Invited Paper

GRAFTING AND CURING

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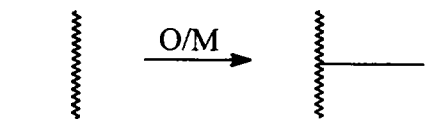
Abstract

Progress in radiation grafting and curing is briefly reviewed. The two processes are shown to be mechanistically related. The parameters influencing yields are examined particularly for grafting. For ionising radiation grafting systems (EB and gamma ray) these include solvents, substrate and monomer structure, dose and dose-rate, temperature and more recently role of additives. In addition, for UV grafting, the significance of photoinitiators is discussed. Current applications of radiation grafting and curing are outlined. The recent development of photoinitiator free grafting and curing is examined as well as the potential for the new excimer laser sources. The future application of both grafting and curing is considered especially the significance of the occurrence of concurrent grafting during cure and its relevance in environmental considerations.

2. INTRODUCTION

Radiation grafting research has been performed since the early 1950's when ionising radiation sources became available as a by-product of the nuclear power industry. An area of interest was modification of naturally occurring macromolecules and synthetic polymers, grafting being chosen as a method for achieving novel properties with these materials [1,2]. Such a technique would also be environmentally attractive since nuclear power was expected to replace atmospheric contaminating coal powered energy plants. In contrast to grafting, curing developments did not seriously begin until the early 1970's when the oil crisis occurred and the conservation of energy became important particularly the application of environmentally friendly processes in the surface coatings area [3]. It is the purpose of this paper to briefly review developments in grafting and curing and to summarise recent trends in both areas.

Grafting and curing initiated by either ionising radiation (gamma ray or electron beam) or UV are mechanistically related [4]. Grafting is essentially the copolymerisation of a monomer/oligomer (M/O) to a backbone polymer (Eq 1) whereas curing is the rapid polymerisation of an oligomer/monomer mixture onto the surface of a substrate (Eq 2). There is no time scale theoretically associated with grafting reactions which can occur in minutes or hours whereas curing processes are usually very rapid, occurring in a fraction of a second.



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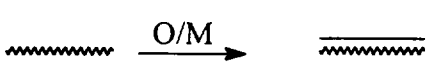

(2)

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 bonding properties of the systems are important in determining their use commercially. Applications of both grafting and curing will be discussed with the future direction of the technology outlined in this presentation.

3. EXPERIMENTAL TECHNIQUES

3.1. Grafting Procedures

Grafting and curing procedures were modifications of those previously reported [5]. For gamma irradiation grafting work, a 1200 Ci Co-60 source was used whereas for grafting a 90W high pressure facility was utilised. For EB curing, two machines were used, namely Nissan 500kV and ESI 175kV units whilst for UV, Primarc (200W/inch) and Fusion (300 W/inch) units were utilised.

4. GRAFTING STUDIES

The earlier grafting work has been reviewed by Charlesby [1] and Chapiro [2]. Since these publications many researchers have participated in the field. The present paper is not intended to be a comprehensive review, only the author's interpretation of the field including their own contribution will be discussed. In the current treatment of grafting ionising radiation systems will be initially examined, followed by UV processes. A number of grafting techniques are available [2,4] involving pre-irradiation, post-irradiation, and a simultaneous method, the last of which will be emphasised in this paper since it is the most important and the most extensively ultilised in practice. A wide variety of substrates have now been modified by radiation grafting using many types of monomers [2,5,6] the essential parameters affecting grafting yields are solvent nature of the substrate, structure of monomer, dose and dose rate, temperature and the presence of additives.

