International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:2, No:7, 2008

Kinetic, Thermodynamic and Process Modeling of Synthesis of UV Curable Glyceryl and Neopentyl Glycol Acrylates

R. D. Kulkarni, Mayur Chaudhari, S. Mishra

***Abstract*—**Curing of paints by exposure to UV radiations is emerging as one of the best film forming technique as an alternative to traditional solvent borne oxidative and thermal curing coatings. The composition and chemistry of UV curable coatings and role of multifunctional and monofunctional monomers, oligomers, and photoinitiators have been discussed. The limitations imposed by thermodynamic equilibrium and tendency for acrylic double bond polymerizations during synthesis of multifunctional acrylates have been presented. Aim of present investigation was thus to explore the reaction variables associated with synthesis of multifunctional acrylates. Zirconium oxychloride was evaluated as catalyst against regular acid functional catalyst. The catalyzed synthesis of glyceryl acrylate and neopentyl glycol acrylate was conducted by variation of following reaction parameters: two different reactant molar ratios- 1:4 and 1:6; catalyst usage in % by moles on polyol- 2.5, 5.0 and 7.5 and two different reaction temperatures- 45 and 75 ^{0}C. The reaction was monitored by determination of acid value and hydroxy value at regular intervals, besides TLC, HPLC, and FTIR analysis of intermediates and products. On the basis of determination of reaction progress over 1-60 hrs, the esterification reaction was observed to follow 2nd order kinetics with rate constant varying from $1*10^{-4}$ to $7*10^{-4}$. The thermal and catalytic components of second order rate constant and energy of activation were also determined. Uses of these kinetic and thermodynamic parameters in design of reactor for manufacture of multifunctional acrylate ester have been presented. The synthesized multifunctional acrylates were used to formulate and apply UV curable clear coat followed by determination of curing characteristics and mechanical properties of cured film. The overall curing rates less than 05 min. were easily attained indicating economical viability of radiation curable system due to faster production schedules

***Keywords*—** glyceryl acrylate, neopentyl glycol acrylate, kinetic modeling, zirconium oxychloride.

I. Introduction

RADIATION Curing is a process whereby reactive liquids are transformed into solid crosslinked polymeric networks by reactions initiated by UV light or electron beam radiation, rather than heat. Rapid UV cure at ambient temperature of solvent free formulations delivers best economic value in terms of faster line speed, smaller floor space, high energy efficiency, and clean/green technology [1], [2]. The output of radiation curing technology in 2004 in China was 25,000 tons per year, while that in US was 50,000 metric tons per year [3]. Although the physical volume of radiation cure materials is relatively small, their economic importance is disproportionate to their volume. They are essential to production of computer chips, optical fibers, printed circuit boards, printing plates and permit easy application on heat sensitive substrates, including paper, plastics, and wood. A number of excellent review articles/ books have been published [4]-[8].

Manuscript received September 15, 2008.

R. D. Kulkarni is with the Department of Chemical Technology, North Maharashtra University, Jalgaon, India. (phone: +91 257 2258420; fax: +91 257 2258403; e-mail: drrdkulkarni@gmail.com)

Mayur Chaudhari is with the Department of Chemical Technology, North Maharashtra University, Jalgaon, India (e-mail: mayur.ec07@gmail.com).

S. Mishra is with the Department of Chemical Technology, North Maharashtra University, Jalgaon, India. (e-mail: profsm@rediffmail.com).

II. UV curing Chemistry and Formulations

A. UV curing Coating Compositions

The photocurable formulations consist usually of multifunctional monomer [e.g., trimethylolpropane triacrylate, pentaerythritol triacrylate, tris(2-hydroxyethyl) isocyanurate triacrylate, 1, 6-hexanediol dicrylate, glyceryl propoxylate triacrylate, tripropylene glycerol diacrylate etc.], monofunctional monomers [e.g., isobornyl acrylate, 1-(2-ethoxy) ethyl acrylate, ethoxylated nonylphenol acrylate], and multifunctional oligomers (epoxy/urethane/polyester /polyether /amine modified acrylate, cationic curable epoxies). Small amount of photoinitiator which generate reactive species (free radicals or ions) on UV exposure and additives (oxygen scavengers, flow and wetting agent, adhesion promoters) best suited for producing polymer networks in relation to applications are also the integral part of formulation. W. A. Green has elaborated the legacy of 40 years of industrial UV curing that revolves around 50 common photoinitiators [9].

