

Coating Compositions for a Can and their Properties

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ABSTRACT

Special requirements are currently imposed on paints and varnishes for the food can insides, associated primarily with the resistance to sterilization in various corrosive environments. Epoxy-phenolic coatings, including those that do not contain bisphenol A, replaced by low-toxic bisphenol E, meet these requirements. Coatings based on such materials possess a number of valuable properties, including good resistance to aggressive environments, drawability, hardness, etc. However, epoxy-phenolic coatings also have a number of disadvantages, which arise from spontaneous conglomeration and association processes that visually can be traced as a viscosity increase at storage. This paper is to evaluate the contribution of each polymer component of the composition in order to eliminate the negative effects of side processes that occur in epoxy-phenolic coatings during storage.

Keywords: can coating, epoxy-phenolic coatings, tin-plate varnishing

INTRODUCTION

Can coating, or varnishing of tin-plate for canning application, refers to various methods of coating with varnishes and enamels [1-7].

- coating sheet and band materials by rolling using rubber/polyurethane rollers;
- electrostatic coating by applying spray substance. As it passes a high-voltage electrostatic field (12-140 kV), varnish particles gain a negative charge as they are sprayed through the slit electrodes. Once they are sprayed, particles deposit on a grounded metal container or band, which is about to be coated. Electrostatic coating is in a common use for varnishing chrome-finished tin plate strips;
- electrophoretic coating of metal or finished packing by applying aqueous film-forming material with little water-soluble organic solvents. This is carried out at a DC voltage of 100-150 V. The article being coated acts here as an anode, while the bath – as a cathode;
- coating using compressed air sprayers or vapor pressure of own solvent (efficiency is little, but the use of solvents is significant). This method is for applying paint to various small cans as they travel the production line, and varnish to stamped cans, if necessary.

Roller coating is now in a common use in the canning industry, as it is a high-performance process that gives a varnish coating of a uniform thickness, which can be easily controlled, and can be applied to surfaces that are easy to manufacture, not mention the ability to switch varnishes [8-12].

Quality control applied to materials that go in coatings is essential for compositions used in coating food/beverage cans and associated articles. Requirements that exist for physical, mechanical and protective properties of can coatings are high. On top of this, cans must be safe for foody contents, considering the long period of storage.

When cans and can lids go from the production line, cured membrane is checked for appearance. By standard, coating has to be uniform, solid, smooth, without cracks and bubbles, and have a color of varnish or enamel. From the inside, coated cans and lids may have some defects (tin plate darkening, signs of coating been rubbed off along

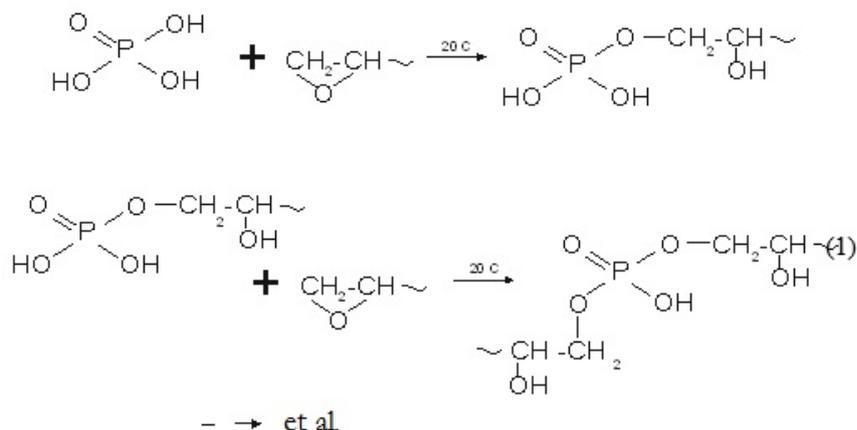


Figure 1. The α -oxide group of epoxy oligomer in reaction with phosphoric acid

a longitudinal seam, multi-shaded effect) if the surface was covered with a second layer of coating from top to bottom, from side to side [9, 11-13].

The inner varnish or enamel coating of cans and can lids must be resistant to sterilization, give no foreign smell and taste to distilled water, and leave no sediments behind when sterilized (sterilization medium must remain light and transparent). After sterilization, there should be no visible changes on the coating. For some aluminum cans that are for fruits and vegetables, inner coating should be without pores when checked using a copper sulphate solution. Lithographed cans and can lids should have a clear imprint of reproduced original with accurate color of approved samples [14-17].

The standard outer coating should be uniform, solid, smooth, without leaks, stains and bubbles, and be resistant to sterilization in water.

