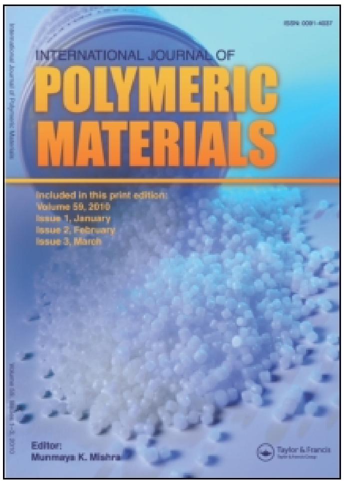


International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Unsaturated Polyurethane Resin Based on Resorcinol

Jitendra M. Patel[a]; Jatin R. Thakkar[a]; Ravji D. Patel[a]
[a] Department of Chemistry, Sardar Patel University, Vallabh Vidya Nagar, Gujarat

To cite this Article Patel, Jitendra M. , Thakkar, Jatin R. and Patel, Ravji D.(1998) 'Unsaturated Polyurethane Resin Based on Resorcinol', International Journal of Polymeric Materials, 39: 1, 73 — 78

To link to this Article: DOI: 10.1080/00914039808041036

URL: http://dx.doi.org/10.1080/00914039808041036

Intern. J. Polymeric Mater., 1998, Vol. 39, pp. 73–78
Reprints available directly from the publisher
Photocopying permitted by license only

Unsaturated Polyurethane Resin Based on Resorcinol

JITENDRA M. PATEL, JATIN R. THAKKAR and RAVJI D. PATEL

*Department of Chemistry, Sardar Patel University,
Vallabh Vidya Nagar 388 120, Gujarat, India*

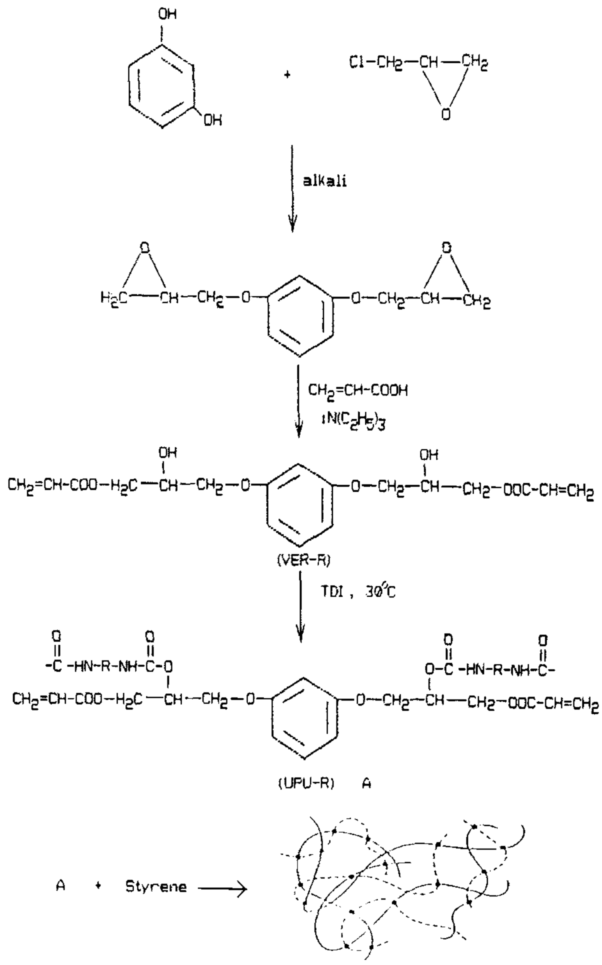
(Received 17 November 1996)

Diglycidyl ether of 1,3-benzenediol (DGER) was prepared and characterized. Vinylester resin of DGER (VER-R) was prepared by the reaction between DGER and acrylic acid. The resin was characterized by their viscosity, number average molecular weight and infra-red spectrophotometry. The polyurethane was prepared by the condensation of VER-R and toluene diisocyanate and characterized. The resultant polyurethane containing two vinyl group was copolymerized with styrene vinyl monomer by varying the proportion of styrene. The properties of resulting materials relative to coating applications were established.