B. Designs of UV cure vehicles

Vehicles for free radical initiated UV cure use acrylated reactants rather than methacrylates, since acrylates cure more rapidly at room temperature, terminate by combination rather than disproportionation and are also less oxygen inhibited. The design of commercial coating formulation relies heavily on the Science and Technology associated with the selection of mono to hexa functionalized monomers (used for reduction

of viscosity, adhesion to substrate) and acrylate terminated oligomers / high molecular weight polymers (used for rapid cure rate, shrinkage and mechanical properties). Empirical correlations of chemical structures of monomers, oligomers and polymers with their chemical and physical properties have been developed; advanced experimental design techniques are increasingly used to create complex coating compositions based on as many as 30 variables in the final system [10], [11]. It is necessary to use number of monomers in order to achieve a balance between speed of cure and properties of the final film. The typical % of monofunctional and multifunctional monomers in UV cure vehicle range from 5-15% and 20-60% respectively [12]. Acrylated epoxies have largest variety of structures; bridge the performance gap between acrylated urethanes, acrylics and polyesters; promote good adhesion, chemical resistance and flexibility and are the dominant oligomers used in the radiation curable coatings [13], [14]. Care must be used in handling them because many are skin irritants / sensitizers [15].

C. Background of Investigation

The synthesis of multi and mono functional acrylates from acrylic acid and polyhydric alcohol is known to be an equilibrium reaction. In order to obtain economical conversions, either one of the reactant is used in excess and/or the resulting water be removed from the reaction mixture using an organic solvent, which is immiscible with water or forms an azeotrope with water. Another major problem in the esterification is the high tendency of acrylate compounds to polymerize owing to their reactive double bonds when exposed to high temperatures. This results in soiling of the apparatus, blockage of pipes and pumps and coating of column trays and heat exchanger surfaces (fouling). The cleaning of the plant is complicated, expensive and environmentally polluting procedure. In addition the yield is greatly reduced. The preparation of acrylates by acid catalyzed esterification of acrylic acid with alkanol has been described [16]. The invention by Derks *et al*. relates to a process for preparation of esters of acrylic/crotonic/ cinnamic acid and polyhydric alcohol/ hydroxyl functional polyesters in presence of acidic catalysts and subsequent in situ neutralization of catalyst through additional esterification and thus eliminating the washing step [17]. The esters formed through this process are claimed to be free from β-OH group and thus hydrolytically stable as against those obtained using Vianoa and BASF processes which requires neutralization of free acrylic acid with epoxides [β-hydroxy forming component] and water washing of catalysts/free acids or alcohols through use of water soluble flocculators respectively [18], [19]. Another process described use of polymerization inhibitor (hydroquinone or it's mono-methyl ether in amount from 200 to 2000 ppm) for suppressing the free radical polymerization and an organic solvent [pentane / hexane / heptane / toluene at 5-50% by weight] which forms azeotropic mixture with water for preparation of acrylates in a stirred reactor that comprises a distillation unit, a reflux column with dumped packing and tubular / Plate type condenser [20]. Part of the column reflux was brought into contact with copper metal/copper alloys with Zn, Ni, Al, and Sn for minimizing polymer formation in the distillation column. Conversions from 95 to 98% were claimed to be obtained without polymer formation in distillation column.

Most of the information associated with preparation of multifunctional acrylates is either scattered or in the form of patents. Kinetic and thermodynamic parameters associated with acid catalyzed esterification are not available thus introducing difficulty in design of reactor. Aim of present investigation was to optimize the process of synthesis of multifunctional acrylates and investigate kinetics and thermodynamics of the process. The present paper reports synthesis of neopentyl glycol (NPG) Acrylate and glyceryl acrylates using zirconium oxychloride as a catalyst and subsequent determination of rate constant 'k' and energy of activation 'E_a'. NPG acrylate is used primarily in UV-curable coating formulation as viscosity reducer. Glyceryl acrylates after propoxylation is used for low skin irritation, reducing surface tension for adhesion to substrate and obtaining water balance properties for offset printing.

