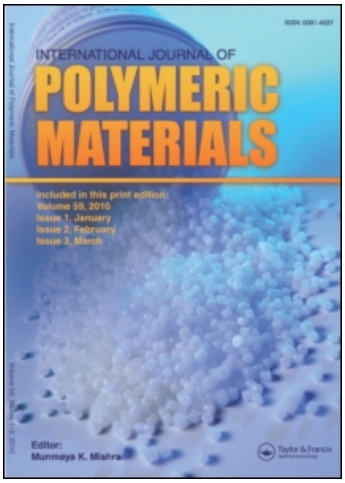

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Novel Unsaturated Polyurethane Coatings from Vinylester Resin Based on Hydroquinone

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

To cite this Article Patel, Jitendra M. , Thakkar, Jatin R. and Patel, Ravji D.(1997) 'Novel Unsaturated Polyurethane Coatings from Vinylester Resin Based on Hydroquinone', International Journal of Polymeric Materials, 38: 3, 291 — 296
To link to this Article: DOI: 10.1080/00914039708041024
URL: http://dx.doi.org/10.1080/00914039708041024

Intern. J. Polymeric Mater., 1997, Vol. 38, pp. 291–296
Reprints available directly from the publisher
Photocopying permitted by license only

Novel Unsaturated Polyurethane Coatings from Vinylester Resin Based on Hydroquinone

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

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

(Received 6 February 1997)

Vinylester resin of *p*-dihydroxybenzene (VER-HQ) was prepared by the reaction between diglycidyl ether of hydroquinone and acrylic acid. Novel unsaturated polyurethane resin (UPU-HQ) from (VER-HQ) was synthesized by reacting VER-HQ with Toluene diisocyanate. The polyurethane resin (UPU-HQ) was coated on mild steel panels. The coated panels were tested for their impact strength, flexibility scratch hardness and chemical resistancy. The addition of vinyl monomer viz., styrene in the resin systems impacts the properties of coatings remarkably.

Keywords: Coatings; polyurethanes; vinylester resins; hydroquinone

INTRODUCTION

The Novel vinylester resins are becoming increasingly important in new industrial applications [1–4]. Considering excellent performance of vinylesters, the present authors decided to develop novel vinylester resins containing urethane groups. Current markets make various demands on technical performance, and different qualities and colours are required. It was expected that the new coatings may meet some of these demands.

RESULTS AND DISCUSSION

Novel polyurethane resin (UPU-HQ) is soluble in common organic solvents such as acetone, chloroform, carbon tetrachloride, dioxane

and N,N'-dimethyl formamide etc. The number average molecular weight ($\overline{Mn}$) of the resins estimated by vapour pressure osmometry is reported in Table I.

The intrinsic viscosity of UPU-HQ measured by a capillary viscometry at 30°C using chloroform as solvent is listed in Table I. The percentage free isocyanate values [5] of UPU-HQ given in Table I.

IR Spectral Study

The IR spectrum of VER-HQ comprises the bands 3555 cm^{-1}, 1720 cm^{-1} and 1630 cm^{-1} due to hydroxyl group, ester group and double bond of vinyl group respectively. Comparing the IR spectrum of VER-HQ and UPU-HQ, we note the absence of band in UPU-HQ due to the hydroxyl group at 3555 cm^{-1} which is present in VER-HQ, with the appearance of new bands around 3340 cm^{-1} due to the N-H stretching vibration. The band around 1530 cm^{-1} may be assigned to N-H deformation vibration, indicating the presence of N-H linkage in the UPU-HQ resin.

DSC Curing Kinetics

An understanding of the curing reaction is very important to control the curing process for the end use of the resin system. In order to study the curing kinetics, the exothermic transition observed in dynamic scans

TABLE I Curing characteristics and kinetic parameters for curing of Novel unsaturated polyurethane resin based on hydroquinone (UPU-HQ)

Resin System	*Styrene Content (% by wt)*	T_i *(°C)*	T_p *(°C)*	T_f *(°C)*	E_a *(± 2 KJ mole^{-1})*	*Order of Reaction n*
UPU-HQ	–	95	119	156	79.0	1.03
UPU-HQ	10	92	113	153	74.3	1.02
UPU-HQ	20	89	108	150	69.2	1.02
UPU-HQ	30	85	105	142	63.6	0.99
UPU-HQ*	–	94	116	148	76.0	1.01
UPU-HQ*	10	91	109	143	71.8	0.99
UPU-HQ*	20	86	104	140	67.7	0.98
UPU-HQ*	30	85	101	136	61.9	0.96

Viscosity of the UPU-HQ resin is 0.047 dlg^{-1}.
%Isocyanate value of the UPU-HQ resin is 0.15.
UPU-HQ* = Addition of N,N'-dimethyl aniline as promoter to the system.

for the formation were analysed to obtain the characteristic temperatures like T_i (initiation temperature), T_p (peak exotherm temperature) and T_f (Temperature at which the curing is completed). The values of T_i and T_f for both the resins (Tab. II) indicated faster curing rate for the UPU-HQ resin. This may be due to catalytic acceleration by secondary and tertiary amino group present in this resin. The incorporation of styrene (Tab. I) into the resin system prior to curing lowers the curing temperature.

The values of activation energy and order of reaction were evaluated by the methods reported in literature [6, 7]. All the reactions followed n^{th} order type Arhenius Kinetics, with the order of reaction of about unity.

