EB Curing and Cure Grafting of Thiol-Enes. Comparison with UV Systems and Potential Industrial Applications of the Products.

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Abstract

Variables affecting the UV/EB curing and cure grafting of thiol-enes on cellulose have been studied. These include effect of varying the type of olefin, increasing the functionality of the thiol, use of acrylate monomers and oligomers in hybrid systems, altering the surface structure of the cellulose and finally the role of air in these processes particularly with EB. Photopolymerisation of the thiol-enes in bulk has also been investigated. The potential of these thiol-ene systems in industrial applications is briefly discussed.

Introduction

Thiol-ene systems are becoming increasingly important in UV curing (1-4). Originally developed in the eighties (5) the thiol-enes ultimately proved to be unsuitable for general commercial applications at the time. Recent work, especially with new thiol-enes, has shown that this system can be attractive in UV cure. Preliminary studies have also been reported for analogous EB curing of thiol-enes (2).

A significant feature of radiation curing of thiol-enes are the unique properties that these materials can impart to the product film. An important aspect of these properties is the adhesion of the coating to the substrate after radiation curing. Adhesion of cured coating can be dramatically improved if concurrent grafting occurs (6, 7). Curing and grafting are depicted in reactions 1 and 2 where O/M denotes the oligomer/monomer resin system.
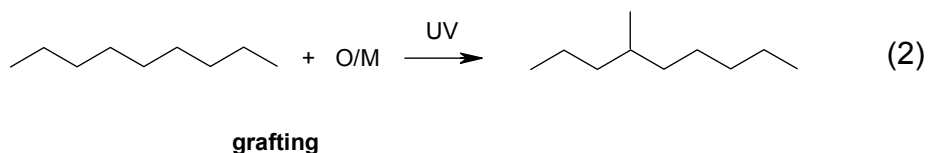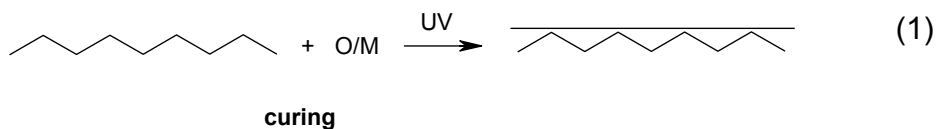
curing (1)

grafting (2)

An important difference between grafting and curing is the nature of the bonding occurring in each process. In grafting, covalent carbon – carbon bonds are formed whereas in curing bonding usually involves weaker Van der Waals or London dispersion forces. The process depicted in reaction 2 has been termed cure grafting to differentiate it from conventional methods such as preirradiation and simultaneous techniques (7). Cure grafting, per se, has been shown to be a useful technique for synthesising novel copolymers possessing unique properties not capable of being achieved by standard preirradiation and simultaneous methods. The scope of the process has been outlined in detail elsewhere (7).

In terms of properties of cured coatings the occurrence of concurrent cure grafting is significant since, if present, cure grafting would not only minimise delamination of the coated film but could also render difficult recycling of the finished product especially if it was cellulose. Hence the conditions for the control and optimisation of cure grafting during radiation curing is important. In this respect there are potential differences in the proportion of cure grafting if UV or EB sources are used. With more energetic ionising radiation such as EB, radicals at sites for grafting are formed more readily than with UV. Thus concurrent cure grafting would be expected to occur more efficiently in EB systems. With UV, in the presence of photoinitiators (PIs) abstraction reactions with the backbone polymer can occur leading to a graft copolymer. Even with PI free systems in curing, the occurrence of cure grafting has been observed and discussed (2).

Thiol-ene systems may be very useful for controlling cure grafting because preliminary studies indicate that concurrent cure grafting in such systems will generally be low even with EB (2). These studies were performed with the trifunctional thiol (PPT, I) and thus the use of other thiol-enes particularly higher functionality materials with other components such as oligomers is relevant. The purpose of this paper is to describe radiation curing of such thiol-enes on cellulose and to compare the trifunctional and tetrafunctional thiols in the process. The use of thiol-enes combined with other oligomer systems to improve surface properties will also be investigated since the thiol-enes may be used as components to induce specific properties into films. The effect of this process in both curing and cure grafting will be discussed. The potential of this work in industrial application will be briefly mentioned.
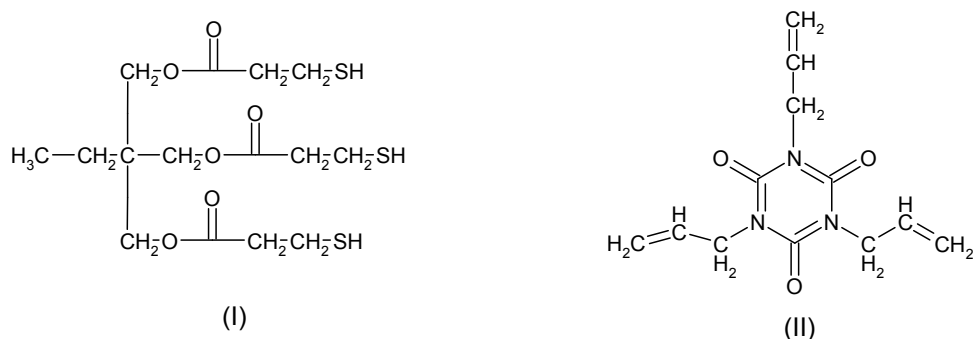
Figure 1. Structures of typical trithiol, trimethylol propane tris(3-mercaptopropionate) (TTP, I) and olefin containing electron rich double bonds triallyl-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione (TAT, II).