III. Materials and Methods

A. Chemicals

Glycerol (98.0 %, s. d. Fine), NPG (98.0% Sisco Research Lab.), pyridine (99.0%, s. d. Fine), acetic anhydride (98.0 %, s. d. Fine), methanol (99.0 %, s. d. Fine), acrylic acid (99.0 %, Loba Chemie), ethyl acetate (98.0%, Qualigens Fine Chemicals) were used as received. $ZrOCl_2.8H_2O$ (96.0 % s. d. Fine) was dried at 80^0C for 05 hrs and cooled in desiccators before its use as catalyst during the synthesis.

B. Synthesis of glyceryl and NPG acrylates

The esterification reaction assembly consisted of a three-neck flask fitted with reflux condenser, stirrer with speed regulator and electrical heating system with energy regulator capable of maintaining reaction temperature within $\pm 0.5^0$C. The polyol and acrylic acid were mixed at a given molar ratio (1:6 or 1:4) together with zirconium oxychloride as a catalyst at 2.5,5,7.5 % by moles on polyol heated to the given reaction temperature ($45/75^0$C) and maintained well mixed there at for the reaction period varying from 1 to 60 hours. Determining the initial and final acid and hydroxyl value (AV and HV) and performing TLC analysis for each reaction batch monitored the reaction progress. The catalyst was recovered by precipitating it from the reaction mixture through addition of diethyl ether/ ethyl acetate as a solvent and subsequent filtration through Whatman filter paper No. 40. Solvent was distilled under vacuum and the product obtained in this manner was analyzed by TLC, HPLC, and FTIR spectrophotometer.

C. Characterization Methods

Acid Value (AV) was determined by titration of 0.5 to 1 gm of reaction mixture in 50 ml 95% neutral alcohol against 0.5N alc. KOH using phenolphthalein as indicator and using following formula:

$$AV = \frac{Titration \cdot reading \times N_{KOH} \times 56.1}{Weight \cdot of \cdot sample}$$

Hydroxyl value (HV) was determined as follows: 0.2- 0.3 gm of reaction mass was refluxed with 10 cc of acetic anhydride-pyridine (1:5v/v) reagent for 2 hrs followed by addition of 20 ml distilled water through condenser and refluxing for additional 30 min. It was then back titrated against 0.5N alc. KOH using phenolphthalein as indicator.

$$HV = \frac{(Blank - sample) \times N_{KOH} \times 56.1}{Wt.of.sample} + AV$$

TLC: The reaction mixture was spotted on silica gel plate using

TABLE I
ESTERIFICATION OF NEOPENTYL GLYCOL WITH ACRYLIC ACID

Reaction Temperature, (°C)	Reactant and catalyst Conc.			Run No.	Reaction Period t (min)	Reaction progress		$k*C_{Ao}$ (min^{-1})
	Functionality Ratio OH: COOH & Molar % of Catalyst on polyol	AV @ t=0 (mg/g)	HV @ t=0 (mg/g)			AV (mg/g)	HV (mg/g)	
75	2:4, 5	492.0	637.7	L1	360	339.3	402.3	$7.12x10^{-4}$
				L2	720	325.8	389.8	
				L3	1100	318.1	380.9	
				L4	1452	315.9	374.4	$2.18x10^{-4}$
				L5	1800	312.8	353.7	
				L6	2160	311.3	350.5	
				L7	3450	290.2	333.1	
	2:4, 2.5	510	641.5	L2C1	720	356.0	405.1	$3.56x10^{-4}$
	2:4, 7.5	505	636.3	L2C2	720	304.6	316.4	$5.68x10^{-4}$
45	2:4, 5	492.0	637.8	L1T1	360	387.8	433.3	$5.89x10^{-4}$
75	2:6, 5	514.6	650.5	H1	363	437.3	507.0	$2.37x10^{-4}$
				H2	720	422.1	485.3	
				H3	1080	410.4	452.0	
				H4	1440	399.5	426.2	$0.98x10^{-4}$
				H5	1800	396.4	409.6	
				H6	2160	393.8	404.2	
				H7	3240	380.2	393.9	
	2:6, 2.5	517.3	651.8	H1C 1	363	449.5	520.8	$2.14x10^{-4}$
	2:6,7.5	512.3	648.6	H1C 2	363	396.2	425.3	$4.13x10^{-4}$
45	2:6, 5	514.6	650.2	H1T	363	470.7	550.8	$1.57x10^{-4}$