Thermogravimetric Analysis

The thermal stability of VER-HQ and UPU-HQ was investigated by thermogravimetry. The nature of the TGA curve was observed to be similar. However, the decomposition temperature varied with the resin system. On the basis of the temperature (T_{max}) at which maximum decomposition occured. the trend of thermal stability was to be VER-HQ (385°C) > UPU-HQ (360°C). The diminished thermal stability of UPU-HQ compared to VER-HQ is due to the presence of flexible urethane linkages between crosslinking sites, resulting in lower degree of crosslinking than in VER-HQ.

Incorporation of styrene into the resin system lowers the glass transition temperature T_g. The observation of a single glass transition temperature for each systems indicates the very good miscibility of

TABLE II Flexibility, impact strength and scratch hardness of the novel unsaturated polyurethane resin based on hydroquinone (UPU-HQ)

Resin	*Styrene Content (% by wt)*	*Flexibility*	*Impact Strength*	*Scratch hardness (gm)*
UPU-HQ	–	Pass	220	1150
UPU-HQ	10	Pass	240	1330
UPU-HQ	20	Pass	265	1480
UPU-HQ	30	Pass	280	1570
UPU-HQ	40	Pass	305	1710

styrene [8]. On incorporation of N,N'-dimethyl aniline (0.1% w/w) as a promoter for curing reaction becomes more rapid.

Flexibility and Adhesion

All resin systems passed flexibility test on 1/4" and 1/8" conical mandrel, which is expected of vinyl ester and urethane based coatings. All the coated mild steel panels passed stripping test for adhesion. These might be due to free hydroxyl group in vinyl ester and isocyanate group in polyurethane which contribute in the strong metallic bond formation with the surface of mild steel panels.

Scratch Hardness and Impact Resistance

The results of testing furnished in Table I reflect that UPU-HQ yields coatings with better scratch hardness and impact strength. In the reaction of VER-HQ with toluene diisocyanate, the urethane linkages are formed. The formation of urethane linkages improves the toughness of the coatings which may be attributed to the higher scratch hardness and impact strength of UPU-HQ. The values of scratch hardness and impact strength observed in VER-HQ resin systems may be responsible for the unsaturation present in the resin structure.

The incorporation of styrene in both the VER-HQ and UPU-HQ should improve their properties as it may increase the toughness of the resin system.

Water and Solvent Resistance

In case of water resistance, coatings based on all the resin systems shows no blistering or change in colour for the times listed in Table I. The panels immersed for 72 hours in solvent, showed no cracking, blistering or change in colour which indicates that all the systems have excellent solvent resistancy.

Acid and Alkali Resistance

The coated panels immersed in 2% acid and 2% alkali solution for 72 hours shows remained unaffected upto 48 hours. At times >48 hours

possibilities of change in colour were noted. These observations reveal that on exposure of the coated panels to 2% NaOH and 2% H_2SO_4, no substantial loss in gloss or change in appearance takes place indicating excellent adhesion as well as good resistance to acid, alkali and organic solvents.

EXPERIMENTAL

Materials

All the chemicals used were of laboratory grade.

Synthesis of Resins

The unsaturated polyurethane resin (UPU-HQ) was prepared by the method described in our earlier communication [9–12].

Preparation of Coating Compositions

Various coating compositions were prepared using thinner, methyl cellosolve solvent and were made free from coarse skin by passing the solutions through a sieve, 150 μm [IS:460–1960]. The composition were applied on mild steel panel using flat brush (IS:384–1964). The coated panels were kept vertically for fast drying. After a specified time, the coated panels were examined for tack free test and then cured tharmally.

Measurements

All the coated panels were tested for flexibility, scratch hardness, impact strength and chemical resistance by following ASTM standard test. The scratch hardness of the film was measured using mechanically operated scheen Scratch Hardness Tester. Flexibility of the coated film was tested on 1/4″ and 1/8″ conical mandrel. The chemical resistance of the film was studied by dipping separately in 2% sulphuric acid, 2% NaOH solution and acetone for specific time at room temperature.

References

[1] Kitazawa, S. and Yasuda, T. (1986). Japan Kokai Tokkyo Koho, JP 86, 91212, *Chem. Abstr.*, **105**, 192282z.
[2] Kuboto, N. (1986). Japan Kokai Tokkyo koho, JP 86 21, 104;1986 *Chem. Abstr.*, 98565y.
[3] Thomas, E. D., Fekete, F., Patrik, J. K. and William, J. P. (1967). US Patent 3, 317, 465; *Chem. Abstr.*, **67**, 120969.
[4] Matsushita Electric Works Ltd, Japan Kokai Tokkyo Koho, JP 84, 71303, *Chem. Abstr.*, **101**, 131876s.
[5] Urbanski, J. (1977). Handbook of Analysis of Synthesis Polymers and Plastics.
[6] Patel, R. G., Patel, R. D. and Patel, V. S. (1987). *Br. Polym. J.*, **19**, 37.
[7] Thakkar, J. R., Patel, R. D., Patel, R. G. and Patel, V. S. (1990). *J. Polym. Material*, **7**, 1.
[8] Paul, D. R. and Newman, S. (1978). Polymer blends (New York: Academic).
[9] Bayer, O. (1947). *Angew. Chem.*, **A 59**, 275.
[10] Guise, G. B., Jackson, M. B. and Maclaren, J. A. (1972). *Aust. J. Chem.*, **25**, 2583.
[11] Terpin, E. T. (1969). US 3, 478, 126.
[12] Guise, G. B. (1977). *J. Appl. Polym. Sci.*, **21**, 3427; *Polym. News*, **7**, 149 (1981).