Experimental

Monomers and oligomers were supplied by Aldrich, BASF, Monocure Pty Ltd and Ballina Pty Ltd and include pentaerythritol tetrakis-3-mercatopropionate (PTP), trimethylolpropane tris (3-mercaptopropionate (TTP, I), triallyl-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione (TAT, II), triethyleneglycol divinyl ether (DVE-3), trimethylol propane trivinyl ether (TMPTVE), hydroxybutyl vinyl ether (HBVE), cyclohexyl vinyl ether (CHVE), maleic anhydride (MA), maleimide (MI), dimethyl maleate (DMMA), hexanediol diacrylate (HDDA), aromatic urethane acrylate (UA), epoxy acrylate (EPA) and polystyrene (PST). Photoinitiators (PIs) were donated by Ciba Geigy (Irgacure series). The procedures used in EB and UV curing and cure grafting including lamp calibrations were modifications of those previously described (2, 6). For the EB work two machines were used, namely Nissan 500 kV and ESI 175 kV facilities. For UV, two lamps were used, a Fusion F300 with H and D bulbs (line speed of 16 mm^{-1} at peak UV intensity of 1.4 Wcm^{-2} and dose of 0.20 Jcm^{-1} per pass together with a mercury lamp facility of 80 Wcm^{-1} with a dose of 0.17 Jcm^{-1} per pass. The UV lines were calibrated with an INT Light IL' 390 radiometer. For the bulk UV irradiations a Philips 90 W medium pressure mercury lamp model 93110ET fitted with a quartz envelope and mounted in a vertical configuration was used.

Results

In both UV and EB work, the data have been expressed as percent curing and percent cure grafting (7). These terms have previously been defined as follows. Curing is the increase in weight of the substrate after being coated, exposed to the radiation source and the coating tested for cure by the conventional solvent rub and delamination procedures. Curing (C) is defined as follows where W_O is the weight of substance before coating and W_C is the weight of the substrate after coating has been cured.

$$C = (W_C - W_O)/ W_O$$

Cure grafting is the weight increase of the substrate after the cured sample has been solvent extracted to constant weight to remove residuals in the traditional radiation grafting procedures originally developed for the conventional preirradiation and simultaneous methods (7). Cure grafting (C.G.) is defined as follows where W_e is weight of coated substrate after solvent extraction.

$$C.G. = (W_e - W_O)/ W_O$$

The cure and cure grafting terms are important since the presence of cure grafting in a cured film can significantly influence the properties of the end product in its final use especially in recycling. These concepts are particularly relevant to the current thiol-ene work since preliminary exploratory work with these systems has indicated the occurrence of poor cure grafting in certain of the cured films (2). The essential difference between radiation curing and cure grafting as defined above is that to obtain the cure grafted material, residuals in the cured film such as unreacted monomers, low molecular weight oligomers and PIs or their fragments need to be removed.

The types of cellulose substrates used in this work have also been specifically chosen since the results will be of particular value to certain industries, especially the graphic arts field including printing, overproof varnishing and label applications. For the data reported in Tables 1-3, three types of papers were examined including Niklakett medium 70 gsm, Algrofiness 80 gsm and Whatman 41. As expected similar degrees of reactivity in curing and cure grafting were observed with all papers thus Whatman 41 was adopted as model paper for most of the EB runs. The results in Tables 4 and 5, especially the former table are particularly relevant to the label market thus the substrate used was a chrome coated label stock paper, coated on one side which is the side used for label printing and coating. The reverse side was uncoated cellulose. If cure grafting was efficient i.e. quantitative, the yield could be predetermined before cure by the weight of coating applied to the cellulose by the metering rod (7). The essential variable influencing coating weight delivered by the rod was the viscosity of the medium, higher viscosities, such as when oligomers were present, generally leading to higher coating weights. In some examples in the tables, high coating weights were deliberately applied in runs to examine specific film properties which are discussed in the relevant sections.