Epoxy-phenolic coatings are demanded compositions for food and beverage cans that occupy 75-77% of the market [16, 18]. By standard, epoxy-phenolic coatings must have a range of properties, such as good resistance to aggressive environments, stamping resistance, adhesive strength, drawability and hardness. These materials are cured in hot drying units, while the very formation of coating occurs in the presence of acid catalyst [19, 20]. However, epoxy-phenolic coatings also have a number of disadvantages, which arise from spontaneous conglomeration processes that visually can be traced as a viscosity increase at storage.

Many authors [21] associate these phenomena with spontaneous formation of hydrogen bonds between phenolic hydroxyl and methylol groups in the phenol-formaldehyde oligomers. Once the probable reason was established, solutions were introduced to prevent phenomena associated with O-alkylation of a phenolic hydroxyl group [21], and with partial replacement of methylol groups by alkoxy groups.

However, despite the decrease in the rate of viscosity increase in epoxy-phenolic coatings, storage-based consistency of coating (its appearance and resistance to sterilization, in particular) is far from high.

Phosphoric acid and its derivatives, which act as curing agents, are in the core of epoxy-phenolic coatings.

At the same time, the α -oxide groups of epoxy oligomers can enter into various reactions with mineral acids even at low temperatures [20].

When the phosphoric acid reacts with the α -oxide group, opening of the epoxy ring occurs and a secondary hydroxy acid group is formed. Because the phosphonic acid is multifunctional, this reaction leads to a partial cross-linking on the oligomeric matrix, causing an increase in its molecular weight and, as a consequence, an increase in system viscosity.

In theory, these processes cause a change in the morphology of a coating when it cures, theory encouraging the appearance of a multitude of surface defects.

Given that oligomers make up 90% of a coating composition, Therefore, even a low concentration of the α -oxide groups will spark side reactions.

Thus, the quality of epoxy-phenolic coatings is dependent upon the oligomeric component and the catalyst system, which portion and quality attributes are essential for a choice.

METHODS

The process of combining epoxy and phenol-formaldehyde resins in the presence of some catalyst is not that simple, considering so many physical processes (association, conglomeration, etc.) that occur spontaneously in

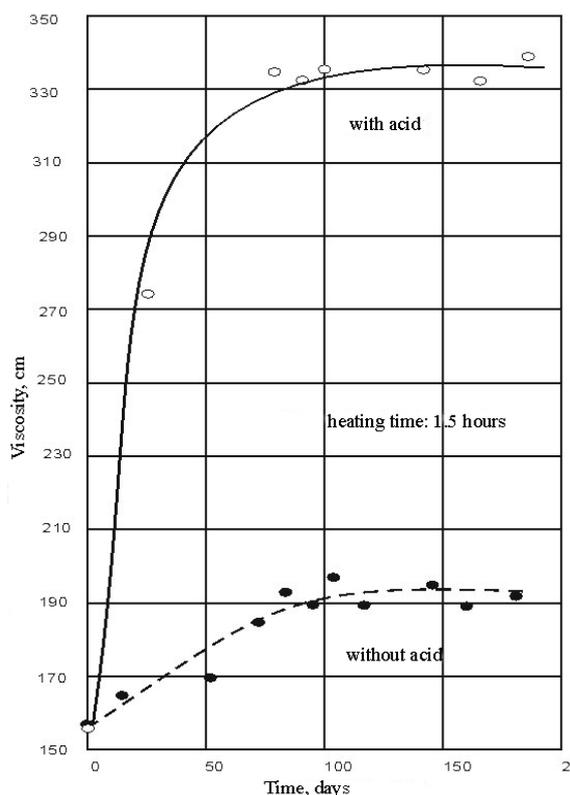


Figure 2. Relative Viscosity Dynamics for Epoxy-Phenolic Systems with and without Phosphoric Acid Added (Heating Time: 1.5 hours)

resin solutions. Therefore, the issue is to assess the character of viscosity increase in epoxy-phenolic coating compositions.

To solve this problem, phosphoric acid was investigated in interaction with various types of epoxy and phenol formaldehyde oligomers under conditions simulating the production and storage of epoxy-phenolic coatings.

Production, which was a process of combining two oligomeric matrices and breaking of intramolecular bonds, especially h-bonds that cause the association of phenolic hydroxyl groups of the phenol-formaldehyde oligomer with the secondary hydroxyl groups of the epoxy resin oligomer, has been performed at 120°C for a certain interval of time.

Because epoxy-phenolic compositions contain phosphoric acid, which is a catalyst, introduced into the system at the final stage of production, interaction analysis applied to both types of oligomers.

