Synthesis of Novel Alkyl-Aryl Polyamide

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ABSTRACT

A laboratory procedure for synthesizing an alkyl-aryl polyamide curing agent for liquid epoxy resins from commercially available, low cost materials is given. The various chemical reactions required to obtain the desired end-product are described, and several properties of the novel polyamide are listed. This agent was found suitable for producing foamed or frothed epoxy products.

INTRODUCTION

Use of dimer acids for the production of polyamide resins has been known since 1940 (1). However, it was not until 1946 that the first feasible commercial process was disclosed (2). Recently, another type of fatty acid dimer has been described that depends upon cationic copolymerization of a conjugated fatty ester with styrene and that also may be used for producing polyamide resins (3-6).

The work described here is basically a simplification and improvement of the latter process. By starting with a commercially available conjugated linoleic acid, an isomerization step is eliminated, and, because of the high conjugated unsaturation content of the precursor, the formation of the dimerized product by reaction with styrene is enhanced greatly. In addition, a more reproducible product is obtainable because the starting material has a uniform fatty acid composition.

EXPERIMENTAL PROCEDURES

Esterification

The precursor is a commercial material known as Pamolyn 380, supplied by Pine and Paper Chemicals Department, Hercules, Wilmington, Del. Their Product Data Sheet Number 7046 lists the following properties for the material: unsaponificables, 1.5%; resin acids, 1.2%; iodine number, 154; fatty acid composition (conjugated linoleic acid), 76%; linoleic acid, 6%; oleic acid, 17%; and saturated acids, 1%.

Into a reaction flask fitted with a stirring device, reflux condenser, and dropping funnel, 1 mole Pamolyn 380 and 2.80 g concentrated sulfuric acid catalyst are added. (The amount of sulfuric acid added represents 1% by wt of the total amount of Pamolyn 380.) The mixture is heated slowly to a temperature of 50 C. Anhydrous methyl alcohol (2 moles) present in the dropping funnel is added dropwise to the heated solution. The reaction mixture is brought up to a temperature of 80 C and left to react for 48 hr. The mixture is collected and washed with a 25 ml portion of water and then is extracted with anhydrous ethyl ether. The extracted etheral layer is dried over anhydrous magnesium sulfate, filtered, and the ether portion evaporated. The end-product is collected by distillation at 180 C under a vacuum of 1 torr.

Styrenation

Into a reaction flask fitted with a stirring device, reflux condenser, and dropping funnel, 1 mole esterification product is mixed with a phosphoric-acid activated bleaching earth copolymerization catalyst. (The amount of copolymerization catalyst added represents 2% of the amount in g of the esterification product.) The mixture is heated slowly to a temperature of 120 C. Styrene (1 mole) present in the dropping funnel is added dropwise to the heated solution. The reaction temperature is maintained at 120 C for 1 hr, heated to 150 C for 1 hr, then to 180 C for 4 hr. The mixture is collected and filtered to remove the catalyst.

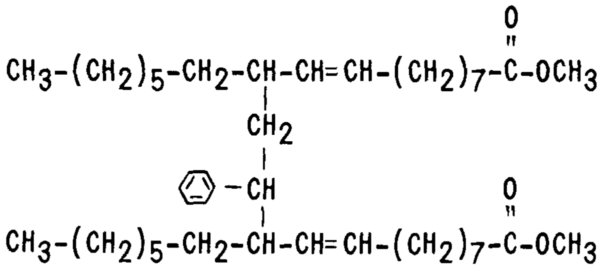
Amidation

Into a reaction flask fitted with a stirring device and reflux condenser, 100 g styrenated product and 27.2 g tetraethylenepentamine (TEPA) are added. At this point, the stoichiometric ratio of styrenated product to TEPA is 1:1/2. The 27.2 g TEPA represent the first half of the total TEPA addition. A Barrett distilling receiver is incorporated to collect the methanol side-product. The reaction contents are stirred and refluxed at 220 C for 3 hr. During this time, samples are removed periodically from the reaction mixture to monitor the rate and degree of amidation. After 3 hr, or when no further amide carbonyl formation is observed, the second portion of 27.2 g TEPA is added to the hot reaction mixture. The stoichiometric ratio is now 1:1. The mixture is allowed to react for an additional 2 hr at 220 C. During this time, reaction samples are evaluated again by IR analysis to ensure complete amidation. If it is observed that the maximum amide carbonyl formation is attained prior to the end of the 2 hr, the reaction may be terminated.