EB Curing and Cure Grafting of Thiol-Enes

In Tables 1 and 2 the EB curing and cure grafting of thiol-ene systems is reported, the results in Table 1 being obtained for curing under nitrogen

whilst those in Table 2 were cured in air. The last two entries in Table 1 are data obtained for the MA and MI charge transfer (CT) complexes with DVE-3 as donor.

Table 1
EB Curing of Thiol-Enes In Nitrogen on Cellulose[a]

Thiol-Ene System	Cure (%)	Cure Graft (%)	Comment
TTP/TAT	34	33	gloss
TTP/TAT	35	32	corona
TTP/TAT + 6% H_2O	29	28	gloss
TTP/HDDA (1:1)	38	20	gloss
TTP/HDDA (1:5)	41	20	gloss
TTP/HDDA (1:1) + 20% PST	17	15	gloss
TTP/DVE-3	16	10	gloss
TTP/TMPTVE	23	21	gloss
TTP/DMMA	25	13	matt
TTP/HBVE	21	10	matt
TTP/UA	31	29	gloss
TTP/EPA	26	22	gloss
MA/DVE-3	27	9	gloss
MI/DVE-3	26	18	gloss

[a]Dose 2.8×10^4 Gy at 40 – 60 m min^{-1}. Reactant ratios (1:1 by weight) unless specified.

Extensive information on curing has been previously been reported for these systems. The current results are included for comparative purposes and are relevant to the mechanism of the thiol process discussed in the following sections. The data in Table 1 show that a variety of enes can be used with the TTP trithiol. TAT is especially useful as the olefin since concurrent grafting with this compound is almost quantitative. Inclusion of water in the system is not detrimental to curing and cure grafting and this may be important since the presence of water in a cured coating can improve the swelling of certain substrates and thus improve adhesion.

Multifunctional acrylate monomers like HDDA are effective with TTP even at higher dilution (1:5). Concurrent grafting in this system is relatively poor, however this situation is significantly improved by the inclusion of a binder resin like PST. Strong donor monomers like DVE-3 and TMPTVE, especially the latter, also constitute effective EB curing systems with TTP. Polar monomers such as DMMA and HBVE cure readily with TTP however the finished coating is matt whereas all others are gloss. This observation would suggest incompatibility in the cured coating of the two components. The result is mechanistically interesting since DMMA is a strong acceptor. Acrylate oligomers, typically aromatic urethanes and epoxies, can also be cured with TTP which is a practically

useful result since the unique properties of these oligomers can be incorporated into the finished coatings. The last two entries in Table 1 are used for mechanistic comparison purposes and demonstrate the reactivity of typical CT complexes in this work. MA and MI are traditionally strong acceptors which have been coupled with a strong donor like DVE-3. Although these latter CT systems are very efficient with EB, concurrent cure grafting yields are not exceptional and contrast markedly with the TTP results.

All data reported in Table 1 have been observed using an inert nitrogen blanket over the film in the EB processing. The possibility that EB curing could be accomplished in air would dramatically reduce the costs for commercial processing. The data in Table 2 show that certain TTP systems can be EB cured in air at doses similar to those used with nitrogen (Table 1). TTP/TAT EB cures well in air, although the concurrent grafting yields are not exceptional even if the substrate is corona treated. These results are in marked contrast to the HDDA system especially at higher dilution (1:5) and particularly in the presence of binder polymer PST. The PST result is consistent with what is found with a traditional CT complex like MA/DVE-3 where inclusion of the binder polymer enables not only curing to be achieved in air but also improves the yield of the concurrent cure graft.

Table 2
EB Curing of Thiol-Enes in Air on Cellulose[a]

Thiol-Ene System	Cure (%)	Cure Graft (%)	Comment
TTP/TAT	19	14	
TTP/TAT	25	14	Corona
TTP/HDDA	18	15	
TTP/HDDA (1:5)	24	23	
TTP/HDDA (1:1) + 20% PST	23	22	
MA/DVE-/PE (3:4:4)	34	33	

[a]Conditions as in Table 1.