chloroform as a solvent. Hexane- ethyl acetate mixture (1:9

TABLE II
ESTERIFICATION OF GLYCEROL WITH ACRYLIC ACID

Reaction Temperature. (°C)	Reactant and catalyst Conc.			Run No.	Reaction Period t (min)	Reaction progress		$k*C_{A}o$ (min^{-1})
	Functionality Ratio OH: COOH & Molar % of Catalyst on polyol	AV @ t=0 (mg/g)	HV @ t=0 (mg/g)			AV (mg/g)	HV (mg/g)	
75	3:4, 5	437.3	740.1	1	360	330.2	529.9	$4.26x10^{-4}$
				2	720	317.2	497.1	
				3	970	310.6	478.8	
				4	1440	299.4	452.1	
				5	3240	281.7	420.3	
	3:6, 5	558.6	717.6	1	365	500.0	583.4	$2.98x10^{-4}$
				2	720	480.5	551.5	$1.28x10^{-4}$
				3	1080	474.7	541.7	
				4	1455	462.7	538.7	
				5	3090	440.7	480.5	
	3:6, 2.5	559.9	718.3	1C1	365	519.8	640.8	$1.63x10^{-4}$
	3:6, 7.5	556.3	716.5	1C2	365	486.9	572.9	$3.28x10^{-4}$
45	3:6, 5	558.6	717.6	1T	365	535.5	707.8	$1.92x10^{-4}$

$$\left[C_{A0}..k.t.(M-1)\right] = \ln\left[\frac{(M - X_A)}{M(1 - X_A)}\right] \quad M \neq 1 \quad (2)$$

v/v) was used as developing solvent.

D . Instrumental Analysis

The FTIR spectra were recorded using NaCl plate thin film deposition technique on Shimadzu FTIR- 8400 Spectrophotometer. The quantitative determination of mono and diester was conducted on Chemito HPLC LC-6600 series model and UV detector set at 210 nm with the mobile phase consisting of HPLC grade methanol.

E. Mathematical Model

The kinetics of esterification between polyol and acrylic acid was examined by application of integral method of analysis using second order rate law for constant volume batch reactor system[21]

Fractional conversion: $$X_A = \frac{(HV_{t=0} - HV_{t=t})}{HV_{t=0}} \quad (1)$$

where A = Polyol B = Acrylic Acid

$$M = \frac{N_{B0}}{N_{A0}} = \text{Initial COOH : OH ratio}$$

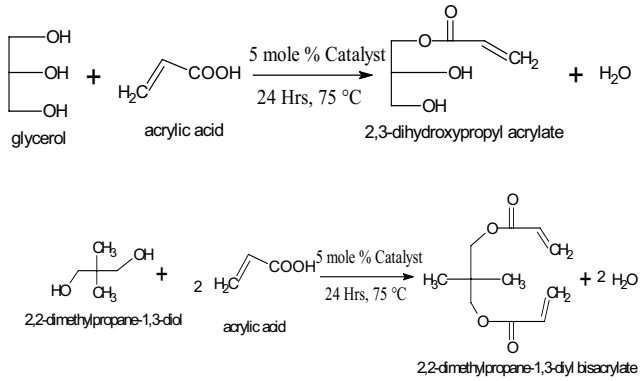
t= time in minutes, C_{A0} = initial HV, (mg / g),
k= second order rate constant, (g) / (mg) (min).