DISCUSSION AND RESULTS

The esterification procedure achieves nearly 98% conversion to the methyl ester as determined by recovered product. The ester was prepared since the free acid group possibly could affect the cationic reaction with styrene. The sectional IR spectrum in Figure 1 shows the carbonyl absorption of Pamolyn 380 prior to and following esterification. The esterification of Pamolyn 380 is noted by a shift of the carboxylic acid carbonyl peak at 5.38 μ to the ester carbonyl peak at 5.72 μ.

The formation of the alkyl-aryl intermediate is solely dependent upon the cationic copolymerization reaction between the conjugated fatty acid ester and monomeric styrene. The process of cationic copolymerization is widely known. It has been performed in the presence of catalysts, such as peroxides, acids, or Friedel Crafts catalysts, and the conditions under which the reaction is performed may be varied widely, depending upon the desired end-product. This particular reaction is, however, enhanced by a cation exchanger in the acid form. The idealized styrenation reaction product is shown in equation 1:



Styrenated conjugated methyl linoleate

The styrenation reaction to form the conjugated methyl linoleate described here should yield the reaction product shown in equation 1. This rationale is based upon the fact that fatty acids undergo diene synthesis with other dienophilic reactants (7). IR spectroscopy was used for ascertaining the gradual disappearance of the absorption bands of the 9, 11 conjugated methyl linoleate as it was copoly-

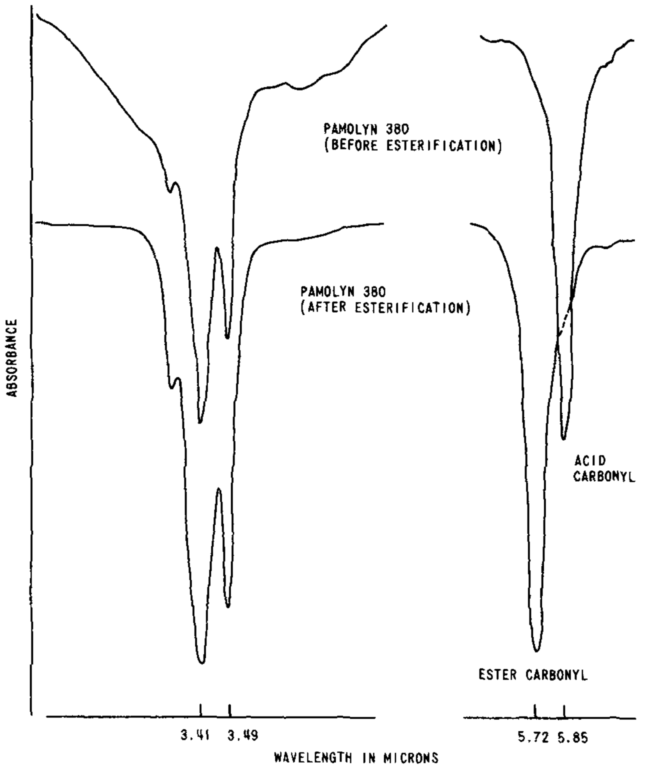


FIG. 1. Sectional IR spectra comparison of Pamolyn 380 before and after esterification with methyl alcohol.

