



Recent developments of thermosetting polymers for advanced composites

H. D. Stenzenberger

*Technochemie GmbH Verfahrenstechnik, * D-6915, Dossenheim, Germany*

The aircraft/aerospace industry is the fastest growing market sector for advanced composites. To use fully the potential of advanced composites for demanding structural applications it requires improved properties of its constituents, the carbon fibres and polymer matrix resins. This article emphasizes new developments of thermosetting polymers such as epoxy resins and bis-maleimides. The concepts to achieve improved thermosetting polymer matrix resins are new monomers (resins and curing agents), thermoplastic modification, liquid crystalline monomers and impact tolerant interleaved systems. The paper highlights thermoset resins and systems which provide improvements in the areas of moisture absorption, fracture toughness and high temperature stability.

1 INTRODUCTION

High performance composites based on glass-, carbon- and aramide-fibres are finding increased application as structural and functional materials, due to their unique mechanical, thermal and electrical properties.

The worldwide market for advanced composites and high performance adhesives in 1987 was about £29 million. This amounted to approximately £15 million of resin sales in 1987. Currently, epoxy resins constitute over 90% of the matrix resin material used in advanced composites. The remaining 10% are unsaturated polyester and vinylester for low temperature applications and cyanate esters, bismaleimides, and polyimides for the high temperatures. The use of thermoplastics, however, which are included in the 10%, will become more important within the next decade. The total usage of advanced composites is expected to grow to around £110 million by the year 1996.¹ The market sectors for advanced polymer composites were 38% aerospace, 31% recreational, 22% industrial, 4% transport, and 5% others in 1987. By far the fastest growing area is aerospace which, according to actual forecasts, will use up to 65% of the total advanced polymer composite production in 1996. In the past, rising fuel prices justified advanced

composite materials in aeroplanes. Boeing began to replace aluminium with fibreglass aboard airlines in the early 1960s, but the fuel crisis a decade later led NASA to examine the advantages of lighter and stronger carbon and aramide in more heavily loaded structures. Several components such as carbon skinned aluminium spoilers for the 737-200 aircraft, carbon skin honeycomb sandwich elevators for the 727, and horizontal stabilizers with solid laminate skin and stringer construction for the 737 were developed under the Aircraft Energy Efficiency Programme sponsored by NASA. This successful introduction of composites justified a greater commitment to advanced composites to the Boeing 757 and 767 advanced aircraft. Ailerons, rudders, elevators and the 767 rudder, which is 420 inches long (10.6 metres) and has a carbon fibre spar, are examples for the successful introduction of resin matrix advanced composites as lightweight materials for civil aircraft.

Airbus Industries in Europe has been using advanced composites extensively since 1979/80. Only 5% of the structural weight was composite in the A300 and has been increased to 15–17% structural weight for the A320 family. Ambitious projects such as the composite fuselage and the all-composite wing will dramatically increase the advanced polymer composite use.

The extensive use of polymer based composites in these demanding structural applications

*A member of the Royal Dutch/Shell Group of Companies.

requires improved properties of its constituents, the carbon fibres and polymer matrix resins.

The properties of the carbon fibres have seen a dramatic improvement during the last ten years. Properties such as tensile strength, tensile modulus and elongation were increased almost by a factor of two. Particularly the strain to failure of 2% and above made it possible to improve composite toughness and damage tolerance. To utilize fully the new carbon fibre properties, matrix resins with a strain to failure of 6–10% are required. Problem areas of thermosetting matrix polymer (thermosets) are brittleness, high moisture absorption, low glass transition temperature (T_g), insufficient thermal oxidation stability and lack of processability for low cost processing techniques such as filament winding, resin transfer moulding and resin injection moulding. Development directions and concepts to achieve improved thermosetting polymer matrix resins are discussed in this article. Such concepts are:

- development/synthesis of new monomers, curing agents and comonomers;
- modification with thermoplastics;
- impact tolerant interleaved systems; and
- liquid crystalline thermosets.

Within this article these new development directions are discussed for epoxy resins and bismaleimides. Similar developments are in progress for other resin families such as vinyl esters, cyanate esters, benzocyclobutenes, acetylene terminated resins and polyimides.

2 STATE-OF-THE-ART THERMOSET RESIN TECHNOLOGY

2.1 Epoxy (EP) resins

The most widely used EP resins are based on 4,4'-bisglycidylbisphenol-A. Given in Fig. 1 are the structure and properties of some typical liquid bisphenol-A epoxy resins. In commercial products, the value of n ranges from about 0 to 25, with typical liquid epoxy resins having n values 0–1. The number average molecular weight (M_n) and the molecular weight distribution determine the resins viscosity. The structures of a number of more widely used speciality EP resins are given in Fig. 2. Shown at the top of the figure are brominated resins which are used in printed circuit boards, usually at levels of about 20 wt% bromine.

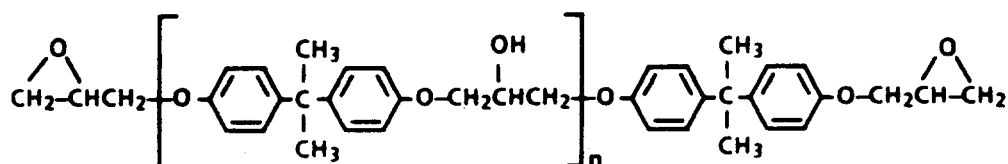
For certain applications it is desirable to modify the brittle bisphenol-A system to improve toughness. This is frequently accomplished by introducing flexibilizing epoxy resins which are based on long chain molecules such as dimer fatty acids and polyglycols. For more demanding uses at higher temperatures, such as aircraft/aerospace, multifunctional epoxy resin systems are used. The epoxy resins based on tetraglycidylmethylenedianiline (TGMDA) cured with diaminodiphenylsulphone (DDS) was the first system to meet the performance requirements of the aerospace industry and still is extensively used today.

Epoxy resins are reactive intermediates composed of a mixture of oligomeric materials containing one or more epoxy groups per molecule. To convert epoxy resins into useful products they must be cured or cross-linked by chemical reaction into a three-dimensional network. Cross-linking agents or curing agents, as they are called, used with epoxy matrix resins for advanced composites are aromatic diamines or anhydrides. A large number of epoxy resin/curing agent combinations are possible which may further be modified with catalysts, reactive diluents, to reduce viscosity, and additives, to provide the desired cured resin properties.

