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GMA grafted sago starch as a reactive component in ultra violet radiation curable coatings

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Abstract

Glycidyl methacrylate (GMA) was successfully grafted onto sago starch using ceric ammonium nitrate as initiator in aqueous medium. The percentage of grafting increased with increasing concentration of GMA monomer in the range studied. A core-shell configuration had been suggested to account for the hydrophobic behavior of the starch-*g*-GMA. Fourier transform infrared spectral analysis provided evidence of the grafting of GMA onto the starch. The acrylic double bond participated in the grafting onto the polysaccharide backbone with the glycidyl groups remaining unaffected.

The graft copolymer of starch and glycidyl methacrylate (starch-*g*-GMA) was incorporated into UV curable formulations using a cationic photoinitiator. In general, the addition of starch-*g*-GMA increased the flexibility of the cured film. The increasing of starch-*g*-GMA concentration in the coatings formulation increased the hardness of cured films. Gel content of the cured epoxy resin remained unimpaired by the addition of starch-*g*-GMA. Increasing the photoinitiator concentration in the coating formulations increased the hardness and as expected decreased the flexibility of the cured film. The gel content increased with increasing photoinitiator concentration. Further experiments are in progress to study the biodegradability of coatings.

Keywords: Starch graft copolymers; Starch; Glycidyl methacrylate; UV radiation; Photoreactive; Starch-*g*-GMA; Cycloaliphatic epoxide; Core-shell structure; Cationic photoinitators

1. Introduction

Modified and unmodified starch products are extensively used for a variety of applications such as sizing agents for textiles and paper, as adhesives for corrugated and laminated paper boards and wall papers, flocculants, binders, fabric printing aids, thickeners, and many other non-food industrial applications. For the production of surface coatings and polymeric moulding compounds, industry relies heavily on synthetic polymeric resins produced from petrochemical resources. Petrochemicals are depletable resource and ever increasing demand for petroleum based products has adversely affected their cost and availability in recent times. Starches are readily available and renewable. The potential of starch based products can be substantially increased if it is possible to alter or correct the inherent defects which limit applications in coatings and shaped articles applications. Hence the use of starch as partial substitute for petroleum derived polymers is currently an active area of research. A further advantage of such a substitution is the low cost and biodegradability of synthetic polymers incorporating the plant-derived materials (Trimnell, Swanson, Shogren, & Fanta, 1993). The starchy portion of the polymer can be easily attacked by microorganisms, leading to environmental breakdown of the material thereby losing its integrity resulting in particles small enough to cause minimal damage to the environment (Patil & Fanta, 1994; Trimnell, Fanta, & Salch, 1996).

Next to cellulose, starch is the most abundant carbohydrate in the world. The raw material is available in sufficient amounts and in high purity. Its total annual world production is estimated to be between 25 and 45 million tons. To fulfill the various demands for the functionality in different starch products, industrially processed starch is modified enzymatically, physically or chemically. In most chemical modifications of starch, usually referred to as chemical derivatisation, the granule form is maintained and the hydroxy groups are partially substituted, yielding starch

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ethers and esters, as well as anionic and cationic starches. Other types of chemical derivatisation are oxidation, cross-linking and grafting of starches (Burgt, Bleeker, Mijland, Kamerling, & Vliegenthartart, 2000).

Grafting has been used as an important technique for modifying physical and chemical properties of polymers. Graft polymerization originates from the formation of an active site at a point on a polymer chain other than its end and exposure this site to a monomer. Most graft copolymers are formed by radical polymerization. In many instances, chain transfer reactions are involved by the abstraction of hydrogen atoms (Athawale & Rathi, 1997).

Starch graft copolymers are becoming increasingly important because of their potential application in industry. The wide range of available vinyl and other monomers suggests that the grafting is a powerful method for effecting substantial modification to starch properties, thereby enlarging its range of applications (Athawale & Rathi, 1997).