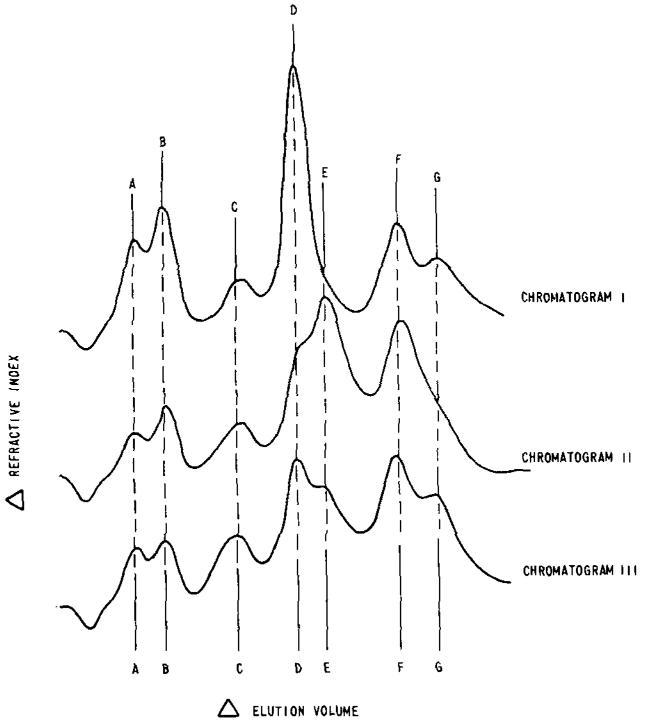


FIG. 2. Gel permeation chromatography analysis of products from styrenation of conjugated methyl linoleate. A,B = styrene oligomers, C = polystyrene, D = methyl linoleate, E = monostyrene-monomethyl linoleate, F = monostyrene-dimethyl linoleate, and G = distyrene-trimethyl linoleate.

merized by the styrene monomer.

It was verified further by studying the copolymerization reaction that two or more conjoint fatty acid esters were linked together between one or more styrene molecules. Gel permeation chromatography (GPC) was used in this work to define the various oligomeric and polymeric styrene-methyl linoleate compounds formed during the styrenation reaction. By regulating the reaction conditions, it was possible, as shown in Figure 2, to synthesize a material possessing a structure inherently equivalent to the copolymer product shown in equation 1. The relative amounts of the styrene-methyl linoleate molecular combinations are affected by changing the stoichiometric amount of catalyst only (chromatogram II) and by changing the amount of catalyst in combination with a change in reaction temperature (chromatogram III). Chromatogram I depicts the results of a styrene-rich reaction condition having considerable unreacted monomeric methyl linoleate and a high degree of oligomeric and polymeric styrene.

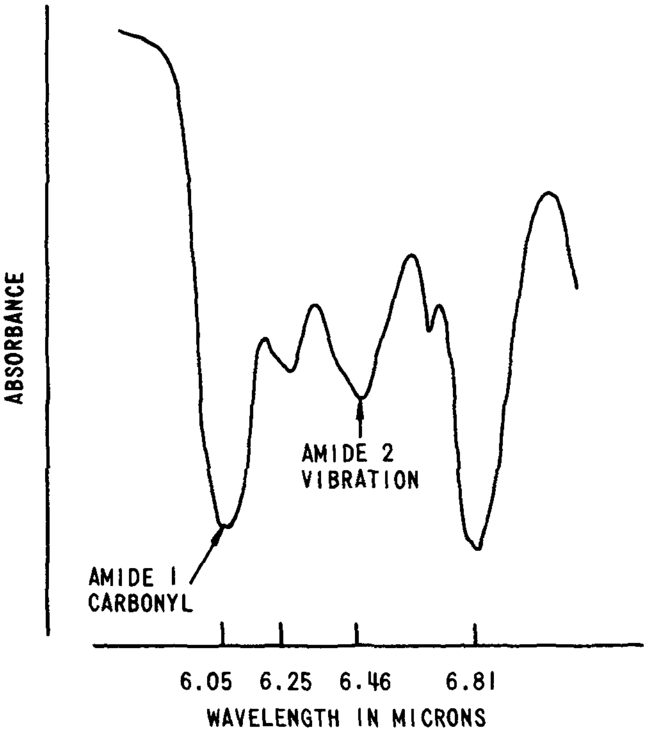
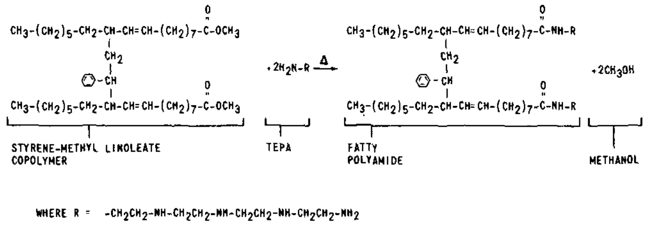


FIG. 3. Sectional IR spectra of the styrene-methyl linoleate copolymer-tetraethylenepentamine reaction product.