2.2 Bismaleimide (BMI) resins

BMI resins comprise bismaleimide monomer, comonomers, reactive diluents and other additives, catalysts, etc. The most important property is that BMI can be polymerized thermally or by catalytic means to form a highly cross-linked network. The maleimide double bond is very reactive and can be engaged in various other chemical reactions. Nucleophiles such as primary and secondary amines, phenols, thiols, etc., undergo a so-called Michael addition reaction. Bismaleimide is a bisdienophile and can undergo Diels-Alder reactions with dienes. Allylphenol reacts with BMI via an 'ene' reaction. Furthermore, vinyl and allyl type ethylenic double bonds can copolymerize either with or without radical type catalysts. Important with respect to enhanced BMI resin cure is the anionic polymerization of the maleimide double bond effected by tertiary amines or imidazoles.²

All commercially available BMI resins comprise 4,4'-bismaleimidodiphenylmethane (Fig. 3) as a building block at a concentration of 50–70%. Other resin ingredients can be comonomers, such as styrene³ or divinylbenzene⁴ reactive diluents,



Typical Properties of Selected Liquid Epoxy Resins

Approximate average molecular weight, Mn	Typical EEW range	Typical viscosity range, poise, 25°C
340	172-178 ^a	40-60
350	178-186 ^b	65-95
370	185-192 ^c	110-150

Examples of commercial resins: ^aEPON® Resin 825, EPI-REZ® 508, D.E.R.® 332; ^bEPON Resin 826, EPI-REZ 509, ARALDITE 6015, D.E.R. 330; ^cEPON Resin 828, EPI-REZ 510, ARALDITE 6010, D.E.R. 331.

EPON is a trademark of Shell Chemical Company; EPI-REZ is trademark of Intereze, Inc.; ARALDITE is a trademark of Ciba-Geigy Corporation; D.E.R. is a trademark of Dow Chemical Company.

Fig. 1. Structure and typical properties of liquid bisphenol-A based epoxy resins.

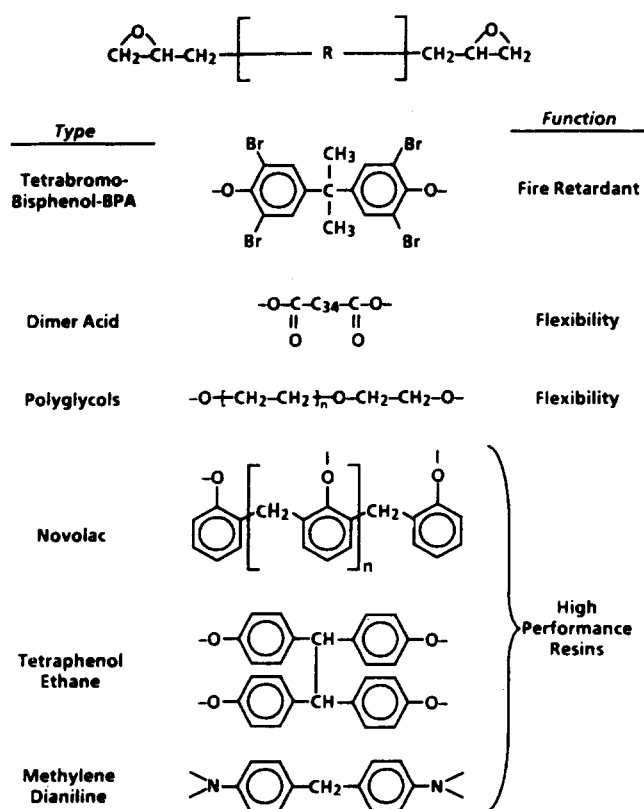


Fig. 2. Speciality epoxy resins.

or chain extenders, such as aromatic diamines⁵ or aminobenzoic hydrazide.⁶

State-of-the-art comonomers are diallylbisphenols⁷ and allylphenol compounds⁸ which provide tough networks. Other interesting comonomers are bis(*o*-propenylphenoxy) com-

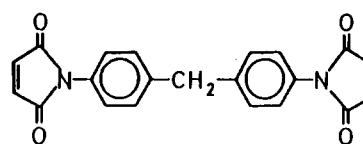


Fig. 3. Chemical structure of 4,4'-bismaleimidodiphenylmethane.

pounds such as bis(*o*-propenylphenoxy)benzophenone⁹ and bis(*o*-propenylphenoxy)diphenylsulphone¹⁰ which provide temperature resistant networks.

3 NEW MONOMERS FOR THERMOSET RESINS

More demanding aerospace applications require improved thermoset resins with respect to:

- toughness and damage tolerance;
- temperature resistance; and
- moisture absorption.

Experts are of the opinion that new monomers with new backbone architecture are necessary to achieve these ambitious targets.

3.1 Chemistry and properties of new high performance epoxy resins

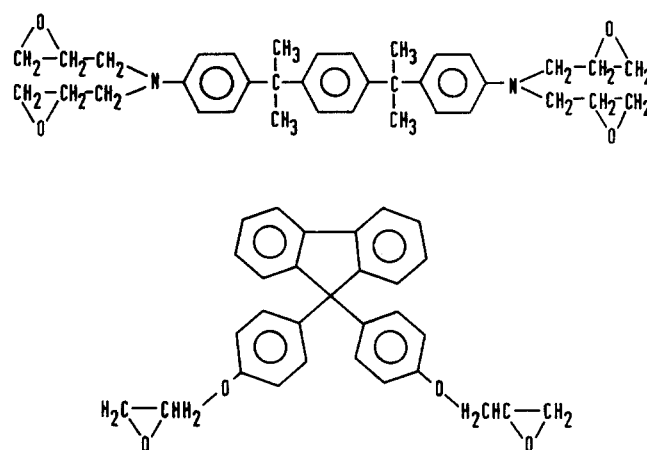
Shell Chemical Company has introduced a new tetraglycidyl amine and a new stiff backbone

diglycidyl ether under the respective tradenames EPON HPT® Resin 1071 and EPON HPT® Resin 1079^{11,12} which have superior hot/wet performance compared to tetraglycidylmethylenedianiline (TGMDA). These two materials are chemically *N,N,N',N'*-tetraglycidyl- α,α -bis(4-aminophenyl)-*p*-diisopropylbenzene and diglycidyl-9,9'-bis(4-hydroxyphenyl)fluorene. Their structures along with uncured resin properties are given in Fig. 4. As can be seen from Fig. 5, the moisture gain (after two weeks immersion in water at 93°C) for EPON HPT® Resin 1071 and EPON HPT® Resin 1079 cured with DDS is 3.7 and 2.8 wt% compared to 5.7 wt% for the corresponding TGMDA system. This results in a much improved hot/wet performance for these two new resins compared to TGMDA. Specifically under hot/wet conditions (samples were tested under water at 93°C after two weeks immersion at 93°C) the TGMDA system retains only 65% of its dry room temperature modulus, whereas the EPON HPT® Resin 1071 and EPON HPT® Resin 1079 retained 85% and 91%, respectively, of their dry room temperature modulus under hot/wet conditions.