IV. Results and Discussion

In general the esterification of acrylic acid with polyol is performed using conventional catalysts such as H_2SO_4, p-toluene sulphonic acid (PTSA). This requires the conduction of reaction at higher temperature and hence necessitates addition of inhibitor for minimization of polymerization during esterification. Use of aromatic or aliphatic hydrocarbons for azeotropic removal of byproduct H_2O is also practiced for driving reaction equilibrium towards right. The process is neither environmental benign route nor supporting prevention of polymerization within reactor as well as in condenser. We observed through preliminary empirical investigation that reaction must be conducted below 100^0C for control of polymerization. Thus an efficient catalytic system permitting esterification at low temperature was essential. Use of zirconium oxychloride as catalyst for ambient temperature high yield esterification of acrylic acid and methanol has been reported [22]. The catalyst can be easily recovered after esterification and reused. Hence we used zirconium oxychloride as catalyst in present investigation. The results of $ZrOCl_2.8H_2O$ catalyzed esterification of acrylic acid with NPG and glycerol at 2 molar ratios viz. 6:1 and 4:1, three catalyst concentrations viz. 2.5, 5, and 7.5% by moles on

polyol, and two reaction temperatures viz. 45, 75^{0}C have been reported in Table I and II respectively. The fall in AV and HV as a function of reaction time indicating progress of the reaction has been presented in Fig. I and II. The plots exhibited two distinct characteristics phases: reaction period (rapid drop in HV/ AV with time) and equilibrium period (plateau formation). These plots have been the typical characteristics of all second order reactions.

The reaction between acrylic acid and glycerol and that between NPG and acrylic acid takes place as follows:



Since glycerol being triol and neopentyl glycol being diol, more than one hydroxyl group may undergo esterification changing reaction stoichiometry from the type A + B → product to A + 2B → product. Since application of second order mathematical model requires knowledge of reaction stoichiometry, the glycerol and NPG esters were subjected to HPLC analysis. Fig. 3 (a) presents HPLC plot of pure acrylic acid and Fig. 3 (b) for NPG acrylate obtained at OH: COOH: 2: 4 ratio and 5 mole % catalyst on NPG. The three sharp peaks corresponding to acrylic acid, monoester (at retention time of 2.96 min), and diester (at retention time of 3.14min) in Fig. 3 (b), clearly indicated absence of any impurities that could have been aroused out of polymerization or any other side reaction. The product composition implied diester as major product. Thus esterification can proceed by either A + B → product pathway or A + 2B → product route. The rate of reaction of free polyol with acrylic acid and that between monoester and acrylic acid will differ, thus the rate constant calculated by second order mathematical model will average out over different permutations and combinations. Hence one finds minor difference between rate constants calculated from initial runs and those from subsequent runs. The average esterification rate constant ($k*C_{A0}$) calculated after substituting the reaction data in (1) and (2) have been reported in Table I and was observed to vary from $1*10^{-4}$ to $7*10^{-4}$ min^{-1}.

The HPLC analysis of glyceryl acrylate synthesized at OH : COOH :: 3 : 4 and 3 : 6 ratio and 5 mole % catalyst on glycerol have been presented in Fig. 3 (c) and Fig. 3 (d), respectively. These HPLC plots again confirmed product synthesis with total freedom from impurities. The striking feature of glycerol esterification is the precise reaction preference for monoesterification. This has been primarily due to triol functionality of glycerol. The rates of individual molecular esterification were thus more or less uniform. The magnitude of rate constant for glycerol esterification calculated after substituting the reaction data in (1) and (2) have been reported in Table II. It was observed to vary from $1.25*10^{-4}$ to $4.25*10^{-4}$ min^{-1}.

The FTIR spectra obtained for NPG acrylate and glyceryl acrylate have been presented in Fig. 4 (a) and 4 (b), respectively. The FTIR spectrum of NPG acrylate indicated following characteristic peaks:

i. 1724 cm^{-1}: ester carbonyl group.
ii. 1625.9 cm^{-1}: acrylic double bond conjugated with
iii. carbonyl double bond.
iv. 2968.2 cm^{-1}: OH stretching frequency of COOH group.
v. 1375.2 cm^{-1}: characteristic frequency of methyl groups.