4.1. Solvent, Dose, Dose-Rate, Temperature, Substrate and Monomer

Generally solvents which wet and swell the backbone polymer are most appropriate for optimising grafting yields. By controlling variables such as solvent, surface and or bulk grafting can be achieved in one step. Typical of the solvents used are those shown in Fig 1 where styrene is grafted to PVC. Solvent effects are particularly evident when grafting to substrates like cellulose where polar solvents such as methanol are attractive whereas hydrophobic materials give low yields but predominately surface grafting. The solvent effect is also influenced by structure of substrate, a wide range of materials containing -CH and the like bonds being amenable to the process. Typical naturally occurring macromolecules such as wool and cellulose and synthetics like polyolefins, PVC and cellulose acetate graft readily by this process [2,5]. As expected, radiation dose and dose-rate affect yields. Thus at constant dose grafting is inversely proportional to dose-rate whilst yield is also directly proportional to dose. Temperature also influences the process [5, 6] e.g. in grafting styrene in methanol to polyethylene film a yield of 29% at 14°C is increased to 42% at 84°C. Finally the presence of functional groups in the monomer also influences grafting efficiency and patterns. Acrylates are the most useful of monomers in this respect, however they suffer from the disadvantage of the presence of competing homopolymer. This problem can be minimised by the use of the styrene comonomer technique [5] or the addition of ions such as Fe^{2+} and Cu^{2+} [7].

4.2. Additives

An important development in grafting was the discovery that certain additives in low concentration could increase yields. The first of these additives used was mineral acid [5]

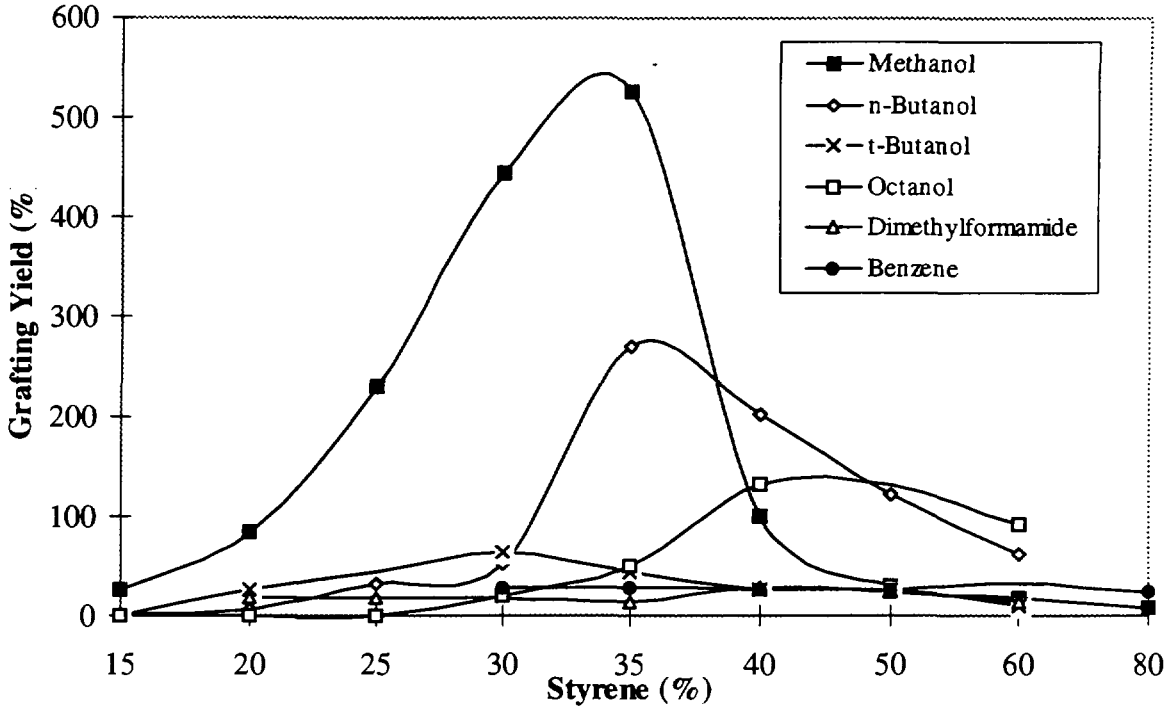

FIG. 1. Solvent Effect in Radiation Grafting Styrene to PVC Radiation conditions; Total dose, 5.0 x 10^{+2}Gy; dose rate, 1.0 x 10^{+3} Gy/h.