Another possibility for further modifying the moisture absorption of epoxy resins is the use of new curing agents. A very attractive aromatic diamine is 2,2'-bis(3,5-dimethyl-4-aminophenyl)-*p*-diisopropylbenzene designated EPON HPT® curing agent 1062 (Fig. 6). As can be seen in Table 1 the moisture absorption and hot/wet properties of EPON HPT® Resin 1079 cured with EPON HPT® curing agent 1062 are outstanding. This new curing agent may also be combined with other epoxy resins to provide both high T_g combined with low moisture absorption.

3.2 Chemistry and properties of new high performance bismaleimide resins

Bismaleimide combined with liquid or low melting comonomers such as *o,o'*-diallylbisphenols^{7,8,13} provide tough networks. There is the possibility of either modifying the backbone chemistry of the BMI or the backbone chemistry of the comonomer to improve their properties. Extensive work is underway to develop coreactants for BMIs which provide high T_g without the loss of toughness. This can be achieved by using extremely stiff backbones terminated with allyl or propenyl functional groups. Recent publications show that comonomers with imide type structural



EPON HPT Resin 1079

Typical Neat EPON HPT Resin Properties

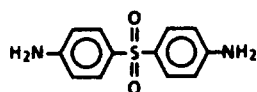
Property	EPON HPT Resin 1071	EPON HPT Resin 1079
Weight per epoxide (WPE) (Shell method HC-427C-81 perchloric acid method)	150–170	240–270
Melt viscosity, Brookfield, Pa. s (p)	18–22 ^b	55–80 ^c
T_g (DSC), °C	23	51–54
Melting point °C (ASTM D3461, Mettler, 1°C/min)	50	139–144

^aTrade name of Shell Chemical Company; ^bat 100°C; ^cat 177°C.

Fig. 4. Structures and typical neat resin properties of EPON HPT® Resin 1071 and EPON HPT® Resin 1079.

backbone fulfil these requirements. Bis(benzocyclobutene-imide)¹⁴ and bis(allynadide-imide)¹⁵ are examples for such imide type comonomers.

Recently, the synthesis of bis[3-(2-allylphenoxy)phthalimides] (Fig. 7) has been reported.¹⁶ They were synthesized via a nucleophilic nitrodisplacement reaction of bis(3-nitrophthalimides) with *o*-allylphenoxy-sodium in high yield. These allylphenoxyphthalimides thermally copolymerize with bismaleimides to provide tough copolymer networks with high glass transition temperatures and excellent high temperature mechanical properties. Toughness, however, is very dependent on the molar ratio between the reactants (Table 2). For a 2:1 stoichiometry of BMI and bis[3-(2-allylphenoxy)phthalimide] fracture toughness is optimum. Within a recent publication, the excellent thermal oxidative stability of carbon fibre



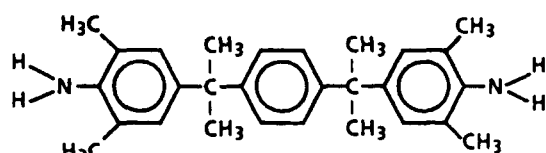
Curing agent Resin	TGMDA ²	EPON HPT Resin	
		1071	1079
Properties			
T_g (tan δ) (°C)	262	249	279
Flexural properties (RT/dry)			
Strength (MPa) (ksi)	138(20)	117(17)	124(18)
Modulus (GPa) (ksi)	3.9(559)	3.9(563)	3.3(485)
Elongation (%)	5.0	3.7	4.7
Flexural properties (hot/wet) ³			
Strength (MPa) (ksi)	76(11)	90(13)	90(13)
Modulus (GPa) (ksi)	2.5(361)	3.0(434)	3.0(433)
Elongation (%)	4.7	4.2	4.1
Moisture gain (wt%) ⁴	5.7	3.6	2.8

¹ Cured with stoichiometric amount of curing agent, cure schedule 2 h at 150°C and 4 h at 200°C.

² Formulation contains 8.2 phr EPI-REZ SU-8 (Interez, Inc.).

³ Tested in water at 93°C after two weeks immersion at 93°C.

Fig. 5. Neat resin properties of EPON HPT® Resins 1071. EPON HPT® Resin 1079 cured with DDS.



EPON HPT Curing Agent 1062

Typical Properties of Neat Curing Agent	
Physical form	Crystalline solid
Colour	Tan to cream
Melting point	151°C–154°C
Approximate equivalent weight/active hydrogen	100

Fig. 6. Chemical structure and typical properties of EPON HPT® 1062 curing agent.

laminates based on BMI/bis(allylphenoxy)phthalamide copolymer was reported.¹⁷

All of the improvements, however, are achieved at the expense of processability. All of the new epoxy resin or bismaleimide comonomers are solids with softening temperatures around 50°C, or melting temperatures around 100°C, respectively, which greatly restricts their versatility in prepreg formulations and other liquid resin processing techniques such as filament winding and RTM (resin transfer moulding).

4 THERMOPLASTIC MODIFIED THERMOSETS

Brittleness is an inherent property of highly cross-linked polymers, such as epoxy resins, bismaleimides and cyanates. Improvements in ductility, fracture resistance and impact strength, however, can be achieved through modification with liquid elastomeric carboxyl terminated butadiene acrylonitrile copolymer.¹⁸ Although this concept provides significant toughness improvements, there is a trade-off in high temperature mechanical properties, in particular elastic modulus and glass transition temperature (T_g). Therefore, the approach of incorporating tough high performance thermoplastics into brittle thermosets is finding increased interest. Thermoplastics such as polysulphone, polyethersulphone, polyetherimide, etc., show a few advantages such as low moisture absorption, and high toughness combined with relatively high elastic moduli, which makes them ideal candidates for improving synergistically the properties of thermoset/thermoplastic blend systems.

