

ADVANCES IN POLYMER SCIENCE

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Crosslinking in Materials Science

Technical Applications

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Crosslinking in Materials Science

With contributions by

B. Ameduri · B. Boutevin · P. Czub · P. Penczek · J. Pielichowski

M. A. Rodríguez-Pérez · A. Taguet



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Unsaturated Polyester Resins: Chemistry and Technology

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Abstract Results of investigations on novel formulations, structure-property relationships, curing, and compositions with fillers and reinforcing fibers (1997–2004) are reviewed with about 200 references to articles and several references to patents. The following topics are considered in particular: novel dibasic acids, glycols, crosslinking monomers, and curing systems, “vinyl ester” resins, fire retardant materials, IPNs and other systems comprising built-in thermoplastic polymers and oligomers with terminal functional groups. Information on unsaturated polyesters manufactured using PET scrap is given. Analytical (mainly spectrometric) methods for studying the chemical structure of crosslinked unsaturated polyester resins are presented. Approaches to the decrease in styrene emission on processing of unsaturated polyester resins are also discussed.

Keywords Unsaturated polyester resins · Reinforced polyesters · Poly(ethylene terephthalate) · Vinyl ester resins · Curing

Abbreviations

ΔH_r	heat released
ρ_v	depolarization ratio
AFM	atomic force microscopy
APP	ammonium polyphosphate
ATH	aluminum trihydroxide $\text{Al}(\text{OH})_3$
BHET	bis(hydroxyethyl)terephthalate
Bis-GMA	2,2-bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]
BMC	bulk molding compounds
BMI	bismaleimide
CDRE	convulsion difference resolution enhancement
CMDB	composite modified double-base
CoHx	cobalt hexanoate
CoNp	cobalt naphthenate
CP/MAS	magic angle spinning
CPD	cyclopentadiene
CTBN	carboxyl terminated poly(butadiene-co-acrylonitrile)
DAD	diode array detection
DCPD	dicyclopentadiene
DD	dipolar decoupling
DEF	diethyl fumarate
DEPT	distortionless enhancement by polarization transfer

DGEBA	diglycidyl ether of bisphenol A
DKGA	diketogulonic acid
DLS	dynamic light scattering
DMA	dynamic mechanical analysis
DMB	2,5-dimethyl-2,5-bis(2-ethylhexanoylperoxy)hexane
DMC	dough molding compounds
DSC	differential scanning calorimetry
DTA	differential thermal analysis
E'	storage modulus
E''	loss modulus
E_a	activation energy
EMTHPA	endomethylene tetrahydrophthalic anhydride
ESR	electron spin resonance spectroscopy
FID	free induction decay
FT-IR	Fourier transform infrared spectroscopy
FUPR	fluorine-modified unsaturated polyester resin
GC/FT-IR	gas chromatography-Fourier transform infrared spectroscopy
GC/MS	gas chromatography-mass spectrometry
G_{IC}	fracture energy
GPC	gel permeation chromatography
GPC-MALLS	multiangle laser light scattering detector
HDT	heat deflection temperature
HPLC	high-performance liquid chromatography
HPN	hybrid polymer network
IPN	interpenetrating polymer network
iTBN	maleimide terminated liquid butadiene-acrylonitrile rubber
k_0	frequency factor
LLCT	lyotropic liquid-crystalline thermoset
LOI	limiting oxygen index
LOM	laminated object manufacturing
LPA	low profile additives
LRP-NMR	low-resolution pulse ^1H -NMR
LSA	low shrink additives
LSE	low styrene emission
\overline{M}_n	number-average molecular weight
\overline{M}_w	weight-average molecular weight
MDI	methylene diphenyl diisocyanate
MEKP	methylethylketone peroxide
MI	maleimides
MMT	montmorillonite
MPD	2-methyl-1,3-propane diol
MTDSC	modulated temperature differential scanning calorimetry
MTGA	modulated thermogravimetric analysis
NBR	acrylonitrile-butadiene rubber
NPI	Novolac-type polyisocyanate
PB	pentabromoethylbenzene
PCL	poly(ϵ -caprolactone)
PD	1,2-propanediol
PDO	<i>tert</i> -butylperoxy-2-ethyl hexanoate
PET	poly(ethylene terephthalate)