UV Curing and Cure Grafting of Thiol-Enes

Essentially the same types of thiol-ene systems as reported in Tables 1 and 2 for EB processing have been studied using UV curing on a similar type of cellulose to that in Table 1. The trithiol, TTP (I), in the presence of the ene, TAT (II), cures in two passes using the Fusion lamp. Cure grafting yields are relatively poor in this system and are even lower with the inclusion of water although this additive speeds up cure. The presence of PI also accelerates cure but does not affect the cure grafting yield significantly. High coating weights and hence high cure yields (>100%, based on an increase in weight of substrate) were deliberately used in these experiments in order to accurately examine the cure grafting yields which were expected to be low. The cure yields i.e.

extremely high or low can be easily controlled by the amount of coating applied to the substrate by the laboratory metering rod. When a multifunctional acrylate (MFA) like HDDA replaces TAT, the UV curing reactivity with TTP is similar to the analogous TAT system, curing occurring in two passes and is accelerated by the inclusion of PI. Extremely poor cure grafting is obtained with the HDDA system, however this is significantly improved with the inclusion of PI as expected. The combination of a strong donor, like DVE-3, with TTP leads to curing in three passes and almost quantitative cure grafting. Addition of water or PI to this system improves cure speed, as does the presence of an acrylate oligomer like an epoxy acrylate (EPA) however cure grafting yields are lowered under these conditions. When the difunctional vinyl ether, DVE-3, is replaced by a monofunctional ether such as CHVE similar results with TTP are observed. TTP itself can also be used in direct combination with acrylate oligomers like the aromatic urethane (UA) and EPA. These results are consistent with the data obtained above for HDDA, especially with UA and EPA oligomers which in commercial practice usually contain up to 20% of an MFA like HDDA to permit easy processing in the plant.

Table 3
UV Curing of Thiol-Enes on Cellulose[a]

Thiol-Ene System	P.C.[b]	Cure (%)	Cure Graft (%)
TTP/TAT	2	340	67
TTP/TAT + 6% H_2O	1	58	0
TTP/TAT + PI	1	470	77
TTP/DVE-3	3	10	9
TTP/HDDA (1:5)	2	250	9
TTP/HDDA (1:5)+ PI	1	330	70
TTP/DVE-3 + 5% H_2O	1	11	10
TTP/DVE-3 + PI	1	13	5
TTP/DVE-3/ 20 % EPA	1	6	2
TTP/DVE-3 + 5% H_2O	1	14	8
TTP/CHVE	3	7	6
TTP/CHVE/ 20 % EPA	1	13	9
TTP/UA	1	84	34
TTP/EPA	1	43	24
MA/DVE-3	3	150	145
MA/DVE-3 + PI[c]	1	100	90
MA/DVE-3/UA	1	56	32
MA/DVE-3/EPA	1	37	27
MI/DVE-3	1	270	110

[a]Ratios of reactants (1:1 by weight). ; PI = 2% Irgacure 2020.
[b]P.C. = passes to cure under UV lamp, Fusion F300, D bulb, at 16 m min^{-1}.
[c]0.5% Irgacure 184.
[d]1.0% Irgacure 184

The last five entries in Table 3 list the results of UV curing and cure grafting of two traditional CT monomer complexes on cellulose, namely MA and MI complexes of DVE-3. These results are shown for comparison purposes with the TTP data and are relevant to the following discussion section.

Effect of Thiol Functionality in UV Curing and Cure Grafting

Preliminary studies of thiol-ene systems in radiation curing has shown that trifunctional thiols are required to achieve efficient crosslinking. Further it would be expected that crosslinking efficiency in the thiol-ene system would be improved with increasing functionality of the ene. Thus the effect of increasing the thiol functionality from the tri to the tetra compound should improve the reactivity of the resulting thiol-ene system. In Table 4, the results of comparing a trithiol, TTP, with a tetrathiol, PTP, in these curing and cure grafting reactions is reported. The cellulose in this work is a chrome coated label stock.

Table 4
UV Curing and Cure Grafting of Thiol-Enes on Chrome Coated label Stock Cellulose[a]

Ene System	Thiol			
	PTP		TTP	
	CURE	C. GRAFT	CURE	C. GRAFT
TAT	7[b]	3	6[b]	0
TAT + PI	12	9	9	3
TAT + 6% H_2O	12	5	6	2
TAT + 6% H_2O + PI	10	3	10	3
DVE-3	14	5	7	3
DVE-3 + PI	14	4	9	2
TMPTVE	8	0	11	6
TMPTVE + PI	32	20	9	2
HDDA	15	2	7	2
HDDA + PI	13	0	13	0
HDDA (1:5)	15[c]	8	6	0
HDDA (1:5) + PI	8	0	8	0
UA (5:1)	47	6	-	-
UA (5:1) + PI	74	35	-	-
EPA	43	39	-	-
EPA + PI	46	38	-	-
EPA (5:1)	65	37	-	-
EPA (5:1) + PI	57	50	-	-

[a]Irradiations with 80 W cm^{-1} mercury lamp. All samples cured in one pass unless specified. As expected MA and DMMA, strong acceptors do not cure with PPT after six passes in reference experiments.
[b]Two passes to cure.
[c]Six passes to cure.

This substrate was specifically chosen as a model so that the work could be optimised for the label industry since much UV curing and printing is performed in that field with this type of cellulose. The paper is coated with an acrylic finish on one side only and the current UV experiments have been performed separately on each side of the paper for comparison.