TABLE 1. COMPARISON OF ACID WITH LITHIUM PERCHLORATE AS ADDITIVES IN RADIATION GRAFTING[a] OF STYRENE FROM METHANOL SOLUTION TO POLYETHYLENE FILM[b]

Styrene (%)	Grafting yield (%)		
	No additive	H_2SO_4 (0.1 M)	$LiClO_4$ (0.2 M)
15	31	32	44
20	64	70	81
25	103	148	192
30	187	240	196
35	193	212	140
40	150	157	114

[a] Irradiation in air at 20°C; dose rate, 3.30x 10^2 Gy/h; total dose, 2.0 x 10^3 Gy

[b] Low density polypropylene film (0.12mm).

TABLE 2. EFFECT OF ADDITIVES ON RADIATION GRAFTING MMA TO CELLULOSE USING STYRENE COMONOMER [a]

System	Grafting yield (%)			
	MMA (%)			
	80	60	40	20
Blank	6.9 (70)	21 (81)	16 (58)	2.1 (33)
N_2	22 (123)	118 (133)	82 (105)	- (72)
AIBN	18 (81)	78 (87)	23 (69)	1.7 (20)
Urea	57 (71)	12 (98)	1.6 (79)	5.0 (42)
H^+	392 (212)	132 (76)	30 (84)	0.1 (52)
DVB	43 (112)	9.0 (110)	12 (75)	56 (34)
AIBN + Urea	58 (66)	20 (90)	47 (62)	50 (43)

[a] Total dose: 2.0×10^3 at 5.0×10^2 Gy.h^{-1}; Additives 1% (w/w); $H^+ = H_2SO_4$ (0.2M); Solvent methanol; Data in brackets for styrene comonomer technique with styrene 20% (v/v) of total monomer.

followed by inorganic salts like lithium perchlorate and nitrate which could be used instead of acid for acid sensitive substrates as the results for the grafting of styrene in methanol to polyethylene show (Table 1). In addition if polyfunctional monomers (PFMs) like divinylbenzene (DVB) are included in additive amounts yields are also enhanced (Table 2), a synergistic effect occurring when both acid and PFM are included in the same monomer solution [5]. In addition, in the presence of nitrogen yields are increased. AIBN is also effective as an additive, decomposing to give additional radicals as well as nitrogen. Inclusion compounds like urea also increase yields. The problem with these grafting systems is homopolymer formation which reduces yields. As previously mentioned utilising the styrene comonomer technique can overcome this problem. Under these conditions longer irradiation times can be used, giving higher yields and the final copolymer is essentially grafted MMA (Table 2). All additives in this table at certain concentrations using the styrene comonomer procedure are seen to enhance grafting when compared with the blank. This comonomer process also yields a better, more uniform product from which residual homopolymer can be easily removed because the viscosity of the grafting solution is relatively low at the completion of the irradiation.

4.3. UV vs Ionising Radiation Systems

UV can initiate grafting reactions analogous to those described above for ionising radiation if sources of the appropriate wavelength are used [2,5,8-12]. UV is a particularly attractive alternative to ionising radiation since the equipment used is simpler, the source does not need extensive encapsulation only a light shield being required and thus can be readily installed in a laboratory without the need for meeting radioactive regulations. The technique is extremely useful for synthesising laboratory scale batches of graft copolymers which possess properties similar to those produced by ionising radiation. One important difference with UV systems is the limitation due to poor penetration of the radiation through a backbone polymer. In order to

overcome this problem photoinitiators have been used to improve the efficiency of the grafting process. Unlike ionising radiation which can indiscriminately break bonds in the backbone polymer to form sites where grafting can occur, UV does not form radicals directly in the backbone polymer unless that substrate has the appropriate functional groups or impurities which can efficiently absorb the incident UV. The graft copolymer from UV reactions needs careful post treatments to remove residual photoinitiator and fragments thereof from the finished copolymer. To the present time this contamination has limited the use of the technique in some applications.