The objective of the present investigation was to prepare a novel starch product containing reactive, pendant glycidyl group with the ability to co-polymerize with epoxy resins. Glycidyl methacrylate monomer (GMA) was employed for the purpose. This monomer was chosen because of its dual functionality—an acrylic group and an epoxy group in the same molecule. Free radical initiator was used to graft the acrylic group onto the starch leaving the pendant glycidyl group for effecting photopolymerization on exposure to UV radiation during a subsequent step. For the purpose of preparing the UV curable compositions, the grafted starch was mixed with cycloaliphatic diepoxide (CAE) and exposed to UV radiation. Photo-curing was induced using a cationic photoinitiator. Cycloaliphatic diepoxide is a petroleum derived resin and is extensively used in Malaysia for a number of applications. The countries demand for the resin is exclusively met by imports. Hence there is a strong economic incentive to replace a portion of the resin by the renewable starch derivative in the coating formulations. The modified starch due to the presence of residual free hydroxyl groups can form an interpenetrating polymer network by a chain transfer mechanism (as discussed in the paper) and this can impart flexibility to the otherwise brittle cycloaliphatic epoxide system.

The studies undertaken in the present investigation consisted of two parts with the following objectives:

1. First to produce a photoreactive starch-*g*-GMA. This required determining the conditions for grafting starch with GMA, so that only the acrylic groups are grafted onto the polysaccharide chain while the glycidyl groups remain unaffected.
2. Secondly, to replace partly the cycloaliphatic diepoxide with starch-*g*-GMA in UV curable formulations and to study the cure behavior of the system induced by cationic photointiator and to determine how much of the starch-*g*-GMA can be incorporated partially with CAE system. For this purpose Response Surface Methodology (RSM) was applied. The results of the RSM will be published later.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

Sago starch (CRAUN/PELITA, Sarawak) was used for graft polymerization. GMA and Ceric Ammonium Nitrate (CAN) used were obtained from Fluka Chemika and used without further treatment. Cycloaliphatic Diepoxide (ERL 4221) and Photoinitiator UVI-6990 were supplied by Union Carbide. All other chemicals and solvents were of analytical grade and used without further purification.

2.1.2. Methods

2.1.2.1. Graft co-polymerization of starch. A slurry of 25 g of starch (dry basis) in 200 ml of distilled water was stirred and sparged with a slow stream of nitrogen gas for 1 h at 25 °C. GMA monomer was added in the range from 1 to 15 g, followed (after approximately 10 min) by addition of a solution of 1.7 g of CAN in 5 ml of 0.5N nitric acid. The CAN solution was added in two equal portions 1.25 h apart. Portion-wise addition of CAN initiator is reported to lead to higher graft molecular weights and improved properties in starch-*g*-poly(glycidyl methacrylate) material (Willett, Kotnis, O'Brien, Fanta, & Gordon, 1998). After adding the second portion of CAN solution, polymerization was allowed to proceed for 3 h at 25 °C. Graft copolymers were separated by filtration, washed with ethanol, neutralized to pH 7 with NaOH solution, and air-dried.

2.1.2.2. Determination of percentage of grafting. Poly (glycidyl methacrylate) homopolymer was removed by extraction with tetrahydrofuran (THF). The PGMA add-on of the starch graft was determined by weight loss on acid hydrolysis. An accurately weighed THF extracted graft copolymer sample (about 5 g) mixed with 450 ml of 0.5N HCl was refluxed for 3 h. PGMA was separated from hydrolyzed starch solution by filtration, followed by drying and weighing.

$$\text{Grafting }(\%) = \frac{\text{weight of polymer grafted}}{\text{weight of graft copolymer}} \times 100$$

2.1.2.3. Confirmation of grafting by FTIR. Fourier transform infrared (FTIR) spectra were acquired on a Nicolet's AVATAR 360 E.S.P. TM FTIR spectrometer system. One milligram of graft copolymer was used for analysis although a smaller amount may give useful spectra. One milligram of graft copolymer were intimately mixed with 99 mg of pure dry KBr followed by pressing into a pellet. FTIR spectra of pure starch and graft copolymer were recorded in the range of 4000–400 cm^{-1}.

Table 1
Mixing conditions

Sample	Cycloaliphatic diepoxide	Raw starch	Starch-*g*-GMA	Photoinitiator
A	10 g	1.5 g	–	0.3 g
B	10 g	–	1.5 g	0.3 g
C	10 g	–	–	0.3 g

2.1.2.4. Preparation of coating formulations. Starch-*g*-GMA which had the highest percentage of grafting (15 g GMA/25 g starch) was powdered in hammer mill to reduce and uniform the particle size. Unmodified starch/starch-*g*-GMA and resin were mixed according to the conditions given in Table 1. The samples were ground in a mortar and pestle to produce a homogenous mixture. Photoinitiator was then added. The mixture was coated by using a hand or roller coater on the glass or aluminum substrate depending on the type of test to be conducted (Table 2).