4.1 Thermoplastic modified epoxy resins

ICI's Victrex 100P, 200P, 300P, etc., were used by Raghava¹⁹ to modify TDMA/DDS systems, but

Table 1. Neat resin properties of EPON HPT® Resin 1079 cured with EPON HPT® 1062 curing agent

Resin system	DDS ^a	EPON HPT curing agent 1062 ^b	
	TGMDA ^a	1071	1079
Properties			
T_g (tan δ) (°C)	262	239	264
Flexural properties (RT/dry):			
Strength (MPa (ksi))	138 (20)	131 (19)	188 (20)
Modulus (GPa (ksi))	3.9 (559)	3.9 (497)	3.2 (462)
Elongation (%)	5.0	4.5	6.4
Flexural properties (hot/wet): ^c			
Strength (MPa (ksi))	76 (11)	96 (14)	90 (13)
Modulus (GPa (ksi))	2.5 (361)	3.0 (441)	2.7 (415)
Elongation (%)	4.7	3.9	4.1
Modulus (wet/dry):			
% Retention	65	89	90
Moisture gain (wt%) ^d	5.7	1.6	1.3

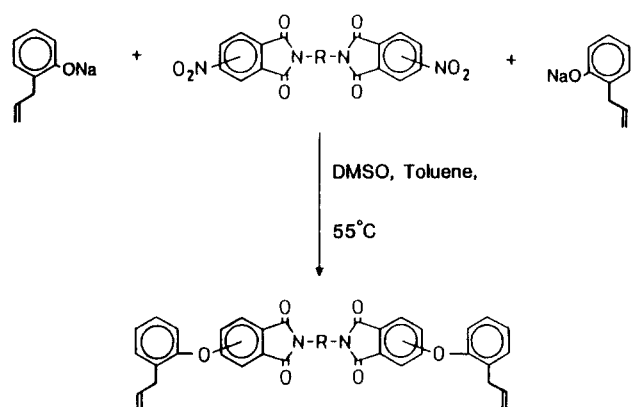
^aTGMDA/DDS/EPI-REZ SU-8: 100/49.4/8.2, cure schedule 2 h at 150°C and 4 h at 200°C.

^bCured with stoichiometric amount of curing agent, cure schedule 2 h at 150°C and 4 h at 200°C.

^cTest in water at 93°C after two weeks immersion at 93°C.

^dAfter two weeks immersion at 93°C.

RT, Room temperature.

**Fig. 7.** Synthesis of bis[3-(2-allylphenoxy)phthalimides].

these combinations showed only marginally improved toughness. In another independent study, Bucknall and Partridge²⁰ reported that DDS and/or DICY cured TGMDA or triglycidyl-*p*-aminophenol showed only very little improvement in toughness with polyethersulphone. Interestingly, phase separation of the thermoplastic occurred with the triglycidyl epoxide cured with DDS and DICY, and phase separation was not observed for TGMDA with the same curing agents.

Recently, it has been reported that the modification of the backbone of an aromatic thermoplastic allows the morphology of an epoxy resin/thermoplastic blend^{21,22} to be controlled.

Although a number of publications have been written about TP toughening of epoxy resins, it is

not 100% clear what is required for an epoxy/thermoplastic pair to develop optimum toughness properties in the hybrid system. However, it became obvious that the toughness obtainable from the thermoplastic modified epoxy resin system depends on several factors, including:

- the type of thermoplastic;
- heterophase morphology;
- interfacial adhesion between the heterophase and the matrix;
- epoxy resin and curing agent;
- cure conditions; and
- molecular weight between cross-links of the epoxy resin.

The engineering thermoplastics which are generally used for epoxy resin toughening are polysulphone, polyethersulphone, polyetherimide and polyimide. The selection of the right thermoplastic for a specific epoxy resin curing agent system is not easy because the thermoplastic has to fulfil at least the following requirements:

- the TP must be soluble in the uncured epoxy resin;
- the T_g of the TP should be higher or at least equal to the T_g of the thermoset (TS) system;
- the elastic modulus should not be below the modulus of the epoxy resin; and
- the molecular weight of the TP has to be high enough for achieving high toughness.

Table 2. Neat resin properties of BMI/2,4-bis[3-(2-allylphenoxy)phthalimido]toluene copolymers

Property	Composition (wt% BAPPT)			
	38	48	49	52
T_g (tan δ) (°C)	286	278.5	284	280.5
Flexural properties ^a (RT/dry):				
Strength (MPa)	94	89	114	115
Modulus (GPa)	4.24	4.00	4.04	4.04
Elongation (%)	2.23	2.31	2.89	2.81
Flexural properties ^a (177°C/dry):				
Strength (MPa)	63	89	94	94
Modulus (GPa)	3.74	3.50	3.53	3.31
Elongation (%)	1.70	2.48	2.65	2.72
Flexural properties ^a (250°C/dry):				
Strength (MPa)	61	86	95	92
Modulus (GPa)	2.95	2.95	3.23	3.18
Elongation (%)	2.08	3.16	3.07	3.17
Fracture energy, G_{Ic} (J/m ²)	88	146	165	207
Moisture gain (wt%) ^b	2.73	2.42	3.19	—

^aCure: 1 h 160°C, + 3 h 180°C, + 4 h 210°C, + 5 h 240°C.^b1000 h, 94% rh, 70°C.

BMI = eutectic bismaleimide blend.

Modifier: BAPPT = 2,4-bis[3-(2-allylphenoxy)phthalimide] toluene.

RT, Room temperature.