Variables influencing UV grafting are similar to those reported for the ionising radiation technique. Thus solvent, presence of nitrogen, light intensity and temperature of irradiation are all significant. Most importantly, the presence of photoinitiator not only speeds up the reaction but also leads to differences in patterns of reactivity when compared to ionising radiation. Thus the position of the Trommsdorff peak usually occurs at higher monomer concentration with UV than in the ionising radiation system. Structure of the photoinitiator strongly influences its efficiency in these reactions. The early work with UV grafting used uranyl nitrate, anthraquinone derivatives, also benzophenone with its charge transfer complexes with amines but these have now been replaced by the aliphatic and aromatic ethers like the Ciba Geigy Irgacure range namely 184, 1700, 1800 and 1850 also Darocure 1173. Typical of the data obtained with these materials using AIBN as reference are those shown in Table 3 for the UV grafting of MMA in methanol to cellulose where the yields with all organic ethers, including benzoin ethyl ether (BEE) and especially the Irgacure materials are high. The corresponding results with the styrene comonomer technique are equally as impressive (Table 3, data in brackets). With UV, homopolymer formation is more of a

TABLE 3. EFFECT OF PHOTOINITIATORS ON UV GRAFTING MMA TO CELLULOSE WITH AND WITHOUT STYRENE[a]

System	Time (h)	Graft (%)			
		MMA (%)			
		80	60	40	20
Blank	16 (24)	3.3 (125)	6.0 (77)	2.0 (9.2)	0.3 (4.7)
N_2	16 (6)	45 (0.5)	53 (0.6)	24 (0.7)	26 (6)
AIBN	3 (24)	2.3 (21)	41 (132)	41 (124)	15 (54)
BEE	3 (24)	2.6 (49)	49 (105)	43 (81)	23 (30)
184[b]	3 (6)	28 (64)	113 (116)	84 (137)	49 (76)
1700[b]	3 (8)	150 (79)	70 (86)	62 (150)	57 (78)
1800[b]	3 (6)	20 (91)	96 (109)	88 (133)	45 (54)
1173[c]	3 (6)	88 (81)	94 (118)	78 (113)	47 (59)

[a] Conditions as in Table 2 except UV used with 90W lamp; [b] Irgacure materials; 184 is 1-hydroxycyclohexyl phenyl ketone; 1700 is 25% bis (2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide DMBAPO + 75% 2-hydroxy-2-methyl-1-phenyl-propan-1-one (HMPP) and 1800 is: 25% bis (2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide DMBAPO + 75% 1-hydroxycyclohexyl phenyl ketone (HCPK)

[c] Darocure 1173 is 2-hydroxy-2-methyl-1-phenyl-propan-1-one.

problem than with ionising radiation since in the former technique if slight precipitation of homopolymer occurs the grafting solutions become turbid and grafting ceases since transmission of light through such solutions is difficult. This situation is not relevant to ionising radiation where full penetration of the solution by the radiation occurs. The remaining additives found to be active in ionising radiation grafting also accelerate the UV processes.