2.1.2.5. UV curing. Coated samples were cured by exposure to medium pressure mercury UV lamp at a conveyor speed of 7 m/min for five passes. Post cure was carried out at 120 °C for 30 min. Samples were stored in desiccators at room temperature for at least 24 h before testing.

2.1.2.6. Determination of properties of the coatings

2.1.2.6.1. Water absorption. The film were weighed and immersed in distilled water for 10 h. After immersion, the films were wiped using tissue paper and reweighed.

$$\%\ \text{water absorption} = \frac{\text{weight after immersion} - \text{weight before immersion}}{\text{weight before immersion}} \times 100$$

2.1.2.6.2. Pendulum hardness (DIN 53157). The pendulum hardness (König) of the cured coating was determined by Erichsen Pendulum Hardness Test Instrument, Model 299/300. It is the time taken for the pendulum to reduce the angle of swing from 6° to 3°. The instrument is equipped with an automatic counter and an acoustic signal.

2.1.2.6.3. Mandrel flexibility (ASTM D 522). The material to be tested was coated maintaining uniform thickness on aluminum plate. After curing, the elongation was determined by bending the aluminum plate successively over the cylindrical mandrels of decreasing diameters until the film cracked. Mandrel flexibility is defined in terms of elongation, which is defined as

$$E = e_1 + tc_1$$

where

E	total elongation, %
e_1	elongation from graph elongation (%) vs mandrel diameter (mm)
t	thickness, mils
c_1	correction factor (for film thickness exceed 1 mil) from graph correction factor vs mandrel diameter as described by the ASTM D 522.

2.1.2.6.4. Gel content. Gel content was determined by extraction with hot toluene in a Soxhelt extraction apparatus.

The cured film was weighed and then was placed in a cellulose extraction thimble in the Soxhlet's extractor. Solvent extraction was carried out in toluene for 2 h. The residue was taken out, vacuum dried and reweighed until it approached a constant weight. Gel content is calculated using the following equation:

$$\%\ \text{gel content} = \frac{\text{weight before extraction}}{\text{weight after extraction}} \times 100\%$$

3. Results and discussion

Confirmation of grafting by FTIR and determination of percentage of grafting by acid hydrolysis.

3.1. FTIR spectroscopy

The FTIR spectra of the raw sago starch and starch-*g*-GMA (15 g per 25 g of starch) are shown in Fig. 1. The FTIR spectra of starch-*g*-GMA indicated the appearance of new peaks in the region of 1731–1735 and 907–909 cm^{-1} confirming the presence of ester carbonyl group (C=O) (Lutfor et al., 2000) and the epoxy groups (Kumar, Woo, & Abusamah, 1999). These two peaks are absent in the raw starch.

FTIR spectra of the samples treated with up to 10 g of GMA per 25 g of starch contained the ester carbonyl groups but the epoxy absorption at 907–909 cm^{-1} were not significant. Either these peaks had been masked by the starch bands in the region or more probably the epoxy groups had been consumed in a parallel ring opening reaction under the acidic conditions caused by the release of

Table 2
Substrates for testing of coating behavior

Testing	Substrate	Substrate dimension	Coater	Coating thickness (μm)
Pendulum hardness	Glass plate	100 mm × 150 mm × 5 mm	Hand coater	60
Mandrel flexibility	Aluminum plate	35 mm × 100 mm × 0.5 mm	Spiral roller coater	60