Table 3. Neat resin properties of thermoplastic modified EPON HPT® Resin 1071/EPON HPT® curing agent 1062

Property	Control	Udel ^a (wt%)			Ultem ^b (wt%)			Resistherm ^c (wt%)		
		6.5	13.0	30	6.5	13.0	30	10	20	30
T_g (tan δ) (°C)	212	236	230	194	226	229	215	212	223	225
Flexural properties (RT/dry):										
Strength (MPa)	109	124	131	139	145	138	125	122	133	143
Modulus (GPa)	3.49	3.38	3.40	3.35	3.52	3.47	3.54	3.48	3.19	3.16
Elongation (%)	3.2	4.4	4.6	4.5	4.9	4.8	3.7	3.6	4.4	5.5
Flexural properties (120°C/dry):										
Strength (MPa)	100	—	—	103	—	—	107	112	109	117
Modulus (GPa)	2.81	—	—	2.77	—	—	2.91	2.85	2.69	2.87
Elongation (%)	4.19	—	—	5.34	—	—	3.91	5.35	5.53	5.58
Flexural properties (175°C/dry):										
Strength (MPa)	52	—	—	17	—	—	74	67	71	80
Modulus (GPa)	1.78	—	—	0.68	—	—	2.45	2.35	2.37	2.52
Elongation (%)	4.78	—	—	> 5.23	—	—	4.49	4.37	4.40	4.26
Fracture toughness, K_{Ic} (kN/m ² × m ^{1/2})	520–568	607	640	1031	770	942	1314	895	1042	1351
Fracture energy, G_{Ic} (J/m ²)	77–95	110	121	386	169	256	488	230	321	578
Moisture gain (wt%) ^d	1.41	1.01	0.98	1.38 ^e	1.04	1.02	1.30 ^e	1.55	1.51	1.72

^aUdel 1700 from Union Carbide Corporation. Test specimens containing 6.5 and 13 wt% Udel were prepared by melt casting the resin systems. The 30 wt% Udel sample was prepared by compression moulding.^bUltem 1000 from General Electric Company. Test specimens containing 6.5 and 13 wt% Ultem prepared by melt casting the resin systems. The 30 wt% Ultem sample was prepared by compression moulding.^cResistherm from Bayer AG. All test specimens were obtained by compression moulding.^dMoisture gain was obtained on test specimens prepared by melt casting after two weeks immersion in water at 93°C, and specimens prepared by compression moulding after 500 h at 94% relative humidity.^eSamples were immersed in 70°C water for 500 h.

RT, Room temperature.

Recently the author studied the toughenability of the EPON HPT® 1071 resin/EPON HPT® 1062 curing agent system with commercially available engineering thermoplastics (Udel 1700 Polysulphone, Ultem 1000 Polyetherimide and Resistherm PH 10 Polyhydantoin).²³ The mechanical properties of the neat and the thermoplastic modified resins are given in Table 3. Addition of thermoplastic to the resin results in an improvement of the flexural strength by 10–30% depending on the system. In the case of the Udel modified epoxy resins, the flexural strength improves with increasing level of thermoplastic. The Ultem 1000 and Resistherm modified systems show higher 175°C strength, modulus and elongation compared to the unmodified resin.

The fracture toughness of all TP modified EPON HPT® Resin 1071 systems increases with an increasing level of thermoplastic. The poly(etherimide) and Resistherm poly(hydantoin) are more effective in toughening the resin than the Udel polysulphone. Interestingly, low polysulphone concentration (6.5–13%) only provides a marginal increase in toughness. For poly(etheri-

mide) a close linear correlation is found for the fracture energy (G_{Ic}) versus the thermoplastic concentration. However, the fracture energies for all three thermoplastic modified systems are below the values that would be expected from the rule of mixtures.

Udel polysulphone, Ultem 1000 poly(etherimide) and one experimental poly(arylene ether) have also been tested as tougheners for the EPON HPT® 1079/EPON HPT® 1062 resin system.²⁴ Again poly(etherimide) provided the highest degree of toughening with very high fracture toughness values at a 20–30% concentration (Table 4). The poly(arylene ether) provided only very low toughness improvements even at 25 wt% concentration. Combining a thermoset resin with a thermoplastic polymer, the following morphologies are in principle possible:

- Thermoplastic polymer and thermoset resin provide a homogenous system without phase separation.
- The TP separates and is present in the form of small spheres with thermoset as the continuous phase.

Table 4. Neat resin properties of thermoplastic modified EPON HPT® Resin 1079/EPON HPT® curing agent 1062

Property	Control	Udel ^a (wt%)			Ultem 1000 ^b (wt%)			PAE-4 ^c (wt%)	
		10	20	30	10	20	30	10	25
T_g (tan δ) (°C)	250	235	235	242	238	235	233	230	231
Flexural properties (RT/dry):									
Strength (MPa)	119	126	112	160	83	91	78	78	93
Modulus (GPa)	3.16	3.08	3.11	3.37	3.19	3.24	3.19	3.19	3.35
Elongation (%)	4.16	4.22	3.94	6.21	2.66	3.00	2.51	2.49	2.87
Flexural properties (120°C/dry):									
Strength (MPa)	99	106	111	118	88	83	69	82	94
Modulus (GPa)	2.73	2.66	2.74	2.92	2.78	2.87	2.83	2.83	2.98
Elongation (%)	4.02	4.78	4.71	5.48	3.35	3.10	2.51	3.06	3.61
Flexural properties (177°C)									
Strength (MPa)	93	91	81	89	86	67	70	90	97
Modulus (GPa)	2.52	2.44	2.50	2.66	2.57	2.57	2.59	2.57	2.74
Elongation (%)	4.99	4.63	4.88	4.98	3.81	2.55	2.91	4.63	4.52
Fracture toughness, K_{Ic} (kJ m ^{-3/2})	577	477	756	1133	701	1222	1373	589	771
Fracture energy, G_{Ic} (J/m ²)	105	74	183	381	154	461	591	109	177
Moisture gain (wt%) ^d	1.50	1.37	1.28	1.22	1.41	1.46	1.43	1.32	1.22

^aUdel 1700 from Union Carbide Corporation.

^bUltem 1000 for General Electric Company.

^cPoly(arylene ether) supplied by P. M. Hergenrother, NASA Langley Research Center, Hampton, Virginia (Ref. 10).

^d500 at 70°C and 98% relative humidity.

RT, Room temperature.

- Thermoset separates in the form of small spheres and thermoplastic polymer forms the continuous phase (inverted systems).
- Hybride morphologies, that is, the presence of more than one of the above morphologies.

The morphology finally achieved in a TP modified epoxy resin is dependent on the solubility parameters, the concentration thermoplastic its molecular weight and molecular weight distribution.

4.2 Thermoplastic modified bismaleimide

Bismaleimide resins can be modified with thermoplastics similar to epoxy resins. High molecular weight non-reactive amorphous polysulphone, poly(etherimide), poly(hydantoin) and polyimide (Matrimid 5218, Ciba Geigy) were incorporated in a bismaleimide resin (Compimide™ 796/Compimide™ 123)^{25,26}. The properties of the unmodified BMI (control) and the thermoplastic (polyhydantoin and polyimide) modified versions are presented in Table 5. All three thermoplastics in this evaluation had T_g well in excess of 250°C.