The behavior of epoxy-phenolic compositions, as well as the behavior of their components, was evaluated by determining conditional viscosity, as indicated in GOST 8420, conditional viscosity using the Ubbelohde Viscometer, and by addressing turbidimetric titration data.

RESULTS

In manufacturing, the effect of side processes that occur in epoxy-phenolic systems can be weakened at the stage when epoxy and phenol-formaldehyde oligomers are combined by heating.

We have evaluated how this process affects the viscosity properties of epoxy-phenolic coatings with time. An epoxy oligomer with a molecular weight of 4.500–5.000 was chosen as the epoxy component to combine with a phenol formaldehyde component represented by a phenol para-tertiary butylphenol formaldehyde oligomer with a molecular weight of 300–400. Oligomers were heated at 120°C. Conditional viscosity was measured using a viscometer B3-4. Once oligomers were heated, phosphoric acid was added to the epoxy-phenolic composition in a formulation quantity. Then, compositions were placed in a sealed dark glass container and stored in dark at 20–30°C. Compositions were regularly checked for conditional viscosity changes using a viscometer B3-4 at 20±0.5°C.

The assay revealed an extremal curve of heating effect versus conditional viscosity with a duration low of 1.5 hours (Figure 2).

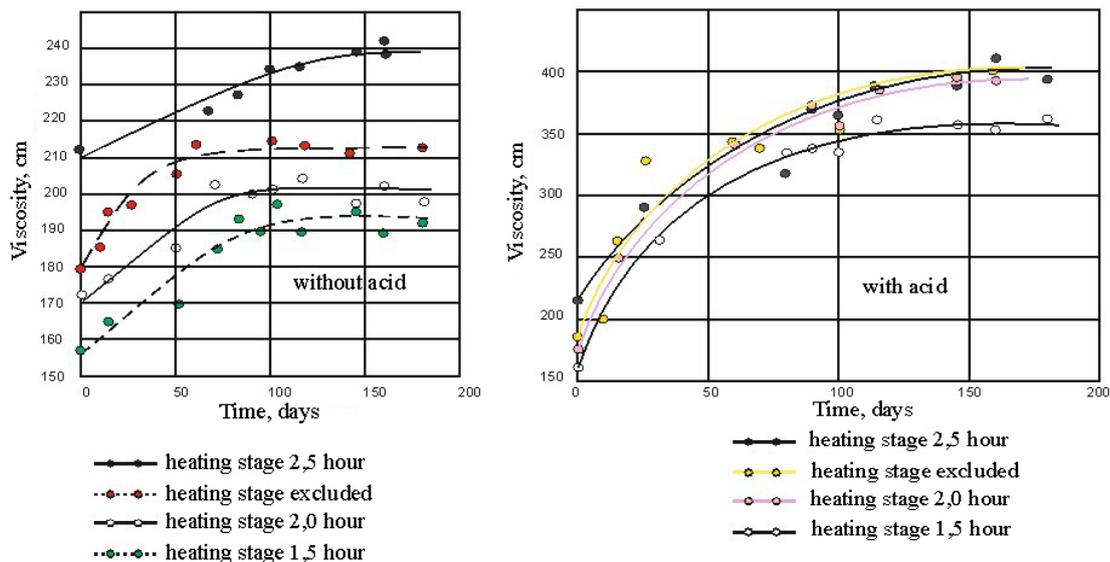


Figure 3. Relative Viscosity Dynamics for Epoxy-Phenolic Systems with and without Phosphoric Acid Added

For epoxy-phenolic compositions made by heating with or without additive, which was a phosphoric acid, viscosity increase was a typical case, which was sharp during the first 100 days, and then more smooth, reaching a high at a 150-day follow-up (Figure 3).

In magnitude, viscosity increase was sharper in compositions containing phosphoric acid than in those without it. The increase in conditional viscosity took place at 200 days of aging in both compositions, but those that had no acid added to them after 1.5 hours of heating displayed an increase by less than 50 seconds, and those that had displayed an increase by almost 200 seconds (Figure 3).

The same is true for all compositions regardless of heating time, including those that were hot heated (Figure 3).

Since heating encourages the destruction of intermolecular bonds in oligomeric structures, the effect that a solvent system has on this process based on composition was also evaluated. Traditionally, epoxy-phenolic compositions use cellosolve solvent in combination with aromatic hydrocarbons, but our system of choice was the ethyl cellosolve - xylene combination.

Evaluation data on the effect that a solvent system composition has on the process of combining epoxy and phenol-formaldehyde oligomers by heating displayed that increase in the polar component reduces product viscosity at heating and at storage (Figure 3).