The data in Table 4 for coatings on the chrome coated paper side are consistent with the previous UV curing and cure grafting results obtained with TTP and a range of enes in Table 3 on relatively pure cellulose. All combinations cured in one pass with the exception of the TAT and HDDA (1:5) systems incorporating PTP and TTP where two passes were required.

Inclusion of PI accelerates the curing to one pass in these slower systems. The significant feature of the data in the table is that cure grafting is very poor in all PI free systems especially with the trifunctional thiol. Inclusion of PI with certain tetrafunctional systems improves these yields. Even though most systems in the table cured in one pass without PI, PI was also included in separate experiments with these systems in order to determine whether the presence of PI improved cure graft yields.

Table 5
UV Curing and Cure Grafting of Thiol-Enes on Chrome Uncoated label Stock Cellulose[a]

Ene System	Thiol			
	PTP		TTP	
	CURE	C. GRAFT	CURE	C. GRAFT
TAT	23	6	-	-
TAT + PI	17	2	-	-
DVE-3	32	2	15	5
DVE-3 + PI	25	5	12	0
TMPTVE	-	-	19	2
TMPTVE + PI	-	-	30	6
HDDA	19	0	10	0
HDDA + PI	23	3	31	0
HDDA (1:5)	30[b]	2	11	5
HDDA (1:5) + PI	24	2	22	5
UA (5:1)	85	81	-	-
UA (5:1) + PI	45	39	-	-
EPA	39	6	-	-
EPA + PI	38	3	-	-
EPA (5:1)	31	3	-	-
EPA (5:1) + PI	91	67	-	-

[a]Irradiation conditions as in Table 4.
[b]Six passes to cure.

Exceptions to the above general observations are the runs containing oligomer acrylates (UA, EPA), where cure grafting results are significantly improved compared to the other formulations.

Similar results to those in Table 4 are obtained when the coatings are cured on the uncoated side of the stock cellulose (Table 5). Again cure grafting is very poor with both tri and tetra systems, the oligomer acrylates especially UA being an improvement in this respect. The HDDA system at high dilution (1:5) with PTP also cures very poorly again consistent with the data in Table 4.

Effect of Thiol Functionality in Bulk Photopolymerisation of Thiol-Enes

Photopolymerisation of thiol-enes in bulk is becoming increasingly attractive to specialised markets, since the process can yield unique products containing thick sections. The data in Table 6 demonstrate the effect of functionality of thiol on the speed of bulk photopolymerisation of various thiol-ene combinations. As expected, the tetrathiol is significantly more reactive than the trifunctional compound except with the trifunctional vinyl ether when both thiols are extremely reactive. This result confirms unequivocally that the higher the functionality of the thiol and ene the faster the rate of photopolymerisation.

Table 6
Comparison of TTP with PTP in Bulk Photopolymerisation of Thiol-enes with and without Photoinitiator[a].

Thiol-ene system	Gel dose (J)			
	PTP		TTP	
	NPI	PI	NPI	PI
TAT	238	1	184	1
HDDA	19	3	42	4
DVE-3	17	1	35	1
TMPTVE	4	0.5	4	0.5
MA/DVE-3	55	1	-	-

[a]Dose rate 1.02×10^{-2} J/s; NPI=no PI; PI=1% Irgacure 2010.

Inclusion of PI dramatically accelerates rates of polymerisation to the degree where it is difficult to distinguish the reactivity of the two thiols. Again the thiol-enes with TAT are the slowest to polymerise consistent with the analogous curing data where these thiol-enes required more passes to cure than the other systems studied. For mechanistic discussion purposes the results for the MA/DVE-3 CT complex are used for comparison and indicate this complex slower in UV bulk polymerisation than any of the thiol-enes studied in the table, however inclusion of PI compensates for this difference.

Discussion

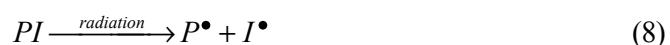*Mechanism of Radiation Curing and Cure Grafting of Thiol-Enes*
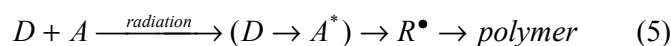
In the earlier thiol-ene UV curing work the possible mechanistic role of thiol-ene CT complexes in the photopolymerisation process was considered (5). Thiol-enes are known to form such CT complexes which have been characterised by spectroscopic techniques. With respect to the current radiation curing and cure grafting work, the problem to be resolved is the degree, if any, these complexes participate in the initiation process of the radiation polymerisation. Other types of CT complexes have already been used successfully in this work (2, 8). Typical donor/acceptor (D/A) complexes donors like DVE-3 with the acceptors MA and MI. Data from EB and UV curing and cure grafting with these DA complexes are reported for comparison purposes in Tables 1-3 and in Table 6 for photopolymerisation in bulk. The data show that the thiol-enes and the DVE-3 CT complexes exhibit comparable reactivities in radiation curing, cure grafting and bulk polymerisation processes with the latter CT complexes in some specific runs exhibiting slower speeds of polymerisation. These results would suggest that there may be common mechanistic pathways between the two systems. With respect to the DVE-3 type CT monomer systems used in this work as reference, extensive studies by a number of authors on the UV initiated process have led to the following mechanism being proposed to explain the curing process. With donors such as DVE-3 and acceptors like MA and MI, reactions 3 and 4 were proposed to explain UV curing with these complexes.

