hardness. A compromise is generally reached between hardness and flexibility depending on the application by adjusting the quantity of the cellulose in the formulation and by controlling the other operating variables, while optimizing the conditions for the desired coating performance.

4.3.3. Mandrel flexibility

Table 4 shows the result of mandrel flexibility. By using the CMC-*g*-GMA in the coating formulation, the mandrel flexibility is 40% higher as compared to CMC, where the value of mandrel flexibility varied from 17.58 to 33.51 and 55.73. The improvement of the flexibility proved that stress transfer across the matrix interface in the cured film is facilitated. The crack propagation of the flexing of the film is kept under check. Grafting GMA onto CMC provides the potential for the chemical bonding between the cellulose and the cycloaliphatic epoxide through the epoxide functionality of GMA. Formation of a covalent bond between the cycloaliphatic epoxide matrix and the cellulose filler during the reaction with the epoxy group of cycloaliphatic epoxide, generally improved the mechanical properties of the coating. It is because the spherical-shell configuration can contribute to flexibility and toughness since spherical-shell can absorb the stress. Coating films with grafted CMC as fillers are able to bear a greater load before deformation.

4.3.4. Gel content

Gel content refers to the percentage of cross-linking that occurs in the coating film. From result given in Table 4, all the formulations show high gel contents of more than 96%. The high gel content shows the high reactivity of cycloaliphatic epoxide. However, the single factor design showed slight decrease in the gel content of coating film, which consists of CMC and CMC-*g*-GMA. So, addition of cellulose affected slightly the performance of curing.

5. Conclusion

GMA was successfully grafted onto CMC polymer chain using CAN as initiator in a homogenous medium. The percentage of grafting increased with the increase of concentration of the GMA monomer in the range studied. FTIR spectral analysis provided the evidence of grafting of GMA onto CMC. The mechanism of the grafting reaction had been suggested. Rheological studies of the solution of CMC-*g*-GMA in CAE system showed (1) that the viscosity of the solution of CMC-*g*-GMA in CAE is less compared to CMC in CAE system. Further (2) CMC-*g*-GMA in CAE system exhibits pseudoplastic behaviour with a hysteresis loop suggestion of thixotropic behaviour. Both the observed rheological behaviours are desirable for the surface coatings. The addition of CMC-*g*-GMA in the coating formulations increased the hardness of cured film. But, the addition does not show any significant effect on flexibility and gel content. The increase of cationic photoinitiator concentration in coating formulation increased the hardness and decreased the flexibility of the cured film. Gel content also increased with the increase of cationic photoinitiator. A spherical core–shell configuration has been proposed to explain the hydrophobic behaviour of the CMC-*g*-GMA.

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