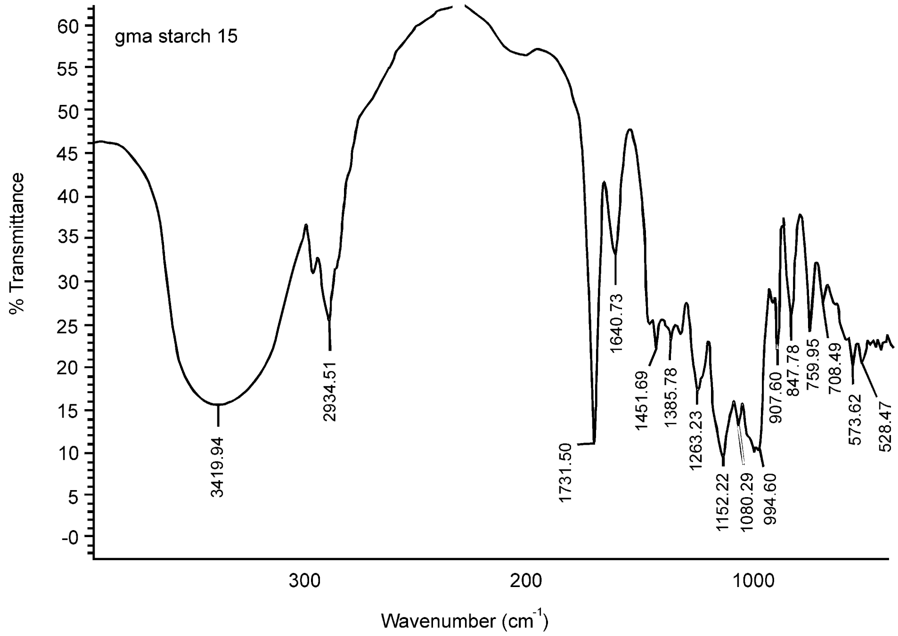

Fig. 1. FTIR spectra of starch-*g*-GMA (15 g GMA/25 g starch).

protons in the redox reaction discussed below. The FTIR spectra of sago starch-*g*-GMA therefore gave supporting evidence that the GMA had been successfully grafted onto sago starch.

The grafting GMA monomer onto sago starch is assumed to follow the same reaction scheme as has been elucidated for the graft co-polymerization of vinyl monomers onto starch macromolecules (Ceresa, 1973; Lutfor et al., 2000).

This scheme is given below:

1. Free radicals are formed on the C_2 of anhydroglucose ring when a ceric ion is used to initiate grafting. The ceric ions are attached to sago starch to produce a sago starch–ceric complex.
2. Ceric ions are reduced to Ce^{3+} ion with the release of a proton.
3. As a result, the bond between C_2 and C_3 is broken and free radicals of sago starch are formed.
4. Free radicals so formed then reacted with GMA to produce the copolymer (Fig. 2).

3.2. Determination of add-on GMA by acid hydrolysis

In order to separate the grafted polymer, the starch-*g*-GMA copolymers were subjected to acid hydrolysis by the method described in Willett et al. (1998). The weight of grafted polymer so obtained was substituted in the equation below and the % of grafting of different concentration of monomer GMA added were calculated.

$$\text{Grafting (\%)} = \frac{\text{weight of polymer grafted}}{\text{weight of graft copolymer}} \times 100$$

3.3. Effect of GMA concentration on the percentage of grafting

From Fig. 3 it is clear that the percentage of grafting increases from as low as 2.012% at 1 g GMA/25 g starch to as high as 48.684% at monomer concentration of 15 g/25 g starch. The same trend was reported by Shukla et al. for the grafting of GMA onto cellulose using CAN as the initiator (Shukla & Athalye, 1994). The enhancement in percentage of grafting could be associated with the greater availability of GMA molecules in the proximity of starch macro radicals (sites for grafting).

3.4. Proposal of core-shell model for the GMA-g-starch

Since the grafting reaction is carried out at room temperature the overall reaction is essentially heterogeneous due to the following reasons:

1. During the period of reaction no dissolution of starch is possible and the particles remained discrete and retained individuality throughout the reaction.
2. Further as the grafting proceeds, the hydrophobic GMA layer gradually and continuously formed on the starch particles is expected not only to prevent any dissolution of starch but also would cause steric stability to the particles. Any possibility of homogeneous reaction would thus be prevented. Hence it is reasonable to assume that the entire grafting process would occur heterogeneously. Under these conditions it is highly likely that the grafting reaction of starch and the GMA results in core-shell configuration consisting of hydrophobic shell around the starch core.