Reaction 3 shows the initial effect of radiation on the DA complex whilst reaction 4 outlines subsequent possibilities depending on the reaction path.
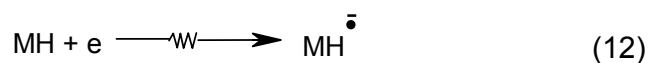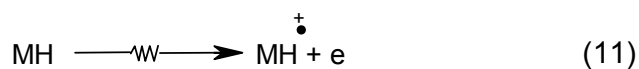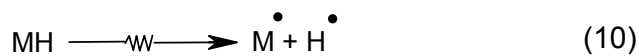

(3)

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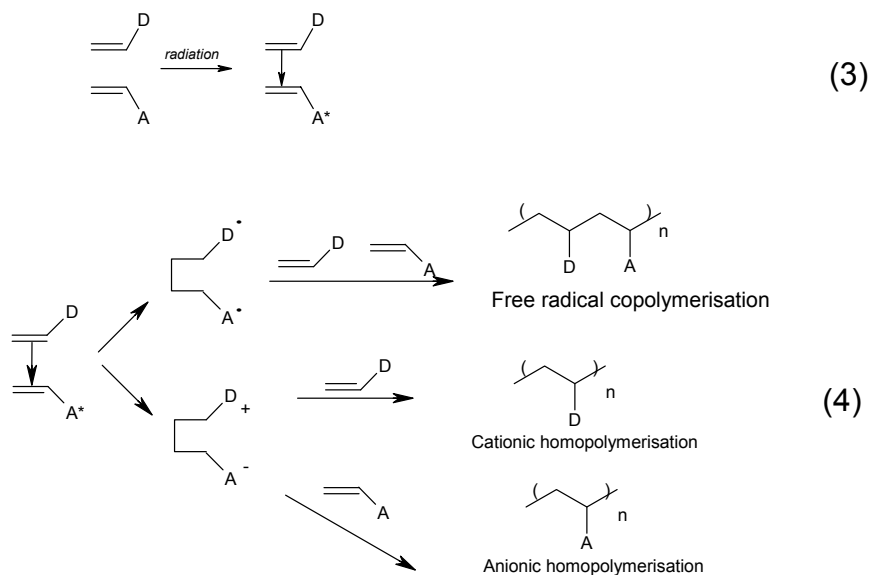
Reaction 4 shows the formation of a zwitterion biradical which leads to (i) free radical alternating copolymerisation or (ii) with excess donor, cationic homopolymerisation or (iii) with excess acceptor, anionic homopolymerisation.

The formation of the intermediate in reaction 3 involves interaction between a ground state donor with an acceptor in the excited state. The above mechanism has also been extended to explain UV concurrent cure grafting (7) in reactions 5-9. Reaction 5 summarises the overall process. Reaction 6 shows site formation in the substrate whilst reaction 7 demonstrates the specific cure grafting process using the radicals formed in reaction 5. Inclusion of PI leads to higher radical concentrations (reactions 8 and 9).

$$D + A \xrightarrow{radiation} (D \to A^{*}) \to R^{\bullet} \to polymer \qquad (5)$$

$$SH \xrightarrow{radiation} S^{\bullet} + H^{\bullet}(SH, substrate) \qquad (6)$$

$$R^{*} + S^{*} \to graft \qquad (7)$$

$$PI \xrightarrow{radiation} P^{\bullet} + I^{\bullet} \qquad (8)$$

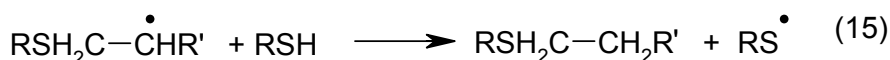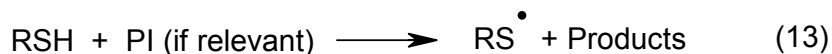$$P^{\bullet} + SH \to PH + S^{\bullet} \qquad (9)$$

