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

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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°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 $1 \times 10^{-4}$ to $7 \times 10^{-4}$.

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].

II. UV CURING CHEMISTRY AND FORMULATIONS

A. UV curing Coating Compositions

The photocurable formulations consist usually of multifunctional monomer [e.g., trimethylolpropane triacrylate, pentaerythriol 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 alkalin has been described [16]. The invention by Derks et al. relates to a process for preparation of esters of acrylic/crotonic/ cinnamic acid and acrylic acid with epoxides [as-hydroxy forming component]. The present paper reports synthesis of neopentyl glycol (NPG) Acrylate and glycerol acrylates using zirconium oxochloride as a catalyst and subsequent determination of rate constant ‘k’ and energy of activation ‘Ea’. 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. ZrOCl2·8H2O (96.0 % s. d. Fine) was dried at 80°C 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 ±0.5°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°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:
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.

\[ AV = \frac{\text{Titrations reading} \times N_{\text{KOH}} \times 56.1}{\text{Weight of sample}} \]

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

TLC: The reaction mixture was spotted on silica gel plate using chloroform as a solvent. Hexane-ethyl acetate mixture (1:9) 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 (1)

\[ X_A = \frac{(HV_{t=0} - HV_{t=\infty})}{HV_{t=0}} \]

where \( A = \) Polyol \( B = \) Acrylic Acid

\[ M = \frac{N_{\text{OH}}}{N_{\text{COOH}}} = \frac{\text{Initial COOH:OH ratio}}{t = \text{time in minutes}} \]

\[ \text{k} = \text{second order rate constant,} \ (g)/(mg) \ (min). \]

IV. RESULTS AND DISCUSSION
In general the esterification of acrylic acid with polyol is performed using conventional catalysts such as \( \text{H}_2\text{SO}_4, \text{p-toluene sulphonphatic acid (PTSA)} \). 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 \( \text{H}_2\text{O} \) 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°C 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 \( \text{ZrOCl}_2\cdot8\text{H}_2\text{O} \) 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...
polyl, and two reaction temperatures viz. 45, 75°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:

\[
\text{glycerol} + \text{acrylic acid} \rightarrow \text{2,3-dihydroxypropyl acrylate}
\]

\[
\text{2,2-dimethylpropyl-1,3-diol} + \text{acrylic acid} \rightarrow \text{2,2-dimethylpropane-1,3-diol bisacrylate}
\]

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 \rightarrow
product to A + 2B \rightarrow 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 3.14 min) 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 \rightarrow
product pathway or A + 2B \rightarrow product route. The rate of reaction
of free polyl with acrylic acid and that between
monooester 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^{-5} to 4.25*10^{-5} 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
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 + 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 mole 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^{-3}, 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°C. The
E/R values were calculated using Arrhenius equation: k =
A*exp(-E_a/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 Glycerol: Acrylic acid Molar ratio

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

[12] Classification System of the Environmental Protection Agency (EPA), title 40, code of federal regulations, part 162.10H.

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 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.