The highest degree of toughening for a thermoplastic concentration of 20 wt% is obtained with the high molecular weight poly(hydantoin) Resistofol N (Fig. 8) and lowest with the poly(hydantoin) PH 10. Morphological evaluation of the fracture surfaces of neat resin specimens were performed by use of scanning electron microscopy (SEM) and provided the following results:

- (1) Poly(hydantoin) Resistherm PH 10 provided a one-phase system.
- (2) Poly(hydantoin) Resistofol N provided a two-phase morphology with polyhydantoin as the continuous phase and BMI present as spheres with no adhesion between the phases.
- (3) Polyimide (Matrimid 5292) provided a phase inverted morphology with BMI present as nodules; however, there is the indication of good adhesion between the nodules and the continuous phase.

At this point it has to be mentioned that the 'degree of toughening' achieved by a thermoplastic toughener is dependent on the thermo-

Table 5. Neat resin properties of thermoplastic modified Compimide™ 796/Compimide™ 123 (65/35) bismaleimide resin

Property	Control	20 wt% PH 10 ^a	20 wt% RN ^b	20 wt% M 5218 ^c	20 wt% P 1700 (PS) ^d	13 wt% Utem ^e	20 wt% PAE-1 ^f	20 wt% PAE-3
T_g (tan δ) (°C)	316	294	280	284	200	220	159.7	180.3
Flexural properties (RT/dry):								
Strength (MPa)	115	115	118	—	0.5	117	114	124
Modulus (GPa)	3.86	3.65	3.51	3.75	3.49	3.72	3.65	3.65
Elongation	3.05	3.09	3.52	—	2.67	3.35	3.21	3.40
Flexural properties (120°C/dry):								
Strength (MPa)	—	95	94	—	37	97	84	108
Modulus (GPa)	—	2.88	2.89	3.13	1.93	3.02	2.60	3.04
Elongation (%)	—	3.44	3.52	—	2.70	3.38	4.06	4.50
Flexural properties (177°C/dry):								
Strength (MPa)	84	91	78	—	—	45	26	30
Modulus (GPa)	3.27	2.77	2.38	2.64	—	1.71	0.64	0.66
Elongation (%)	2.73	4.52	4.74	—	—	2.99	6.61	> 7.20
Fracture toughness, K_{Ic} (kN m ² × m ^{1/2})	573	822	1322	929	763	805	1521	1235
Fracture energy G_{Ic} (J/m ²)	85	185	498	230	167	174	634	418
Moisture gain (wt%) ^g	2.72	3.01		3.23			2.88	2.77

^aPolyhydantoin (Bayer); ^bpolyhydantoin (Bayer); ^cpolyimide (Ciba-Geigy); ^dpolyethersulphone (UCC); ^eUtem 1000 (General Electric); ^fPAE = poly(arylene ether).

^gMoisture gain was obtained on test specimens after 500 h at 94% relative humidity.
RT, Room temperature.

plastics molecular weight. Usually between 15 and 30% of thermoplastic is used in modified thermoset systems with the aim of maximizing the systems toughness but without sacrificing processability.

Recently, the fracture toughness and morphology spectrum of BMI/PEI moulding compounds have been investigated.²⁷ The BMI system consisted of a commercial BMI resin (Compimide™ 796) and 4,4'-bis(*o*-propenylphenoxy)benzophenone (Compimide™ 123). Due to morphology changes, K_{Ic} (fracture toughness) is lower than expected at PEI contents of 30–40% w/w (Fig. 9). Between 50 and 100% w/w PEI the

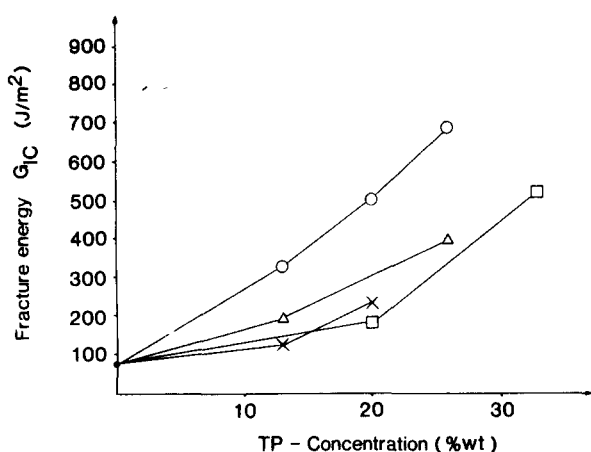


Fig. 8. Fracture energy (G_{Ic}) of thermoplastic modified bismaleimide resin as a function of the thermoplastic polymer concentration. Δ , Ultem 1000; \square , Resistherm PH 10; \circ , Resistafol N; \times , Matrimid 5218.

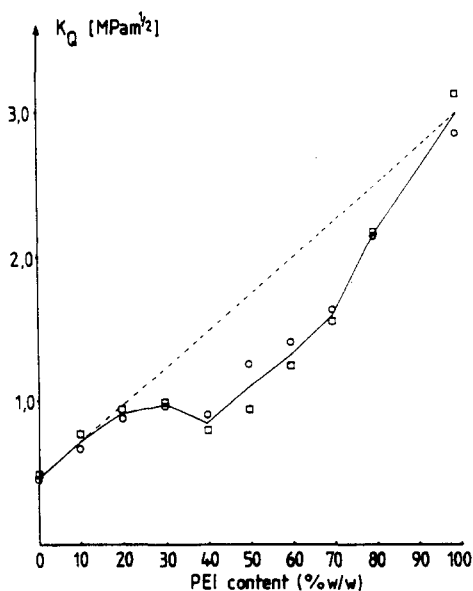


Fig. 9. Fracture toughness (K_{Ic}) spectrum of polyetherimide modified bismaleimide. \circ , MCT; \square , 3 PB specimens.

toughness increases significantly and almost linearly with PEI content; however, all K_{Ic} values for the materials with PEI concentrations above 20% are lower than predicted by the rule of mixtures. Particularly interesting is the fact that the particle size of the separated BMI nodules embedded in the continuous PEI phase decreases with increasing PEI concentration. It has been demonstrated that small nodules of separated particles in a tough continuous phase are required to achieve good composite toughness when such a two-phase resin is used as a composite matrix.²⁸

The most important concern of researchers in this area is that good neat resin toughness, measured by means of K_{Ic} , can be translated into composites toughness measured by CAI (compressive strength after impact). For the BMI/Resistherm PH 10 system it could be shown that improved neat resin toughness translates into improved composite CAI strength²⁹ (Fig. 10).