Keywords: Vinylester resin; viscosity; number average molecular weight; polyurethane; coating

INTRODUCTION

Recent reviews on vinylester resins based on diglycidyl ether of bisphenol-A (DGEBA) suggest that they are becoming increasingly important in new industrial applications such as metal foil laminates, automotive parts, fiber reinforced composites and coatings [1–8]. This has given rise to a widespread research interest in developing vinylester resins and improving their properties for various applications [9–11]. Considering the excellent applications of such vinylesters, the present authors decided to develop novel vinylester resins containing urethane group. Hence the present communication containing synthesis characterization and copolymerization of vinylester resin (VER-R). The synthesis is outlined in Scheme 1.



SCHEME 1

RESULTS AND DISCUSSION

The number average molecular weights determined by vapor pressure osmometry were about 380 and 556 for VER-R and UPU-R respectively, while the intrinsic viscosity in chloroform measured by a capillary viscometry at 30°C were found to be 0.04 $\mathrm{dl\,g^{-1}}$ and 0.046 $\mathrm{dl\,g^{-1}}$ respectively for VER-R and UPU-R.

The acid value and iodine value of VER-R were about 0.25 and 25.0 respectively, while the percentage free isocyanate value [13] for UPU-R was found to be 0.13.

Both the resins, VER-R and UPU-R are soluble in common organic solvents such as acetone, chloroform, dioxane, carbon tetrachloride, tetrahydrofuran and N, N-dimethyl formamide.

Infra-red Study

The following characteristic frequencies of VER-R should be noted; at 3550 cm^{-1} (due to hydroxyl group), 1720 cm^{-1} (due to ester group) and 1630 cm^{-1} (due to double bond of the vinyl group). By comparing the IR spectra of UPU-R and VER-R, the major change observed is that the band observed due to the hydroxyl group at 3550 cm^{-1} in VER-R vanishes in UPU-R, with the appearance of new bands around 3340 cm^{-1} due to the N—H stretching vibration. The N—H deformation vibration is also observed at 1530 cm^{-1}, indicating the presence of N—H linkage in the resins. The data are given in the Table I.

DSC KINETIC STUDY

The dynamic scans for the formulations described in Table II were analyzed to obtain the various characteristic temperatures [14] such as temperature T_i of initiation, peak exotherm temperature T_p and temperature T_f at which the curing is complete for the curing reactions. It is evident from the Table II that values of T_i and T_f for

TABLE I Some important IR spectral data for VER-R and UPU-R

Probable Assignment	*VER-R (in cm^{-1})*	*UPU-R (in cm^{-1})*
Bond O—H stretching	3680–3100 (br)	–
—C=O stretching	1720	1720
—C=C— stretching	1630 (sh)	1625 (sh)
—C=C—H in plane C—H bending RCH=CH$_2$	1420	1420
—C—O—C— sym. stretching (arylether)	1080	1080
C—H bending 1, 3-disubstituted benzene derivative	760	760
N—H stretching	–	3340
N—H deformation	–	1530

TABLE II Curing characteristics and kinetic parameters for curing of VER-R and UPU-R resin using peroxide (1% by weight) as catalyst

Resin Sytem	*Styrene Content (% by wt)*	T_i *(°C)*	T_p *(°C)*	T_f *(°C)*	E_a *(± 2 KJ mole^{-1})*	*Order of Reaction n*
VER-R*	–	103	144	177	84.2	1.11
VER-R	20	90	128	161	73.8	1.09
VER-R	40	85	117	151	68.5	1.09
UPU-R**	–	93	118	155	79.1	1.05
UPU-R	20	88	107	149	68.8	1.01
UPU-R	40	76	102	133	61.9	0.97

VER-R* = Vinyl ester resin based on resorcinol.
UPU-R*** = Unsaturated polyurethane resin based on resorcinol.