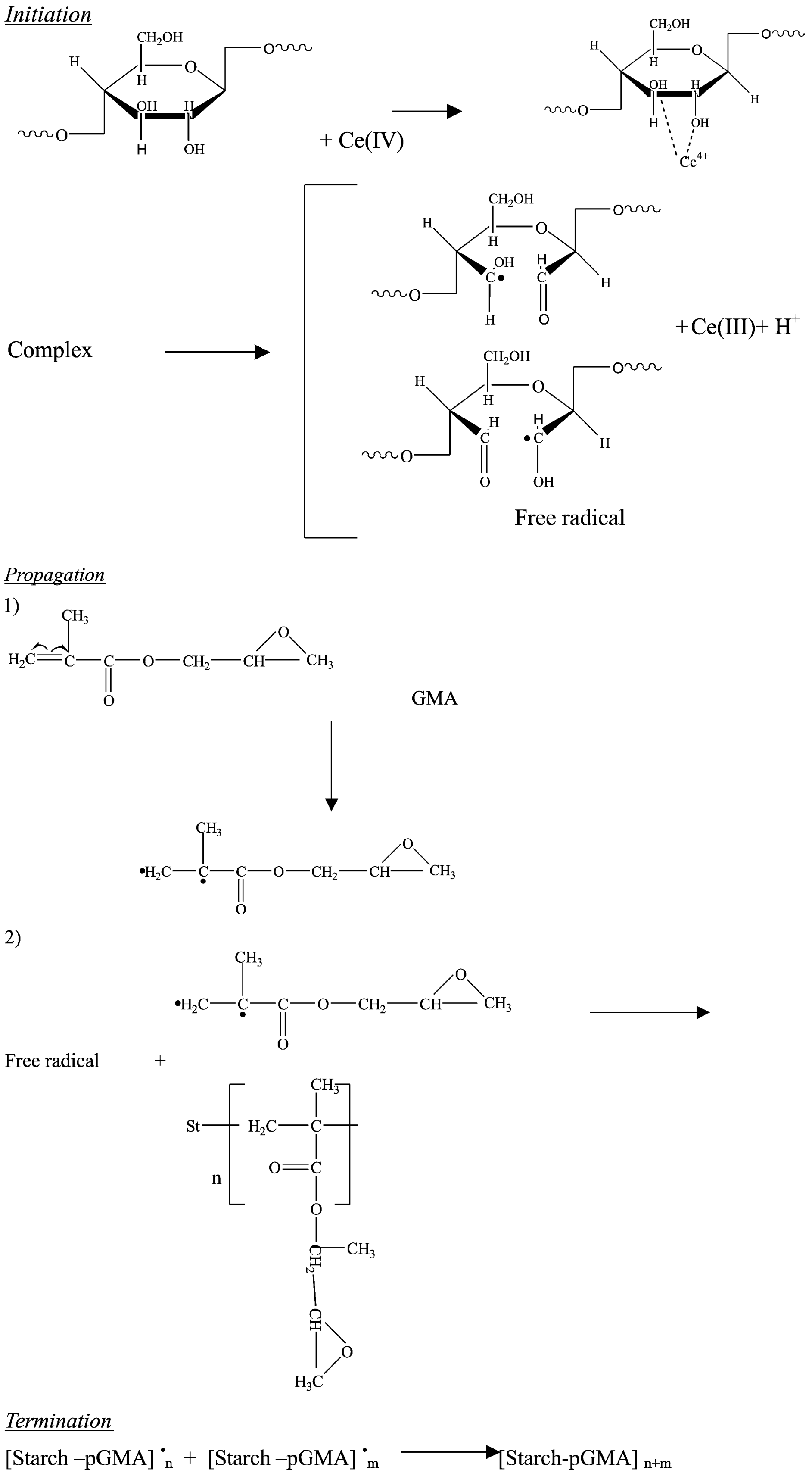

Fig. 2. Graft co-polymerization reaction of GMA onto sago starch.

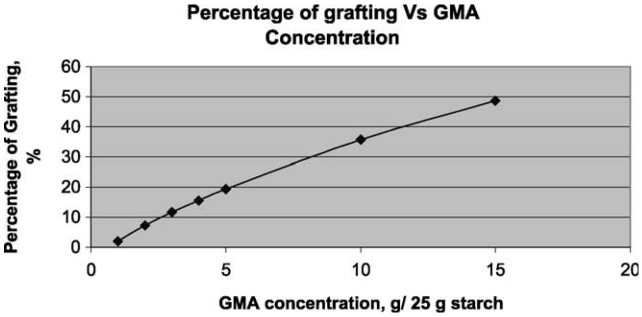

Fig. 3. Effect of GMA monomer concentration.

3.5. UV curable coating formulations based on the grafted GMA-*g*-starch

As described earlier, starch-*g*-GMA has a core-shell configuration. Besides the epoxy groups which constitute the shell, there are also free OH groups of starch. Both these groups are important in the UV curable formulations induced by cationic photoinitiators. While the epoxy groups on the starch particles can co-polymerize with the CAE, the OH groups can act as chain transfer groups and are potential sites for the formation of inter penetrating polymer network. This is shown in Fig. 4.