5 IMPACT RESISTANCE THROUGH INTERLEAFED LAMINATES

The approaches to impact tolerant laminates which have been traditionally followed are the development of high strain fibres and tough resins. Because the weak link in composites is the ply interface, the approach of reinforcing the ply interface through interleaving with a second tough resin or thermoplastic film was developed.³⁰ A thin layer of resin or thermoplastic is added to one side of standard prepreg tape (Fig. 11).

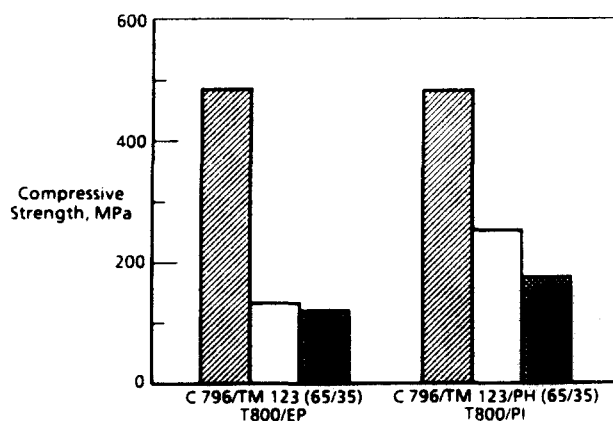


Fig. 10. Post-compression after impact resistance of thermoplastic modified bismaleimide. Impact level: \square , no impact; \square , 3.3 J/mm; \blacksquare , 6.6 J/mm. Test: Boeing specification support standard 7260. Laminate lay up: $[(\pm 45/0/90/0/90)_2 \pm 45/0/90/\pm 45]_3$.

There are two key factors to this approach:

- (i) the interlayer resin used must have a large ultimate strain; and
- (ii) the interlayer must remain a discrete layer after the laminate has been cured.

Interleafing film materials, both thermoset and thermoplastics, are usually 0.0125 mm thick (1/10th of the standard prepreg thickness). The total resin content of the interleaved system is approximately 40% by weight.

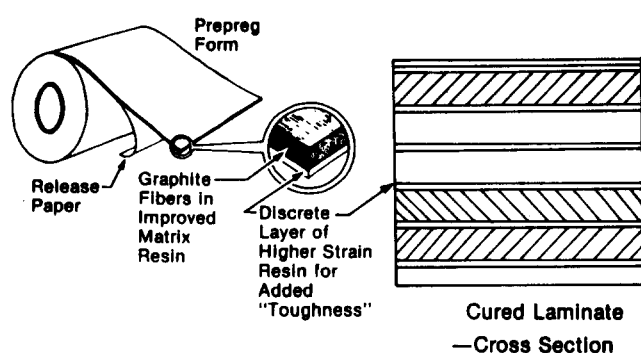


Fig. 11. Interleafed prepreg and cured laminate illustrating retention of discrete layer of tough resin.

Typical toughness and impact tolerance data generated by American Cyanamid on their epoxy and BMI systems on IM-6 fibres are given in Table 6.

In conclusion, interleaving of graphite/thermoset resin prepreg with a thermoplastic film increases the CAI by approximately 80%. Mode I strain energy release rate is only minimally affected, whereas Mode II strain energy release rate is significantly improved. The concept of interleaving brittle prepreg with tough film provides an effective tool for arriving at damage tolerant composites.

6 LIQUID CRYSTAL THERMOSETS

Liquid crystal polymers (LCPs) are recognized as having great potential for the development of new materials which have exceptional physical and mechanical properties. In general, LCPs consist of polymer chains containing structural units (mesogenic groups) which may be incorporated into the polymer backbone, as pendant group or both. It is the objective of various research groups

Table 6. Toughness and CAI data of interleaved epoxy and bismaleimide prepreg

Prepreg	G_{Ic} (kJ/m ²) (in-lb/in ²)	G_{IIc} (kJ/m ²) (in-lb/in ²)	Residual compression strength (MPa) (ksi)
<i>Epoxy matrix</i>			
AS4/1808			
Uninterleafed	0.231(1.32)	1.37(7.84)	220(32.0)
Film A	0.290(1.66)	3.29(18.8)	410(59.6)
Film C	0.222(1.27)	2.87(16.4)	329(47.7)
Film E	0.366(2.09)	3.68(21.0)	326(47.3)
IM6/1808			
Uninterleafed	0.263(1.50)	1.29(7.36)	202(29.3)
Film A	0.329(1.88)	3.37(19.26)	368(53.4)
C6000/1827			
Uninterleafed	0.219(1.25)	1.23(7.0)	218(31.6)
Film E	0.322(1.84)	2.52(14.4)	315(45.7)
AS4/907			
Uninterleafed	0.400(2.29)	2.05(11.7)	276(40.1)
<i>Bismaleimide matrix</i>			
IM6/3100			
Uninterleafed	0.343(1.96) ^a	0.73(4.15)	143(20.7)
Film E	0.635(3.63) ^a	2.42(13.8)	216(31.3)
IM6/3100-21			
Uninterleafed	0.255(1.46) ^a	0.84(4.8)	148(21.5)
Film E	0.380(2.17) ^a	2.00(11.4)	252(36.6)

^aFibre bridging observed in these laminates.

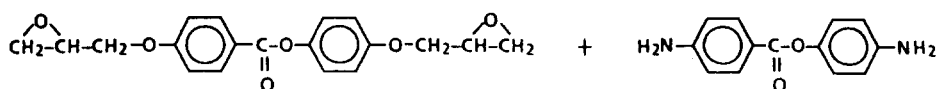


Fig. 12. Chemical structure of liquid crystalline epoxy resin/curing agent system.

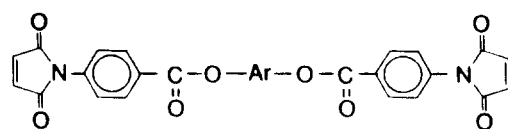
to integrate crystalline behaviour into the field of thermoset polymers. One version of liquid crystal thermoset (LCT) concept involved synthesizing new monomers consisting of a rigid, rod-like central unit, a characteristic of conventional liquid crystals, capped at both ends with well known cross-linking moieties such as epoxy or maleimide. The general concept of LCTs has been addressed in the patent literature but not sufficiently developed to evaluate the full potential of these materials. Very few physical or mechanical properties were reported although it was stated that these materials showed very low shrinkage upon curing.