5. CURING

Curing involves rapid polymerisation of an oligomer/monomer mixture to give a film which can also be crosslinked. Whereas gamma sources are used for ionising radiation grafting, EB are preferred in analogous curing because high doses of radiation are needed at a particular site in a fraction of a second to achieve fast cure. EB machines for this purpose are low energy facilities of 180 keV and above. In UV systems photoinitiators and high performance lamps up to 600W/inch are used to achieve fast rates of polymerisation. The polymer system used in both these radiation curing processes involves an oligomer (usually molecular weight 2000-3000) and is commonly a urethane, epoxy, polyester or polyether acrylate, although non acrylated oligomers such as vinyl ethers are progressively being introduced. Oligomers require the addition of monomers as reactive diluents, to adjust the rheological properties of the resin for application and to speed up the cure by crosslinking. The structure of the reactive diluent is important in determining the properties of the finished film such as flow, slip, wetting, swelling, shrinkage, adhesion and migration within the film. The reactive diluent can be either monofunctional or multifunctional, the latter being preferred because of enhanced crosslinking during cure due to its polyfunctionality. The properties required in the diluent are cutting power, solubility, lack of odor, ability to reduce the viscosity of the medium, volatility, functionality, surface tension, little shrinkage during polymerisation, appropriate glass transition (T_g of the homopolymer), effect on the speed of the overall cure and toxicology. Monomers with low skin irritancy as determined by the Draize rating are preferred, like tripropyleneglycol diacrylate (TPGDA).

5.1. Incentive to use Radiation Technology

The current advantages and limitations of radiation curing are shown in Table 4. One of the essential features of the technology is that it is environmentally friendly. The original purpose of utilising radiation cure was to replace solvents in processes like inks and coatings, such solvents being economically wasteful, toxic and an environmental hazard. During utilisation of the technology over the past twenty five years additional advantages have emerged, particularly the fact that novel products not capable of being formed by other techniques can be obtained. There are of course limitations to the technology (Table 4), however these problems are currently being solved and the technology is expanding steadily at 10% per annum world wide.

6. APPLICATIONS OF GRAFTING AND CURING

With respect to grafting a wide range of products have been synthesised however only a limited number of these processes have been commercialised. Thus grafted films have been used as battery separators, ion exchange resins, membranes for separation processes, in textiles (small scale) for flame retardency, dyeing, soil release and antistatic properties and super water absorbing materials for use as diapers and napkins. In the biological field, grafted systems are used for immobilisation of enzymes, antibodies, cells and drugs with potential medical applications (diagnostic and therapeutic), and industry (fermentation, bioseparation and catalyst supports.).

In contrast to grafting, radiation curing is expanding rapidly in a wide range of fields. In Table 5 are listed the areas of major use of the technology together with those of strongest growth and finally the emerging fields where the technology is beginning to be applied. The largest area of use is in inks and coatings. Theoretically any solvent based ink or coating process can be replaced by the radiation equivalent. One extremely large application where the technology still encounters problems is in coil coating. This is because extremely high line speeds are needed, leading to shrinkage of cured film with subsequent poor adhesion directly onto the metal surface. In terms of novelty of product one unique demonstration where the technology can produce a product difficult to obtain by other means is the UV cured banknote which has now become standard currency in Australia [13].

6.1. Significance of Concurrent Grafting with Curing

One of the most potentially largest and most important applications of grafting is its occurrence in curing. As previously mentioned, curing generally involves physical bonding

TABLE 4. ADVANTAGES AND LIMITATIONS OF RADIATION CURING

Advantages	Limitations
No solvent- greenhouse effect	Economics- equipment/ material costs
Environmentally attractive	Pigmentation difficult (UV)
Fast cure- increased productivity	Application at 100% solids
Improved physical properties	No FDA approval for food
Room temperature cure	Recycling of waste
Lower costs and maintenance	Wider chemistries needed
Energy reduction	Adhesion, formability difficult
High gloss	Line -of-site cure
Process flexible, versatile	Weatherability

TABLE 5. CURRENT STATUS OF RADIATION CURING PROCESSES

Major Use	Strong Growth	Emerging Processes
Clear coatings- graphic arts	Flexo inks wide web	Powder coating
Inks-litho, screen	Metal decorating	UV pigmented
Wood finishes	Silicone release	UV durable coatings
Plastic coating + printing	Pipe coating	Water reducible UV
Flooring finishes	Paper coatings	Sprayable coatings
Banknotes	Automotive	Mechanical devices
Optical fibers	Adhesives	Laser curing