Following characteristic peaks were observed in the FTIR spectrum of glyceryl acrylate:

i. 1722.3 cm^{-1}: Characteristic ester carbonyl group.
ii. 1058.9 cm^{-1}: C-O stretching frequency of primary – OH group.
iii. 1631.7 cm^{-1}: Acrylic double bond conjugated with carbonyl double bond.
iv. 3415.7 cm^{-1}: OH stretching frequency of COOH functionality.

The IR spectra provided additional confirmation of inferences based on HPLC findings.

The overall rate constant is composed of thermal and catalytic components and is given by $k = k_u + c_c k_c$ where k_u represents rate constant for uncatalysed reaction (thermal component), k_c represents contribution to rate constants by catalyst and c_c = catalyst concentration. In order to evaluate k_u and k_c, the esterification run were conducted at 3 different catalyst concentrations: 2.5, 5.0 and 7.5 % by moles on polyol mole. The k_u and k_c values calculated thus for NPG acrylate and glyceryl acrylate were as given below:

NPG Acrylate: $k_u = 1.1*10^{-4}$ $k_c = 6.88*10^{-3}$

Glyceryl Acrylate: $k_u = 2.62*10^{-5}$, $k_c = 9.12*10^{-3}$

In order to determine energy of activation 'E_a' of esterification, additional run were conducted at 45^{0}C. The E_a/R values were calculated using Arrhenius equation: $k = A*e^{-Ea/RT}$ and found to be 1531.5 and 1621.5 for NPG and glycerol esterification, respectively.