The above mechanism developed for UV processes can also be used to explain radiation curing and cure grafting of these complexes in the presence of EB sources. Because EB sources are more energetic than UV then additional reactions to those found for UV are expected for EB. In EB, radicals, cations and anions are formed during irradiation with the first process predominating (reactions 10-12 where MH is monomer).

$$MH \xrightarrow{\quad\quad} \overset{\bullet}{M} + \overset{\bullet}{H} \qquad (10)$$

$$MH \xrightarrow{\quad\quad} \overset{+}{\overset{\bullet}{MH}} + e \qquad (11)$$

$$MH + e \xrightarrow{\quad\quad} \overset{\bar{\bullet}}{MH} \qquad (12)$$

Ionic reactions can thus contribute to the overall EB process, however, in practice free radical reactions tend to predominate under most processing conditions. As the data in the relevant tables show, there are differences in reactivity in specific runs between the thiol-ene and the DVE-3 complexes. Recent studies by other authors using UV initiation

have indicated the difficulty of interpreting the curing of the thiol-enes in terms of the participation of the analogous CT complex, in particular the degree to which the thiol-ene CT complex may be involved in the initiation step. Specifically the problem is that thiyl radicals (see below) are only produced slowly from the complex whereas in radiation processes, a large flux of additional radicals are produced by radiolysis (or photolysis as relevant). Detailed kinetic studies thus need to be performed with the thiol-ene system before this aspect of the mechanism can be resolved.
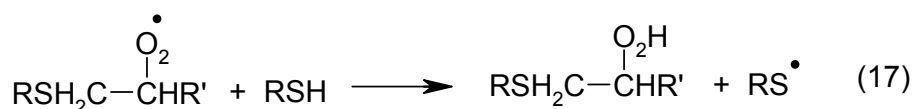
With respect to the thiol-ene system it is generally accepted that the basic reaction occurs by a addition mechanism that is propagated by a free radical chain process involving the addition of a thiol group across an ene double bond as shown in reactions 13-15 (1).

$$RSH + PI \text{ (if relevant)} \longrightarrow RS^{\bullet} + \text{Products} \qquad (13)$$

$$RS^{\bullet} + H_2C{=}CHR' \longrightarrow RSH_2C{-}\overset{\bullet}{C}HR' \qquad (14)$$

$$RSH_2C{-}\overset{\bullet}{C}HR' + RSH \longrightarrow RSH_2C{-}CH_2R' + RS^{\bullet} \qquad (15)$$

In the current work, when comparing EB and UV as initiating systems, differences between the two thiol-ene systems are observed. Thus while cure grafting of thiol-enes with EB is efficient, the corresponding yields with the lower energetic UV system, even with PI present, are relatively poor, this result presumably reflecting the ability of the energetic electrons from EB to generate sites on the substrate where grafting may occur. The relatively fast line speeds of EB (500 m/min) can lead to problems in adhesion i.e. cure grafting can be difficult even with polar substrates like cellulose. The fact that with the thiol-ene system, being essentially a step growth process involving a free radical chain mechanism, gelation occurs late in the free radical chain process and the medium does not become viscous until the later stages of the polymerisation. This property has the effect of effectively increasing the residence time of the coating, whilst still low in viscosity, on the substrate before cure, thus enhancing the penetration of coating into the substrate leading to grafting. In this respect the post curing contribution to grafting would also be increased under these conditions since ultimate gelation is delayed and complete curing would not be achieved until some time after removal from the source.

Effect of Oxygen in EB Curing and Cure Grafting

An important observation from earlier UV thiol-ene photopolymerisation was the lack of oxygen inhibition in curing (5). This was attributed to the reaction between the betathioether carbon radical species (reaction 14) and molecular oxygen to yield a betathioether peroxy radical in a co-oxidation process (reaction 16).

$$RSH_2C-\overset{\bullet}{C}HR' + O_2 \longrightarrow RSH_2C-\overset{\overset{\bullet}{O_2}}{\underset{|}{C}}HR' \qquad (16)$$

$$RSH_2C-\overset{\overset{\bullet}{O_2}}{\underset{|}{C}}HR' + RSH \longrightarrow RSH_2C-\overset{\overset{O_2H}{|}}{C}HR' + RS^{\bullet} \quad (17)$$

This peroxy radical may then undergo a chain transfer reaction with the thiol to preserve the propagation radical (reaction 17). The insensitivity of the thiol-ene process to oxygen can thus be attributed to the fact that the thiol can undergo a rapid chain transfer reaction with the peroxy radical. By contrast, in acrylate and methacrylate systems, the analogous peroxy intermediates are chain stoppers, resulting in the formation of nonpropagating species.