TABLE 6. PHOTOINITIATOR FREE UV GRAFTING TO CELLULOSE AND POLYPROPYLENE WITH AND WITHOUT STYRENE[a]

System	Additive	Time(h)	Graft (%) Monomer (%)			
			80	60	40	20
MMA/MeOH[b]	Blank	16 (24)	3.3 (125)	6.0 (77)	2.0 (	0.3 (4.7)
MMA/MeOH[b]	TPGDA	5 (24)	2.4 (11)	3.0 (31)	3.4 (68)	2.3 (2.7)
MMA/MeOH[b]	DVE-3	5 (24)	1.8 (250)	3.1 (296)	1.9 (339)	11.1 (1.0)
MMA/MeOH[b]	CHVE	5 (24)	8.4 (248)	2.7 (308)	16.8 (35)	1.3 (63)
MMA/MeOH[b]	HBVE	5 (24)	3.2 (107)	3.6 (95)	2.8 (59)	1.7 (1.5)
MMA/ACN[c]	Blank	24	-	0.2	-	-
MMA/ACN[c]	CHMI	24	-	0.1	-	-
MMA/ACN[c]	CHVE	24	-	66	-	-
MMA/ACN[c]	CHMI/ CHVE	24	-	102	-	-

[a] Conditions as in Table 3; Data in brackets for MMA solutions containing styrene (20% by volume of MMA); Additives 1% (w/w); DVE-3 is 3, 6, 9, 12-tetraoxadeca-1, 13-diene; CHVE is cyclohexane 1,4-bis[(vinyloxy) methyl]; HBVE is 1-butanol, 4-(ethyenyloxy); CHMI is cyclohexylmaleimide; MeOH is methanol and ACN is acetonitrile.
[b] Cellulose; [c] Isotactic polypropylene

whereas grafting concerns covalent bonding. Intuitively, it would be expected that the occurrence of grafting with curing would lead to improvements in the final product since delamination would be more difficult. With the more energetic ionising radiation sources, radicals at sites for grafting are formed more readily than with UV. Thus, in curing, the occurrence of concurrent grafting would be expected to occur more efficiently in EB systems. However, with UV, in the presence of photoinitiators, abstraction reactions with the backbone polymer can occur thus leading to graft copolymer. Whilst concurrent grafting during curing can be beneficial in reducing delamination in the final product, it can also be a problem, particularly with coated paper and its recycling. If the film is grafted to the paper during cure, covalent bonds are formed and these are difficult to break, thus removal of surface coating to enable recycling of the paper by repulping can become difficult. Typical commercial examples of this problem have been found in EB and UV systems. Thus in the EB coating of paper for metallising in the label field, it was necessary to develop special EB coatings which were soluble in 0.1% alkali at room temperature but insoluble in water to achieve recycling. In like manner in the UV ink field, paper recycling has been a problem since the recycled product invariably is "spotty" and can only be reused in restricted applications usually as core in cardboard manufacture. These problems with recycling predominantly occur with cellulosic type materials whereas recycling of coated synthetics can generally be achieved more readily.

7. MECHANISMS OF RADIATION GRAFTING AND CURING

Radiation grafting and curing are mechanistically related in that both are predominately free radical reactions with ionic processes capable of participating in specific examples. Thus ionising radiation leads to radicals and ions as a consequence of the interactions of electrons and gamma rays with the substrate. UV, via photoinitiators, leads to both free radicals and to a lesser degree ionic processes by the use of photoinitiators like the aryl sulphonium salts [14]. In grafting the effect of ionising radiation on a backbone polymer (e.g. cellulose, CeOH) is to create grafting sites (Eq 3). Monomer then can graft at this site via a free radical process. With UV the photoinitiator, PI, absorbs energy to yield radicals which can then abstract H atoms from substrate to create grafting sites (Eqs 4-5).