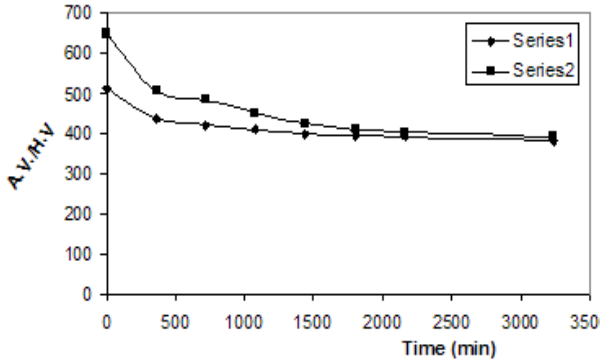


Fig. 1 NPG Esterification progress

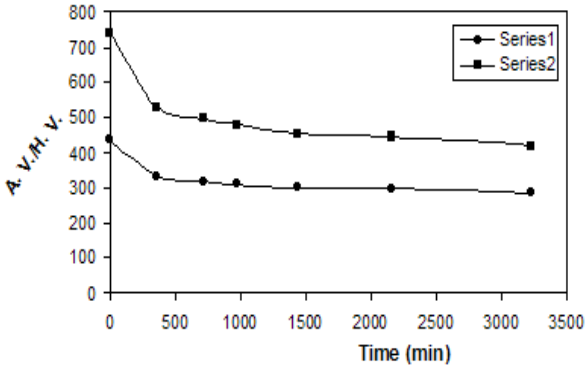


Fig. 2 Glycerol Esterification progress

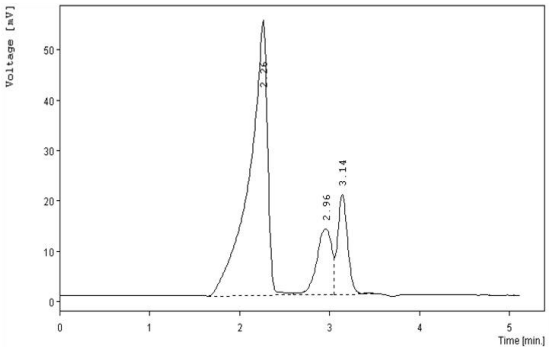


Fig. 3 (b) HPLC plots for Neopentyl glycol acrylate

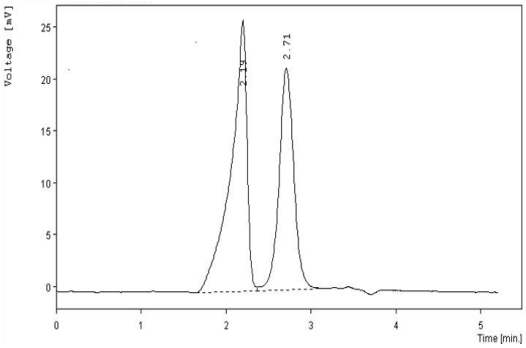


Fig. 3 (c) HPLC plot of Glyceryl acrylate obtained at 1:6 Glycerols: Acrylic acid Molar ratio

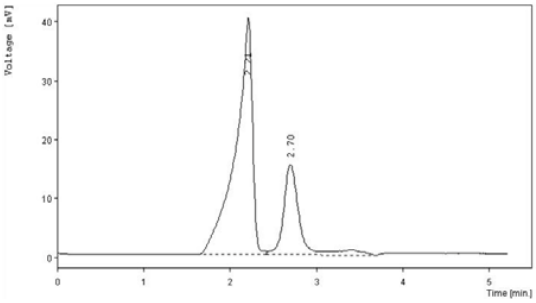


Fig. 3 (d) HPLC plot of Glyceryl acrylate obtained at 1:6 Glycerol: Acrylic acid Molar ratio

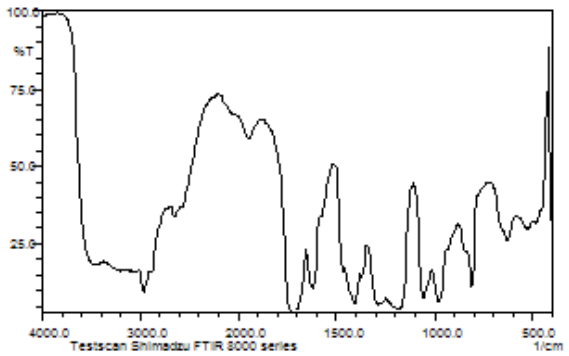


Fig. 4 (a) IR spectrum of NPG acrylates

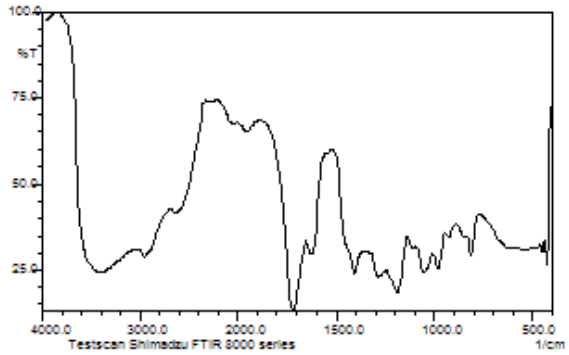


Fig. 4(b) IR spectrum of glyceryl acrylates

V. A Note on Reactor Design

Three basic reactor options are available for homogenous catalyzed esterification: batch, continuous mixed flow and continuous plus flow. Since the reactions are slow and governed by equilibrium considerations, variations of above basic options are utilized in commercial practice. Removal of byproduct water through azeotropic distillation is a semi batch variation of batch option. Cascading of multiple stirred tank reactors and partial recycle of product stream are the variations proposed for mixed flow and plug flow reactors, respectively. The design of reactors covering various options requires calculation of holding/ space time and volume of reactor; which in turn requires knowledge of various kinetic and thermodynamic parameters including rate constants, catalyst activity, and energy of activation. The calculations of k, E_a and catalytic rate constants for synthesis of glyceryl and NPG acrylate have been thus performed to fulfill the essential requirements of reactor design. A conclusion section is not required. Although a conclusion may review the main points of the paper, do not replicate the abstract as the conclusion. A conclusion might elaborate on the importance of the work or suggest applications and extensions.

