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Characterization of tertiary amine and epoxy functional all-acrylic coating system

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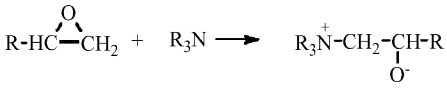
ABSTRACT

For many years the coating industry has been working on developing and/or improving non-isocyanate (NISO) coating systems to meet environmental and safety concerns without sacrificing their performance. The approach of all acrylic (AA) resins, in general comprises of anhydride/hydroxyl, tertiary-amine/epoxy, carboxy/epoxy, or activated hydrogen/ketimine functional groups. The objective of this study is to show that the functional groups in tertiary amine acrylic and epoxy acrylic resins can be determined by means of FTIR and Pyrolyzer GC/FID.

1. Introduction

Environmental regulations and ecological concerns compel the industry to develop isocyanate-free coatings to replace an acrylic urethane system. Research efforts have focused on reducing the volatile organic compounds, while avoiding the use of toxic materials.

High performance requirements are still the most important criteria for the market application, including machinery, protective coatings, industrial maintenance, automotive industry, etc. One of the systems developed for isocyanate-free coatings is the "All Acrylic" (AA) system. AA system is based on acid–epoxy chemistry, anhydride–hydroxyl reactions, epoxy–tertiary amine and other combinations [1,2]. The epoxy and tertiary amine functional polymers are preferred due to their exterior durability with gloss retention equivalent to that of 2 K urethane system.



Various sensitive analysis techniques such as FTIR and Pyrolyzer-GC/FID have been used in the characterization of coating systems.

Fourier Transform Infra-red (FTIR) the infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs. Examination of the transmitted light reveals how much energy was absorbed at each frequency (or wavelength) [3] (Fig. 1).

Analysis of the position, shape and intensity of peaks in this spectrum reveals details about the molecular structure of the sample. This technique works almost exclusively on samples with covalent bonds. The technique has been used for the characterization of very complex mixtures [4].

Pyrolysis GC/FID, pyrolysis is the breakdown of organic molecules by the application of heat in the absence of oxygen and the separation and detection of the pyrolysis products by GC [5]. Pyrolysis GC/FID has been used routinely for characterization of coating resin systems. The molecular structures for characterizing natural resin and oils found in coatings are often polar compounds, containing carboxylic acid and other groups that require derivatization. Thermally assisted hydrolysis and methylation (THM) is a technique utilized in derivatization of compounds that are typically nonvolatile in the presence of a derivatizing agent such as tetramethylammonium hydroxide (TMAH) [6,7].

2. Experimental

2.1. Materials

2-(Dimethylamino) ethyl methacrylate (DMAEMA; MADAME) and glycidyl methacrylate (GMA) were procured from Evonik and AGI Corporation. They were used as references for tertiary-amine and oxirane functionalized (meth)acrylate, respectively.

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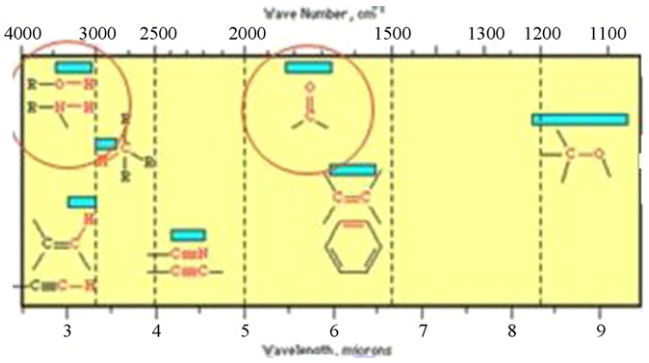


Fig. 1. Typical Infrared absorption frequencies.

Table 1
Epoxy-, or amino- functional copolymers.

Polymer #	Monomer content (%)					
	GMA	DMAEMA	MMA	ST	BA	HEMA
1	15			55	30	
2	30			40	30	
3	100					
4		10	30	40	20	
5		20	25	30	20	5
6		100				

2.2. Synthesis

Several copolymers that contain monomers having functional groups were synthesized (Table 1). The resins were prepared by conventional free-radical solution polymerization techniques. The polymerizations were conducted under nitrogen in a jacketed, 2 L glass reactor equipped with a stirrer, thermometer, and reflux condenser. The monomer mix and initiator were combined and metered into the reactor containing solvent at a prescribed temperature over a 5 h period. After the monomer and initiator addition was complete, polymerization was continued for an additional hour [8].

Table 2
Equipment parameters.

FTIR	
Model	Perkin Elmer precisely spectrum one
Wavelength	4000 cm^{-1} to 400 cm^{-1}
Resolution	4 cm^{-1}
Sampling technique	KBr pellet
GC Schimadzu 2010	
Injector	320 °C
Oven	40 °C for 5 min
Column	5% Ph Me Si
Carrier gas	He
Detector	FID
Pyrolyzer frontier single-shot	
Oven	320 °C
Pyrolyzer	750 °C
Elapsed time	1 min
Sampling technique	Both underivatized and derivatized form that made it utilized by TMAH.

2.3. Characterization techniques for functional groups

FTIR spectra and pyrograms were collected for all synthesized acrylic copolymers. Equipment parameters are given in Table 2.

3. Results and discussion

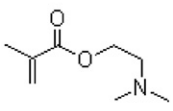
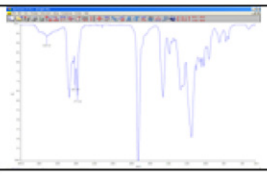
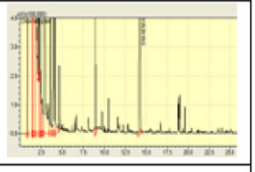
FTIR spectra and pyrograms of reference functional groups; i.e. “DMAEMA” and “GMA” for “Component I” and “Component II”, respectively, are given in Table 3.

3.1. “Component I” results

3.1.1. FTIR results

FTIR spectra of samples having various amount of DMAEMA showed that, the heights of peaks at 3445 cm^{-1}, 2820 cm^{-1} and 2770 cm^{-1} bands were increased with increasing concentration of DMAEMA. The results were given in Table 4. This results validated with expected spectrum, i.e. 2820 cm^{-1}, 2770 cm^{-1} bands in green circles were results of stretching of $CH_2N(CH_3)_2$ (tertiary-amine) and 3445 cm^{-1} band in red circle caused by NH stretching.The

Table 3
FTIR spectra and pyrograms of references.

Functionalized Monomer	Structural Formula	FTIR Spectrum	PYR-GC-FID Pyrogram
2-(Dimethylamino)ethyl Methacrylate (DMAEMA)			
Glycidyl Methacrylate (GMA)