PFPE	perfluoropolyether
phr	weight parts of additive per 100 parts by weight of resin
PPF	poly(propylene fumarate)s
PTSA	<i>p</i> -toluenesulfonic acid monohydrate
PU	polyurethane
PVAc	poly(vinyl acetate)
Py-GC	pyrolysis-gas chromatography
RDA	rheometric dynamic analyzer
RO	rapeseed oil
RTM	resin transfer molding
S	antimony trioxide, Sb ₂ O ₃
SBR	styrene-butadiene rubber
SCRIMP	Seemann composites resin infusion molding process
SIN	semi-interpenetrating polymer network
SLS	static light scattering
SMC	sheet molding compounds
TTT	time-temperature-transformation
SPE	solid-phase extraction
T_1^H	proton spin-lattice relaxation time
$T_{1\rho}^H$	spin-lattice relaxation time in the rotating frame
T_2	spin-spin relaxation time
T_g	glass transition temperature
$\tan \delta$	loss tangent
TCTFE	1,1,2-trichloro-1,2,2-trifluoroethane
TDI	toluene diisocyanate
TEM	transmission electron microscopy
TFA	trifluoroacetic acid
TGA	thermogravimetric analysis
TMS	tetramethylsilane
TSR	thermal scanning rheometry
TX/PCL	fluorinated macromers/poly(ϵ -caprolactone)
TXCL	poly(ϵ -caprolactone)-perfluoropolyether-poly(ϵ -caprolactone) <i>block</i> copolymer
UP	unsaturated polyesters
UPR	unsaturated polyester resin
VARTM	vacuum-assisted resin transfer molding
VE	vinyl ether
VEUH	vinyl-ester-urethane hybrid
VER	vinyl ester resin
VTBN	vinyl terminated poly(butadiene- <i>co</i> -acrylonitrile)
x	order of reaction
ZSA	zero shrink additive

1

Introduction

Unsaturated polyester resins (UPRs) have been known for many years. The production of UPRs started in the 1930s. Recently, their manufacture has reached a peak level. UPRs are, along with polyurethanes, the most important crosslinkable polymeric materials. The importance of UPRs is due to their important fields of application, mainly in glass fiber reinforced plastics. The rapid increase in the share of UPRs in the plastics market, comprising also highly filled materials, coatings, and cast objects etc., is due to their simple processing.

The chemistry of UPRs involves the synthesis of unsaturated polyesters (UPs) by polyesterification or step-by step ionic copolymerization. The thus synthesized UP is then dissolved in an unsaturated monomer and crosslinked applying the radical polymerization approach. Thus, the chemistry of UPRs involves the polycondensation or ionic polymerization methods and crosslinking by peroxide or photochemically initiated radical polymerization.

Thanks to the various types of chemical reactions being applied in the manufacture and processing of UPRs and to the versatility of industrial applications, the progress of research and development in UPRs is very fast. The industrial progress in UPRs is accompanied by intense research, design and processing activities making the UPR industry an important component of polymeric materials science and technology.

2

Major Raw Materials

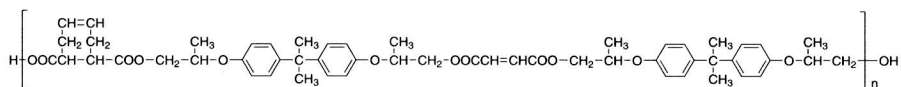
A classification of methods for the synthesis of unsaturated polyesters on the basis of conceptions of condensation and polycondensation as well as addition and polyaddition has been proposed [1]. The presented methods were characterized taking into account a regularity of the distribution of unsaturated bonds and the appearance of side reactions. A model to estimate the average number of chain branches and of chain ends of UP prepolymers has also been proposed [2]. Fundamental molecular parameters, i.e. hydroxyl and carboxyl values, Ordelt saturation (reaction of hydroxyl groups with double bonds) extent, mass polydispersity index, short- and long-chain branch distribution, and composition of starting reactants were included in the proposed model. The real molar mass, especially the molecular mass of the linear backbone chain, as well as the carboxyl and hydroxyl functionalities of UP prepolymers [3] could be estimated using the described model. The obtained results should be very useful for developing UP sheet-molding compounds (SMC) thickening technology.