VI. Use of Acrylates in UV Cure Coating

The synthesized multifunctional acrylates were subsequently reacted with Bisphenol- A Epoxy Resin (EEW-350) to obtain epoxy acrylates. The clear coating was formulated using Irgacure 651 (Ciba) as photoinitiator. The clear coat was applied at 15 micron thickness using wire applicator and cured under UV Lamp of intensity 18 W. The overall curing rates less than 05 min. were easily attained indicating economical viability of radiation curable system due to faster production schedules. The scratch resistance and adhesion properties of UV cure coats were found to be satisfactory.

References

[1] Dan Sweet wood and Michael Kelly, www.PCIMAG.com, , Nov. 2007, pp.78-80.
[2] K. Lawson, *RadTech. Rep*., 12 (1), 1998, pp. 25.
[3] Wang Qingfeng and Wenfang Shi, "Growth and Use of Radiation Curing in China", JCT *CoatingTech*., pp. 48- 54, Oct 2005. Available :http://www.coatingstech.org
[4] Vincent D. McGinniss, "Radiation Curing", in *Kirk Othmer Encyclopedia of Chemical Technology*, 4th Ed., Vol. 20, Wiley-Interscience, New York, ,1996, pp. 830-859.
[5] Belfield, K. D., J. V. Crivello, Eds., 'Photoinitiated Polymerisation', *ACS Symp. Ser. 847*, American Chemical Society, Washington DC, 2003.
[6] Koleske, J. V., 'Radiation Curing of Coatings', ASTM International, West Conshocken, PA 2002.
[7] P.K.T. Oldring,, Ed., '*Chemistry and Technology of Formulating UV Cure Coatings', Inks and Paints*,' Vol. 1-5, SITA Technology, London, 1991-94.
[8] Christian Decker and Khalil Mousssa, "Recent advances in UV Curing Chemistry", *J. Coat Technol.*, 65(819), pp.49-57,1993.
[9] W. A. Green, "Photoinitiators Old and New Food for thought", *Surface Coating International*, 90 (02), pp. 69-75, 2007.
[10] V. D. McGinniss, *Org. Coatings Plast. Chem.* 39, 1978, pp. 529-537.
[11] G. C. Derringer*, J. Quality Tech*., 12 (4), 1980, pp. 214-219.
[12] Classification System of the Environmental Protection Agency (EPA), tital 40, code of federal regulations, part 162.10H.
[13] Hoyle Charles E., James F. Kinstle, Ed. 'Radiation Curing of Polymeric Materials, *American Chemical Society*, Washington DC, 1989, pp.1-16.
[14] Chattopadhya D. K., S. S. Pande, K. V. S. N. Raju, "Thermal and mechanical properties of epoxy acrylate /methacrylates UV cured coatings", Progress *in Organic Coatings*, 54, pp.10-19, 2005.
[15] R Golden, J. *Coat. Technol.*, 69(871), p. 83, 1997.
[16] Takashi Ohara, Takahisa Sato, Noboru Shimizu, Gunter Prescher, Helmut Schwind, Otto Weiberg, *Ullaman's Encyclopedia of Industrial Chemistry*, Vol. A1, VCH 1985, pp. 161-172.
[17] Franciscus J. M. Derks, Michae A. C. Van Dijck**,** "Process for the preraration of esters of (metha) acrylic acid", US Patent 6838515 B2, Jan., 04, 2005.
[18] *EP* 054105 A1 assigned to Vianova, 1982.
[19] *EP* 0933353 A1 assigned to BASF, 1999.
[20] F. G. Martin, G. Nestel , J. Schroder, "Method for producing (meth) acrylic acid esters", US Patent 20040030179 A1, Feb. 12, 2004.
[21] Levenspiel Octave, "*Chemical Reaction Engineering*", 3rd Ed., John Wiley and Sons, Singapore, 1999, p. 43.
[22] Hong-Bin Sun, Ruimao Hua & Yingwa Yin, "$ZrOCl_2{:}8H_2O$: An efficient, Cheap and Reusable Catalyst for the Esterification of Acrylic acid and other Carboxylic Acids with equimolar amounts of Alcohols" *Molecules*, 11, pp. 263-271, 2006. Available: http://www.mdpi.org