At the Materials Research Symposium in Hamm, Germany, in 1988³¹ a poster paper reported the synthesis and properties of a liquid crystalline epoxy resin. The chemical structure is provided in Fig. 12, which, when cured while it is in the nematic state (2.5 h 120°C + 16 h 160°C) provides neat resin properties which are superior to resin cured under 'normal' conditions. In particular, the strain to failure and impact strength are dramatically improved.

Recently, the synthesis of a series of maleimide endcapped ester monomers using unsubstituted rigid central groups was reported.³² These compounds are shown in Fig. 13. The materials show very high melting transitions; therefore, melting is immediately followed by cross-linking. If thin films of cross-linked material are observed between crossed polarizers, a nematic texture can be seen which indicates that the liquid crystalline order had been preserved during cross-linking.

7 CONCLUSION

The development of improved high performance composites based on thermosetting polymers can only be achieved by simultaneously improving resin, fibre and interface properties. Significant property improvements with respect to temperature resistance, moisture absorption and moisture resistance, and damage tolerance are made possible by:



Compound	Ar	T _m °C (1)
4		270
5		299
6		287

(1) Melting point determined by DSC

Fig. 13. Chemical structures and properties of ester maleimide monomers.

- using resins, curing agents and comonomers with new backbone chemistries, which provide networks with reduced moisture absorption;
- modification of the thermoset resins with thermoplastics to take advantage of the high toughness of the thermoplastic polymer; and
- incorporating tough thermoset or thermoplastic films in the form of interleaved systems.

A fascinating new area is the development of liquid crystalline thermosets and their use as matrix resins in advanced composites. This technology, however, is in its embryonic phase.

REFERENCES

1. Fast, R. A. & Eckert, C. H., *Int. SAMPE Symp.*, **33** (1988) 369.
2. Stenzenberger, H. D., Herzog, M., Römer, W., Scheiblich, R., Pierce, S. & Canning, M., *Nat. SAMPE Symp.*, **30** (1985) 1568.
3. Stenzenberger, H. D. *et al.*, *Int. SAMPE Tech. Conf.*, **19** (1987) 372.

4. Street, S., *Nat. SAMPE Symp.*, **25** (1980) 366.
5. Bergain, M., Combet, A. & Grosjean, P., *Brit. Pat. Spec.* 1190718, 1970.
6. Stenzenberger, H. D., US Patent 4 211 861, 1980.
7. King, J., Chaudhari, M. & Zahir, S., *Nat. SAMPE Symp.*, **29** (1984) 392.
8. Stenzenberger, H. D., König, P., Römer, W., Pierce, S. & Canning, M., *Nat. SAMPE Symp.*, **29** (1984) 1043.
9. Stenzenberger, H. D., König, P., Herzog, M., Römer, W., Pierce, S. & Canning, M., *Nat. SAMPE Symp.*, **32** (1987) 44.
10. Stenzenberger, H. D., König, P., Herzog, M., Römer, W., Pierce, S. & Canning, M., *Nat. SAMPE Tech. Conf.*, **18** (1986) 500.
11. Bauer, R. S., *Int. SAMPE Symp.*, **31** (1986) 1226.
12. Bauer, R. S., *Int. SAMPE Tech. Conf.*, **18** (1986) 510.
13. Stenzenberger, H. D. & König, P., *High Performance Polymers*, **1** (3) (1989) 239.
14. Loon Seng Tan, Arnold, F. E. & Soloski, E. J., *J. Polymer Sci., Polymer Chem. Ed.*, **26** (1988) 3103.
15. Chaudhari, M. A., Lee, B. & King, J., *Int. SAMPE Symp.*, **32** (1987) 597.
16. Stenzenberger, H. D. & König, P., *High Performance Polymers*, **1** (1989) 133.
17. Stenzenberger, H. D., König, P., Römer, W., Herzog, M. & Breitigam, W., *Int. SAMPE Symp.*, **36** (1991) 1232.
18. Siebert, R., In *Rubber Modified Thermoset Resins*, ed. K. C. Riew & J. K. Gillham. ACS Advances in Chemistry Series 208, American Chemical Society, Washington, DC, 1983, p. 179.
19. Raghava, R. S., *Nat. SAMPE Symp.*, **28** (1983) 267.
20. Bucknall, C. B. & Partridge, I., *Brit. Polym. Journal*, **15** (1983) 71.
21. Sefton, M. S. *et al.*, *Int. SAMPE Tech. Conf.*, **19** (1987) 700.
22. Almen, G., Maskell, R. K., Malhotra, V., Sefton, M. S., McGrail, P. T. & Wilkinson, S. P., *Int. SAMPE Symp.*, **33** (1988) 979.
23. Bauer, R., Stenzenberger, H. D. & Römer, W., *Int. SAMPE Symp.*, **34** (1989) 899.
24. Bauer, R., Stenzenberger, H. D. & Römer, W., *Int. SAMPE Symp.*, **35** (1990).
25. Stenzenberger, H. D., König, P., Herzog, M. & Römer, W., *Int. SAMPE Symp.*, **33** (1988) 1546.
26. Stenzenberger, H. D., In *Proc. 2nd Ann. Int. Conf. on Crosslinked Polymers*, Lucerne, 1988, May 30–June 1, p. 61.
27. Rakutt, D., Fitzer, E. & Stenzenberger, H. D., *High Performance Polymers*, **2** (2) (1990) 133.
28. Rakutt, D., Fitzer, E. & Stenzenberger, H. D., *High Performance Polymers*, **3** (2) (1991) 59.
29. Stenzenberger, H. D., Herzog, M., König, P., Römer, W. & Breitigam, W., *Int. SAMPE Symp.*, **34** (1989) 1877.
30. Masters, J. E., Characterisation of impact damage development in graphite/epoxy laminates. In *Toughened Composites*, ed. N. J. Johnston. ASTM STP 937, American Society for Testing and Materials, Philadelphia, PA, 1987, p. 413.
31. Meier, H. M., Braun, D. & Eigenbach, C. D., BMFT Symposium for Material Research, Proceedings, Hamm, Vol. II, 1988, p. 1529.
32. Hoyt, A. E. & Benicewicz, B. C., *ACS Polym. Preprints*, **30** (2) (1989) 536.