Formulations were therefore made by incorporating GMA-*g*-starch with cycloaliphatic diepoxide in UV curable coatings induced by cationic photoinitiator (Triphenyl sulfonium hexafluoro phosphate) and the following properties of the cured films were determined.

1. Water absorption
2. Pendulum hardness
3. Mandrel flexibility
4. Gel content

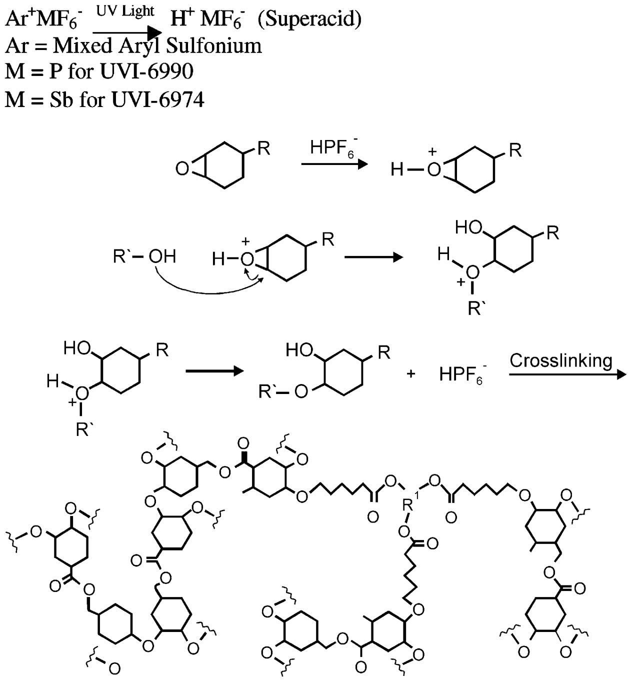

Fig. 4. Cross-linking reaction of cycloaliphatic diepoxide through hydroxy group.

Table 3
Comparison of properties of UV cured films based on modified and unmodified starch

Sample	Water absorption (%)	Pendulum hardness	Mandrel flexibility	Gel content (%)
A	0.5875	104	31.36	99.31
B	0.4025	112	30.54	99.43
C	0.1696	142	7.51	99.26

These properties were compared with unmodified starch. Six samples were used as replicates and the statistical analysis of the data, viz. ‘within the treatment variations and between the treatment variations’ was carried out. In general, differences between the properties of the grafted and ungrafted samples were statitstically significant at 5% level or $p < 0.05$. Similar determinations were also conducted on the control samples consisting of pure cycloaliphatic diepoxide and the photoinitiator.

3.5.1. Effect of starch modification on the water absorption of the cured film

Table 3 shows that the addition of raw starch into the UV curable formulations increased the water absorption from 0.17 to 0.59%. But the starch grafted with GMA reduced the water absorption of the UV cured film from 0.59 to 0.40%, a 32.20% improvement in the water resistance. The reduction of the water absorption is due to the formation of a protective shell of GMA around the starch particles as shown in Fig. 5.

This modification by grafting is, however, confined only to the surface of the starch granules with the bulk of the interior remaining unaffected with the formation of a hydrophobic shell on the surface of the sago starch granule as mentioned earlier. The shell layer further reduces the intermolecular hydrogen bonding in starch and

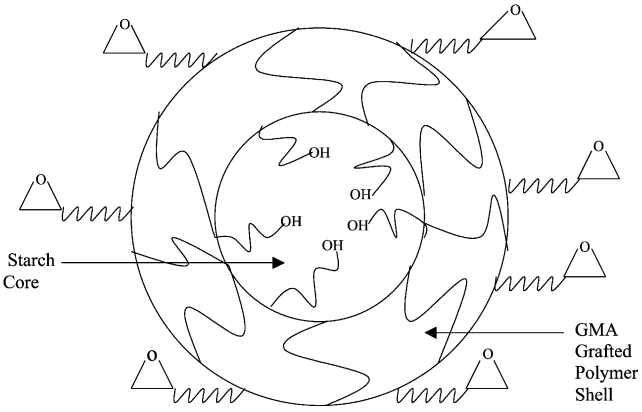

Fig. 5. Depiction of core-shell structure of starch-*g*-GMA.