Thus, combining oligomers by heating can be beneficial, if heating time is optimized. The fraction of new structures, formed from h-bonding between phenolic hydroxyl groups of the phenol-formaldehyde oligomer and secondary hydroxyl groups of the epoxy resin oligomer, can be reduced by increasing the share of non-polar solvents in the epoxy-phenolic composition.

Heating does not guarantee the elimination of spontaneous increase in viscosity during storage, but phosphoric acid will make it significant, if added. This contribution was assessed by evaluating the effect of acid on each component of the epoxy-phenolic composition.

The effect of epoxy component on the acid-based composition's stability was evaluated by tracing conditional viscosity of epoxy oligomer solutions in a mix of ethyl cellosolve and xylene (60/40 ratio).

With the solution of epoxy-based oligomer of phosphoric acid (0.73% by weight), the system viscosity increases by 15% even at a temperature of 200°C. When this happens, one can observe a jump in the figure during the first hour, but then, the viscosity of system does not display any significant changes (Figure 4). If plotted, this change is at some point plateaued, probably because of the balancing of association and structuring processes in the presence of a solvent, which affected the intermolecular bonds between macromolecules.

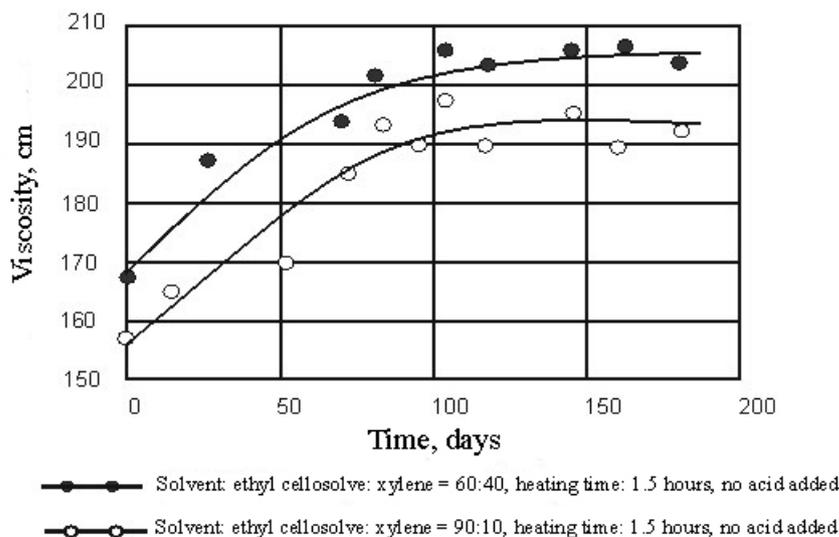


Figure 4. The Effect of Ethyl Cellosolve – Xylene System with Different Component Proportion on Relative Viscosity of Epoxy-Phenolic Compositions at Storage