VER-R and UPU-R, the faster curing rate of the urethanized resins may be due to catalytic acceleration by tertiary and secondary amino groups present in the urethane derivatives. The incorporation of styrene in this resin system prior to curing lowers the curing temperature.

Data analysis for the activation energy and order of reaction were carried out by the methods reported in the literature [14, 15]. All the reaction followed the simple n^{th} order type Arrhenius kinetics, having orders of reaction of about unity.

THERMAL STUDY

The nature of TGA curves of both resins is similar. However, the decomposition temperature varied with the resin system. On the basis of the values of T_{max}, the temperature at which maximum decomposition occured, the trend of thermal stability was to be VER-R (370°C) > UPU-R (350°C). The diminished thermal stability of urethanized derivative of acrylated resin is due to the flexible urethane linkages between the crosslinking sites, resulting in lower degree of crosslinking than found in the acrylated resin.

The glass transition temperature T_g decreases on the incorporation of styrene into the resin system. However, a single glass transition temperature was observed for each system, indicating a very good miscibility of styrene [16].

EXPERIMENTAL

Material

All the chemicals were of laboratory grade.

1) Synthesis of vinylester resin based on resorcinol (VER-R)
The vinylester resin of resorcinol was synthesized by the method reported in the literature [10] (Scheme 1)
2) Synthesis of unsaturated polyurethane resin based on resorcinol (UPU-R)
This was prepared by condensation of equimolar proportion of VER-R and toluene diisocyanate. To a well stirred solution of VER-R (0.01 mole) in dimethyl formamide solvent. Toluene diisocyanate was added at 0°C. The resultant resin was washed by ether several times.

Characterization of Resins

IR spectra were recored on a Perkin Elmer IR 983 spectrophotometer using KBr cell. DSC scans were recored on DuPont 9900 thermal analyzer connected to a DuPont 910 differential scanning calorimeter module was used to measure heat flow as a function of temperature. TGA analysis of both the resins was carried out by DuPont Model 951 thermal analyzer at heating rate 10°C/min.

References

[1] Matsushita Electric Works Ltd, Japan Kokai Tokkyo Koho, JP 85, 21243, *Chem. Abstr.*, **103**, 38307p (1986).

[2] Kitazawa, S. and Yasuda, T. (1986). Japan Kokai Tokkyo Koho, JP 86, 91212, *Chem. Abstr.*, **105**, 192282z.

[3] Buist, J. M. and Gudgeon, H. (1968). 'Advances in Polyurethane Technology', New York.

[4] Damusis, A. and Frisch, K. C. (1967). in 'Film Forming Compositions', ed., Myers, R. R. and Long, J. S. Dekker, New York, Part I.

[5] Saunders, J. H. and Frisch, K. C. (1964). 'Polyurethanes', Wiley, New York, Part II, Chap X.

[6] Chang, W., Scriven, R., Pfeffer, J. and Porter, S. (1973). *Ind. Eng. Chem. Prod. Res. Dev.*, **12**(4) 278.

[7] Thomas, E. D., Fekete, F., Patrik, J. K. and William, J. P. US. Patent 3, 317, 465; *Chem. Abstr.*, **67**, 120969.

[8] Balestic, F., Box, G. and Maradon, Y. (1975). Fr 2, 209, 939. *Chem. Abstr.*, **75**, 37490j.

[9] Matsushita Electric Works Ltd, Japan Kokai Tokkyo Koho, JP 84, 71303, *Chem. Abstr.*, **101**, 131876s.

[10] Takashi, H. (1977). Japan Kokai Tokkyo Koho, JP 77, 00509, *Chem. Abstr.*, **87**, 109445w.