This rationale developed for UV thiol-ene systems can theoretically be extended to EB curing of the same systems. With EB, efficient curing of acrylates can only be achieved in an inert nitrogen atmosphere, an observation consistent with the above discussion. Acrylates generally have been the predominant technology used commercially in EB curing of coatings to the present time, hence the requirement for inert conditions during curing.

The data in Table 2 demonstrate the conditions where curing can be observed on cellulose using a range of thiol-ene systems in the presence of air. Even if acrylates are one of the thiol-ene components, EB curing in air is still possible with this hybrid system. This result is consistent with earlier UV studies of hybrid thiol acrylate systems where rapid photopolymerisation uninhibited by oxygen was observed (5). The result of EB curing in air is particularly significant for systems involving dilute thiols in acrylates (TTP/HDDA-1:5, in Table 2) where oxygen inhibition is minimised. In this system, the process is essentially an acrylate homopolymerisation carried out in the presence of a strong chain transfer agent such as the thiol which acts to attenuate the effects of oxygen. The MA/DVE-3 CT complex with unsaturated polyester will also cure in air under these EB conditions, whereas the CT complex

itself cures only with difficulty. In this latter system, the unsaturated polyester scavenges the oxygen, permitting the polymerisation of the CT complex to occur readily. With respect to cure grafting, it is significant that this reaction also occurs efficiently in air with EB, This result suggests that ionic processes may also be involved in the mechanism of this reaction to complement the free radical process. Oxygen, especially at the surface of cellulose, is known to react readily with impinging electrons according to reaction 18, the resulting O_2^- species, being desorbed from the surface, may well influence the resulting cure grafting process via an ionic process.

$$O_2 + e^- \rightarrow O_2^- \qquad\qquad\qquad (18)$$

UV Curing of Thiol-Enes in Bulk

Thiol-enes are potentially useful in a range of areas where bulk photopolymerisation properties are important, such as in composite formation. A number of the thiols particularly the tri- and tetra-derivatives with a trifunctional ether can gel at reasonably low UV doses without the necessity of using a PI as the data in Table 6 show. The ability of the thiol-ene to crosslink efficiently is thus important. In this respect the higher functional tetrathiol is more efficient than the trithiol with the divalent ene system in the bulk photopolymerisation process. However in these UV systems care still needs to be exercised to obtain uniform polymerisation in the bulk due to the relatively poor transmission coefficient of UV through such systems. The photopolymerisation in bulk systems is further complicated if performed in the presence of air. Generally, in air, the reaction between the thiol and olefin essentially involves the addition co-oxidation process whilst in low air concentrations the addition reaction predominates (5). In bulk photopolymerisation two situations arise, (i) at the surface (the air interface) a high concentration of air is expected whilst (ii) in the bulk further removed from the interface, a lower concentration of oxygen is present. When the concentration of oxygen in the thiol-ene mixture is low, the expected addition chain transfer-addition process predominates, whilst in the presence of excess oxygen the co-oxidation process is predominant. These two processes thus yield different intermediates during the polymerisation process depending upon the concentration of oxygen present at a particular position in the bulk at the time of the irradiation. Thus in such bulk photopolymerisation, the nature of the properties and polymer formed at the interface and in the bulk may vary significantly. Uniformity of product formation in bulk runs may thus be detrimentally affected and may significantly influence the physical properties of the final product especially the strength of the product.

Commercial Potential of Thiol-Ene EB/UV Curing and Cure Grafting Processes

The thiol-ene system has recovered its potential as an excellent monomer in UV curing after an unsatisfactory start in the eighties with the W.R. Grace process in floor tile work. Even since that time thiol-enes have continued to be used in small scale niche markets. There has now been renewed interest in the thiol-enes with the advent of new technology. The results of the present studies show that the process, using either EB or UV, provides an efficient coating process which can be used, either alone, or with a variety of other systems as hybrids, including acryate monomers and olgimers and the CT complexes typified by the DVE-3/MA, MI systems. With EB, the thiol-enes are particularly attractive since they can be cured in air which is a significant economic advantage. With both EB and UV, the thiol-enes can be used to modify substrates by cure grafting (as distinct from curing) technologies. This system complements the conventional radiation grafting processes using the simultaneous and preirradiation techniques.

Conclusions

UV and EB are shown to be efficient initiators for the curing and cure grafting of thiol-enes on cellulose. Changing the structure of the olefin in the thiol-ene affects the reactivity of the system. Acrylate monomers and oligomers when used with the thiols constitute useful hybrid systems for these polymerisation processes. Increasing the functionality of the thiol enhances the speed of polymerisation in the system. EB curing and cure grafting of these thiol-enes in air can be accomplished. A plausible mechanism for the processes has been proposed. The UV/EB curing and cure grafting of the thiol-enes is shown to be of value in a number of industries, such as the graphic arts, especially for printing and coating on paper.

Acknowledgments

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