The final step in the synthesis of the fatty polyamide is amidation of the styrenated product. This is accomplished by reacting the styrene-methyl linoleate copolymer with the correct stoichiometric amount of the polyamide, TEPA, as shown in equation 2:



Styrene-methyl linoleate copolymer reacted with tetraethylene pentamine to form fatty polyamide

The reaction between the amine and the copolymerized fatty acid ester is interesting, since TEPA has both primary and secondary amino groups. Both may be considered as potential reaction sites with the ester group in forming this amide. The secondary nitrogens possess a greater basicity and are, therefore, expected to have greater reactivity with the ester group than the primary amine nitrogens. The point being made is that the greater the degree of secondary amine reaction with the ester, the greater the amount of free primary nitrogens; conversely, the more primary amine nitrogens that react with the ester, the greater the amount of free secondary amine nitrogens. Since greater epoxy-

TABLE I

Typical Properties for Alkyl-Aryl Polyamide Derived Using Synthesis Procedure Described

Property	Value
Refractive index at 25 C	1.5236
Molecular weight (VPO)[a] (g/mole)	1,000
Amine value[b]	440
Viscosity, CPS[c] at 25 C	5,000

[a] VPO = vapor phase osmometry.

[b] Amine value represents the determination of total amine nitrogen within the compound and does not differentiate between primary, secondary, or tertiary amines.

[c] CPS = centipoise.

amine crosslinking reaction is achieved with primary amine nitrogens than with secondary amine nitrogens, the manner in which the amines react with the ester group will determine the eventual reactivity of the polyamide with epoxide groups.

It was determined that the rate of addition of the TEPA to the styrene-methyl linoleate copolymer was an important factor in governing the structure of the polyamide. IR analysis was a useful tool for monitoring the progress of the reaction. The IR spectrum of the fatty polyamide derived from the reaction between the copolymer and the polyamine is shown in Figure 3. The structure of the amide can be correlated to the amide 1 carbonyl absorption at 6.05 μ and the amide 2 vibration appearing in the 6.46 μ region. The sections of the spectrum not pictured were representative of the structures inherent to the copolymer and the remaining R-group of the polyamine.

Listed in Table I are some typical properties for the alkyl-aryl polyamide derived using the synthesis procedure described.

The product was found to be quite soluble in liquid epoxy resins and readily converts them into hard, infusible compositions by the curing mechanism of the amine and amide groups with oxirane linkages. In addition to curing epoxy resins, the alkyl-aryl polyamide has the capability of stabilizing cells of air which have been whipped into a mixture of the polyamide and a liquid epoxy resin. This property makes the material suitable for use in the preparation of foamed or frothed compounds. A typical formulation used for patching external voids in molded rigid urethane foam parts or filling cells in paper honeycomb is given in Table II.

TABLE II

Formulation and Processing Parameters for Foamed Patching Compound

Components	Wt (g)
Epon resin 826	110
Versamide 140	74
Alkyl-aryl polyamide	15
Phenolic microballoons	35
Cab-O-Sil, M-5	4
Mixing conditions[a]	**Time (min)**
Resin and amides[b]	
92 rpm	1
170 rpm	1
Resin, amines, and filler[b]	
92 rpm	1/4
170 rpm	1
Properties	**Values**
Density (lb/ft^3)	22
Hardness (Shore A)	96

[a] Using a Hobart Kitchen Aid mixer.

[b] Mixing temperature = 100 F.

In addition to the above application, the polyamide material was employed successfully as a catalyst-crosslinking agent in rigid urethane foam systems.

ACKNOWLEDGMENTS

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