2.1

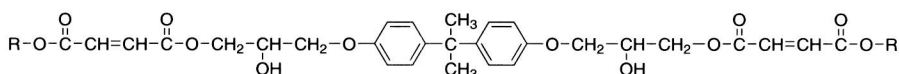
Dicarboxylic Acids and Acid Anhydrides

The introduction of dicarboxylic acids or acid anhydrides with cycloalkene configuration into the polyester chain results in an increase in impact strength, chemical resistance and resistance against UV light as well as a decrease in refractive index and surface tackiness. UP resins were prepared (Scheme 1) from *cis*-4-cyclohexene dicarboxylic anhydride (tetrahydrophthalic anhydride), diethylene glycol, propylene glycol and 2,2-di(4-hydroxypropoxyphenyl)propane [4]. An improvement of mechanical properties, shortening of drying time of the casting surface, lowering of refractive index, more than twofold decrease in water absorption as well as a considerable increase in the Martens temperature of cured UPRs were observed when phthalic anhydride was replaced with tetrahydrophthalic anhydride. Next, partial substitution of maleic anhydride (Table 1) with an eutectic mixture of anhydrides of cyclic non-aromatic dicarboxylic acids (hexahydrophthalic anhydrides and three isomeric tetrahydrophthalic anhydrides) was studied [5]. Crosslinked UPRs prepared from the mixture of acid anhydrides were characterized by improved mechanical properties (Table 2) and considerable resistance to sunlight, particularly in regard to the impact strength and heat resistance. Epoxyfumarates formed by the addition of acrylic or methacrylic acid or acid esters of maleic or fumaric acid to epoxy resins (Scheme 2) are an important group of chemically resistant resins, sharing advantages of UPRs and epoxy resins [6]. The synthesis consists of the following stages:

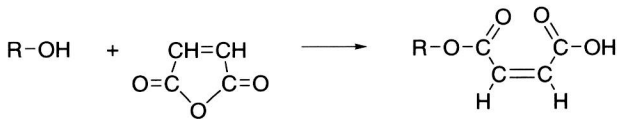
- addition of an alcohol to maleic anhydride to form an alkyl hydrogen maleate/fumarate;
- addition of the thus obtained acid maleate (hydrogen maleate) to the liquid epoxy resin;
- catalytic *cis-trans* isomerization of the thus obtained addition product (the maleate) to form the corresponding fumarate;
- dissolution in styrene of the thus obtained fumarate followed by peroxide-initiated radical copolymerization (crosslinking).



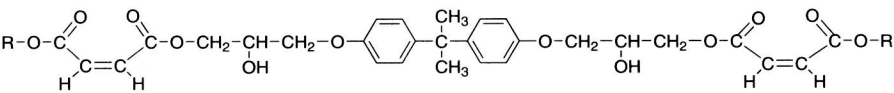
Scheme 1



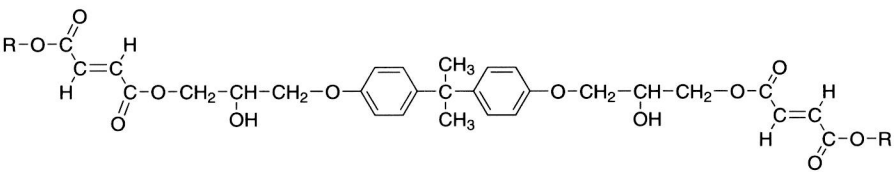
Scheme 2



Scheme 3



Scheme 4



Scheme 5

Table 1 Composition of the studied UPRs. Reprinted from (1995) Polimery 40:669 [5] with permission

Resin	Mixture of anhydrides	Maleic anhydride	Components [mol]			
			Diethylene glycol	Propylene glycol	Glycerol	Xylene
1	1	1	2.1	–	–	0.072
2	1	1	–	2.1	–	–
3	1	1	–	2.0	0.07	–

