Macromol. Symp. ***187****, 243–247 (2002)*

Epoxypolyesters as Film-Forming Materials

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Summary: A series of solid epoxypolyesters were prepared by the condensation of glycols, 1,2,3,6-tetrahydrophthalic anhydride and dicyclopentadiene followed by the epoxidation of the double bonds in the unsaturated polyester. The polyesters were characterized and then subjected to photoinitiated cationic polymerization using triarylsulfonium salt as the photoinitiator. It was demonstrated that the coatings prepared from these epoxypolyesters exhibited good hardness, impact strength and degree of drying. The straightforward synthesis and high reactivity in cationic UV curing make these epoxypolyesters attractive as film forming materials.

Keywords: unsaturated polyesters; epoxidation; epoxypolyesters; UV-curing; epoxypolyester film

Introduction

Epoxy resins based on bisphenol A[1-3] are the most important thermosetting polymeric materials. They have many excellent properties, such as high thermal stability, adhesion, mechanical and electrical properties and they are widely utilised in the field of coatings. However, it is well known that the commonly used epoxy resins are not resistant to UV light. The poor UV resistance of epoxy resins based on bisphenol A greatly limits their use as components of coatings for exterior applications.[4] Lots of efforts have been made to improve the UV resistance of the cured epoxy resins. One of the possible approaches consists in using epoxypolyesters that contain epoxy groups along and at the ends of the molecular chains.

This paper reports the synthesis and properties of a series of dicyclopentadiene modified epoxypolyesters, which were synthesised by epoxidation of double bonds in solid unsaturated polyesters.

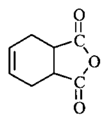
The cationic photopolymerization and the mechanical properties of photocured epoxypolyester films were examined.

 CCC 1022-1360/00/$ 17.50+.50/0

Synthesis of unsaturated polyesters

For the synthesis of solid unsaturated polyesters following materials were used: 1,2,3,6-tetrahydrophthalic anhydride (THPA, **1**), neopentyl glycol (NPG, **2**), 1,4-butanediol (BD, **3**), ethylene glycol (EG, **4**) and 4-cyclohexene-1,2-dimethanol (CHDM, **5**). For the purpose of increasing the crosslinking density, terminal dihydrodicyclopentadienyl ester groups were inserted into polyester chains by an addition of dicyclopentadiene (DCPD, **6**) to the carboxylic groups in the polyester.

The polyesters were obtained by two-step reaction (Scheme 1). Optimum content of DCPD in polyester composition (6% w/w) was settled referring to the analysis of properties of polyesters based on THPA, NPG and DCPD. The properties of polyesters are given in Table 1.



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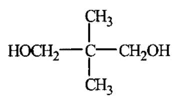

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$HOCH_2-CH_2-CH_2-CH_2OH$

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$HOCH_2-CH_2OH$

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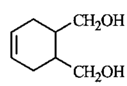

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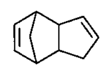

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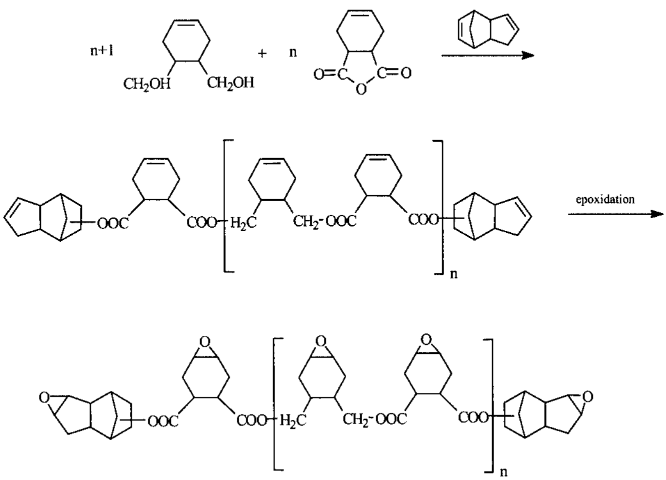

Scheme 1

The optimum properties: the highest softening point (102°C), high iodine number (83 g I_2/100g) and additional double bond derived from the cyclohexene ring were reached with the product that contained CHDM as a glycol component of the polyester (Table 1).