$$CeOH \longrightarrow CeO^{\bullet} + H^{\bullet} \quad (3)$$

$$PI \longrightarrow P^{\bullet} + I^{\bullet} \quad (4)$$

$$CeOH + P^{\bullet} \longrightarrow CeO^{\bullet} + PH \quad (5)$$

In a similar manner, in curing, e.g. with UV, the photoinitiator yields radicals which then react directly with the oligomer/monomer mixture to initiate rapid polymerisation and crosslinking. Additives in the tables are shown to accelerate these grafting reactions. In related studies [15, 16] additives like the multifunctional monomers such as TPGDA and also oligomers like the urethane and epoxy acrylates accelerate these grafting processes. The latter additives are also used as basic materials in curing to achieve fast reaction. The mechanistic relationship between grafting and curing is thus further accentuated.

The mechanism of the additive effect in grafting has been attributed to two concepts, a physical parameter involving partitioning of reagents and a chemical parameter involving an initial increase in concentration of radicals in the presence of additive thus influencing the kinetics of the process via an increase in chain initiation. Partitioning in grafting is due to the fact that in the presence of appropriate additives the concentration of monomer in the grafting solution absorbed by the backbone polymer is higher than in the bulk grafting solution itself thus increasing the concentration of monomer available for grafting at a particular site. In like manner, partitioning of reagents can occur in curing. Thus the low molecular weight monomer in the oligomer/monomer mixture can be partitioned into the upper layers of the substrate, this process influencing the properties of the final product.

8. FUTURE DEVEOPMENTS-PHOTOINITIATOR FREE GRAFTING AND CURING- EXCIMER LASER SOURCES

Developments in radiation grafting and curing, particularly UV curing, over the past five years have been significant, especially the ability to cure highly pigmented systems. A very important recent advance has been the discovery of photoinitiator free UV grafting [15] and curing systems [17]. Associated with this development in chemistry is the use of excimer laser sources to initiate these grafting and curing processes. Typical of the systems used in preliminary studies of photoinitiator free UV grafting are those shown in Table 6, where it is observed that vinyl ethers in additive amounts accelerate photoinitiator free UV grafting of MMA in methanol to cellulose at certain concentrations. Likewise, CHVE, being representative of vinylethers, also enhances photoinitiator free UV grafting of MMA in acetonitrile to polypropylene. The yield is increased further when cyclohexylmaleimide is added to this grafting solution. The important feature of these results is that these maleimide and vinyl ether additives are also used in photoinitiator free UV curing and thus a mechanistic relationship would appear to exist between the two systems ie during curing, concurrent

grafting would be expected to occur under certain radiation conditions with the practical implications such grafting would impose on the properties of the resulting cured products such as recycling efficiency and alike.

The other outstanding development in radiation curing recently has been the emergence of excimer laser sources. This technology currently complements EB and UV processing however in future there is the prospect that it may well replace conventional UV processing. The excimer laser technology, in terms of the IAEA programs, has potential in developing countries since it may be used in those areas where EB is too expensive. With respect to the developed countries the excimer laser technology will provide additional advantages, in particular, new chemistry will be developed concurrently with the improvement in the excimer laser sources. This chemistry involves photoinitiator free formulations leading to cheaper processing costs. The excimer laser process will be a very powerful tool in the radiation processing field and there is strong justification for employing this technology in future IAEA Processing Programs.

8. CONCLUSION

Radiation grafting and curing are shown to be mechanistically related processes and to possess strong potential in future commercial applications. Grafting *per se*, has only limited industrial use, however when it occurs concurrently with curing, the process becomes very important. The significance of concurrent grafting with cure is of environmental value especially where recycling of radiation cured products are involved. The emergence of excimer laser curing provides a new process to complement current EB and UV curing techniques. The onset of photoinitiator free grafting and curing systems indicate strong potential for future growth of radiation processing especially as both are environmentally attractive.

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