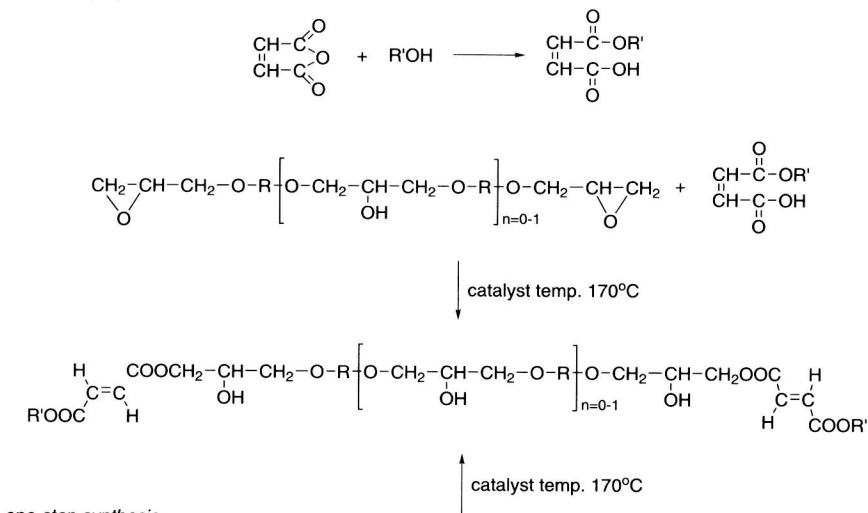
Table 2 Properties of cured UPRs prepared from a mixture of acid anhydrides (according to Table 1) and commercial reference resin. Reprinted from (1995) Polimery 40:669 [5] with permission

	Resin			Polimal 103
	1	2	3	
Flexural strength [MPa]	67	69	72	60
Compression strength [MPa]	190	82	102	102
Static stress at break [MPa]	32	35	26	20
Impact strength [kJ/m ²]	9.6	3.4	4.0	2.3
Heat deformation temperature (Martens) [°C]	58	75	76	55
Water absorption [%]	0.34	0.2	0.1	0.3
Hardness [MPa]	85	147	160	103

Similar to the vinyl ester resins, the cured epoxyfumarate resins are distinguished by enhanced chemical resistance (e.g. in aqueous 20% NaOH at 60 °C), heat deflection temperature and flexibility. The chemical composition of the *R* group (methyl, ethyl, *n*-butyl, benzyl, cyclohexyl) influences the properties of the crosslinked epoxyfumarate resins [6]. If the *R* group contains bromine (e.g. tribromoneopentyl or 2,3-dibromopropyl), the cured resins are fire retardant [7]. Moreover, the brominated resins are distinguished by increased Martens heat deformation temperature and low water absorption.

To further increase the crosslinking density and thus the Martens heat deformation temperature, an allyl group was built into the molecule of epoxyfumarate resin (Scheme 6) [8]. A Martens heat deformation temperature exceeding 100 °C could be reached.

two-step synthesis



one-step synthesis

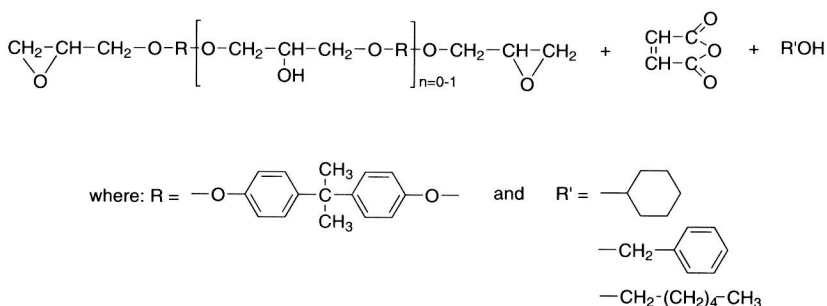


Fig. 1 One- and two-step syntheses of the studied epoxyfumarate resins. Reprinted from (2000) J Appl Polym Sci 77:3077 [11] with permission