the affinity for water. It was also interesting to observe that when both the native starch and the modified starch samples were boiled in excess water for 10 min, the native starch underwent gelation and the gel occupied the entire volume with no visible phase separation between the dispersed phase and the dispersion medium. On the other hand the modified starch remained essentially unaffected after the boiling, retained the particulate integrity and remained discrete after the boiling. The mixture could be centrifuged and the dispersion medium (water) remained as clear liquid over the unagglomerated particles of modified starch. There was no trace of agglutination. This showed that the hydrophobic shell caused by the grafting of GMA onto starch allowed the starch particles to survive the boiling test. There was, however, minor swelling.

This core-shell structure is expected to impart adequate dimensional and mechanical stability to the cured film while at the same time allowing an eventual possibility for biodegradation since the core constitutes of predominantly ungrafted starch. Work is underway to study the biodegradation of the UV cured film consisting of grafted starch to confirm the above. The core-shell configuration also promotes good adhesion between starch particles and the matrix resin of the UV curable coating system.

3.5.2. Effect of starch modification on the pendulum hardness of the cured films

Results tabulated in Table 3 show that the pendulum hardness decreased from 142 to 104 by addition of raw starch into the coatings formulation. But by using the starch-*g*-GMA, slightly higher pendulum hardness 112 is obtained. The decrease in hardness in both the cases is due to the increased flexibility imparted to the rigid cycloaliphatic diepoxide. The reason for the increased flexibility is discussed below. While achieving increased flexibility, it is generally inevitable that there is a trade off in film hardness. While optimizing the conditions for the desired coatings performance, a compromise is generally reached between hardness and flexibility depending on the application. Starch-*g*-GMA while conferring adequate flexibility, can impart better hardness to the cured films compared to the addition of raw starch thereby achieving a good compromise between these properties.

3.5.3. Effect of starch modification on the mandrel flexibility of the cured films

The results in Table 3 show the raw and modified starch both increased the flexibility of the cured film from 7.51 to 31.33 and 30.54 by as much as 318 and 307%, respectively. This improvement of the flexibility is due to the fact that starch as well as the starch-*g*-GMA being basically polyols, functions as chain transfer agent in the cationic curing of the CAE, get integrated into the polymeric network thereby serving as internal plasticizers. The crack propagation during the flexing of the film is kept under check. Grafting of glycidyl methacrylate onto starch provides the potential for the chemical bonding between the starch and the cycloaliphatic epoxide through the epoxide functionality of the GMA. The epoxide can react with the epoxy group of cycloaliphatic epoxide and resulting covalent bonding between the cyocloaliphatic epoxide matrix and the starch filler. This imparts some rigidity to the film. Thus the flexibility of film containing starch-*g*-GMA is somewhat less than pure starch. Compromise between the hardness and flexibility can thus be achieved. And subsequently improved the mechanical properties of the coatings generally. Further as mentioned earlier the core-shell configuration can contribute to better water resistance than pure starch.

3.5.4. Effect of starch modification on the gel content of the cured film

Gel content refers to the percentage of cross-linking that occurs in the coatings film. In this experiment, almost all the formulations show an excellent gel content result, which is more than 99%. The high gel content even at relatively high concentrations of starch and starch-*g*-GMA is again due to the formation of an interpenetrating polymer network as a result of chain transfer caused by the OH groups of starch and the starch-*g*-GMA.

It can therefore be concluded that the addition of starch or starch-*g*-GMA into the formulation did not affect the curing performance under the conditions employed in the present studies.

4. Conclusion

Free radical grafting of GMA onto sago starch was effected in aqueous medium using ceric ammonium nitrate as initiator. The acrylic groups were involved in the grafting while glycidyl groups were left as reactive pendant groups. A core-shell configuration has been suggested to account for the hydrophobic behavior of the starch-*g*-GMA. FTIR spectral analysis provided evidence of the grafting of GMA onto the starch. UV curable coating formulations induced by cationic photoinitiator were made using the grafted starch as partial replacement up to 25% of cycloaliphatic diepoxide. Starch-*g*-GMA imparts flexibility to the cured film without adversely affecting other properties such as hardness and gel content. Participation of the hydroxyl groups of starch in the chain transfer reactions resulting in cross-linking is considered to be the cause of the observed behavior.

Acknowledgements

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