Table 1. Properties of unsaturated polyesters made of THPA, DCPD and various glycols

No.	Composition			Properties		
	THPA	Glycol	DCPD (6%)	AN	IN	SP
1	+	NPG	+	7.6	101	82
2	+	BD	+	4.0	90	83
3	+	EG	+	2.4	100	73
4	+	CHDM	+	3.9	83	102

AN, acid number (mg KOH/g)
IN, iodine number (g I_2/100g)
SP, softening point determined by the "ring and ball" method (°C)

Epoxidation of double bonds in unsaturated polyesters

Unsaturated polyesters were epoxidized with the following reagents: aqueous solution of peracetic acid[5,6] (PAA), a solution of PAA in organic solvents (ethyl acetate or dichloromethane) and m-chloroperoxybenzoic acid (MCPBA) (Table 2, 3).

Table 2. Epoxy numbers (mol/100g) of epoxypolyesters epoxidized with vario-us epoxidation agents

Epoxidation agent		A	B	C	D
Unsaturated polyester (Table 1) No.	1	0.33	0.06	0.07	0.17
	2	0.21	0.07	0.08	-
	3	0.21	0.05	-	0.21
	4	0.26	0.04	0.05	0.19

A: aqueous solution of PAA
B: solution of PAA in ethyl acetate
C: solution of PAA in dichloromethane
D: m-chloroperoxybenzoic acid

The highest yield was obtained from the reaction of polyesters with aqueous solution of PAA, which was prepared directly before epoxidation. PAA was obtained by the reaction of acetic acid with 60% aqueous solution of H_2O_2 in the presence of sulfuric acid, buffer salt (sodium acetate) and stabiliser (sodium polyphosphate).[6]

Table 3. Efficiency (%)* of epoxidation of unsaturated polyesters

Epoxidation agent		A	B	C	D
Unsaturated polyester (Table 1) No.	1	67	19	21	50
	2	60	19	23	-
	3	54	14	-	55
	4	79	12	14	57

Efficiency of epoxidation was calculated referring to theoretical epoxy number, which is equal to iodine number given in mole I_2/100g.

Curing of epoxypolyesters

Epoxypolyesters (No. 1A and 4A) were chosen to UV curing because of the highest content of epoxy groups and the high efficiency of epoxidation of initial polyesters.

Solid epoxypolyesters with 0.5% cationic photoinitiator (50% solution of triarylsulfonium hexafluorophosphate **7** in propylene carbonate) were dissolved in a volatile solvent, spread on a glass plate and UV irradiated after evaporating of the solvent. The crosslinked films were smooth and of uniform gloss. They exhibited high surface hardness, good impact resistance and high degree of drying. Properties of the epoxypolyester films and obligatory standards for cured lacquer films are presented in Table 4.

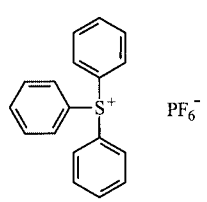

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Table 4. Properties of solid epoxypolyester films in comparison to obligatory standards for cured coating films

Parameter	No. of film		Requested value	Obligatory standard
	1a	4a		
Degree of drying	6	7	min. 7	PN-79/C-81519, corresponding to DIN 53150-71
Impact resistance (Du Pont, cm)	45	50	min. 50	PN-54/C-81526, corresponding to ISO 6272:1999
Surface hardness	0.5	0.7	min. 0.5	PN-79/C-81530, corresponding to ISO 2815:2000

Conclusions

Four epoxypolyesters containing DCPD as terminal groups were synthesized and used as film forming materials. The mechanical properties of the cationic UV cured films were investigated. From the experimental results, following conclusions were drawn:

1. Epoxidation of double bonds in unsaturated polyesters with aqueous solution of peracetic acid was found to be the most effective method of preparing of epoxypolyesters.
2. The epoxypolyesters can be used as a solid film forming material while crosslinked by cationic photopolymerization. The film properties conform with obligatory standards for cured coating films.

Acknowledgements

The authors are grateful to the Polish Committee of Scientific Research for the support of this work (grant No. 3 T09B 086 16).

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