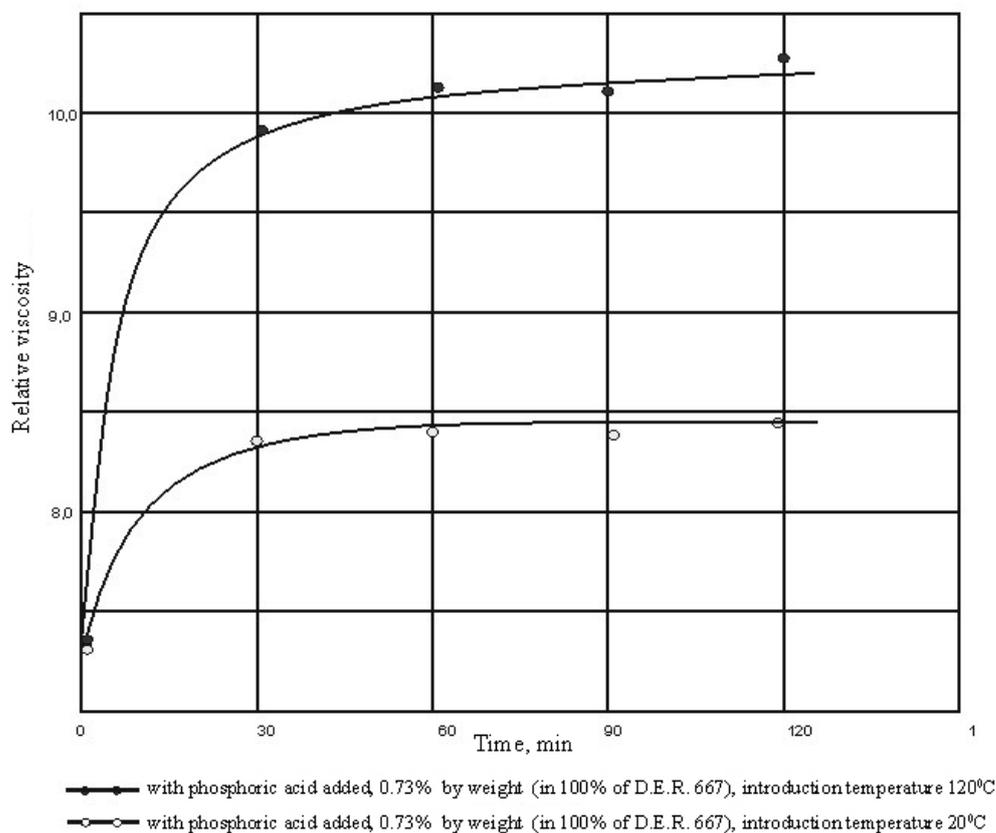


Figure 5. Relative Viscosity Dynamics for Epoxy Oligomer in Presence of Phosphoric Acid Added at Different Temperatures

The turbidimetric growth curves in [Figure 6](#) suggest that an increase in the molecular weight of an epoxy oligomer took place in the presence of phosphoric acid. In this case, three-dimensional spatial cross-linking does not occur only due to the linear structure of the initial oligomer.

With temperature increasing up to 120° C, which is the temperature of making epoxy-phenolic compositions by heating, in the presence of phosphoric acid, system viscosity increased by as much as 40% ([Figure 5, 6](#)).

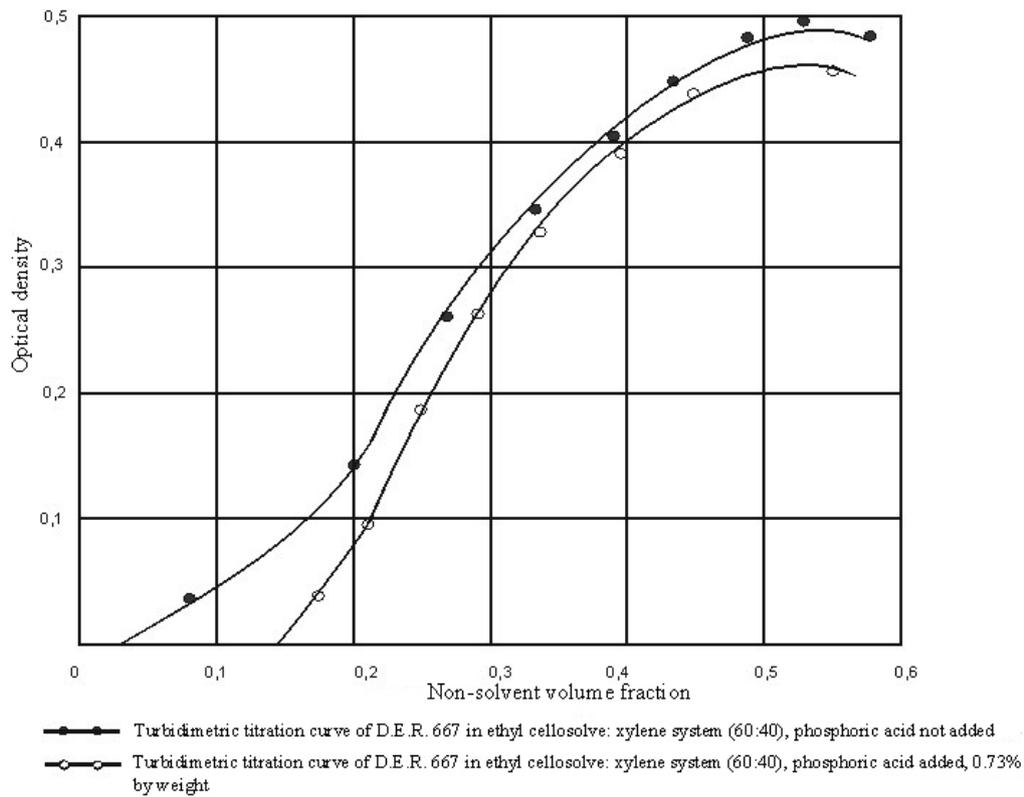


Figure 6. Turbidimetric Titration Curves of Epoxy Oligomer Solution with and without Phosphoric Acid

The increase in the activation energy means intensification of the secondary processes of association and structuring.

As expected, a change in the concentration of phosphoric acid also affects the viscosity of solutions of the epoxy oligomer (**Figure 7**). The higher this concentration is, the greater is the jump in viscosity.

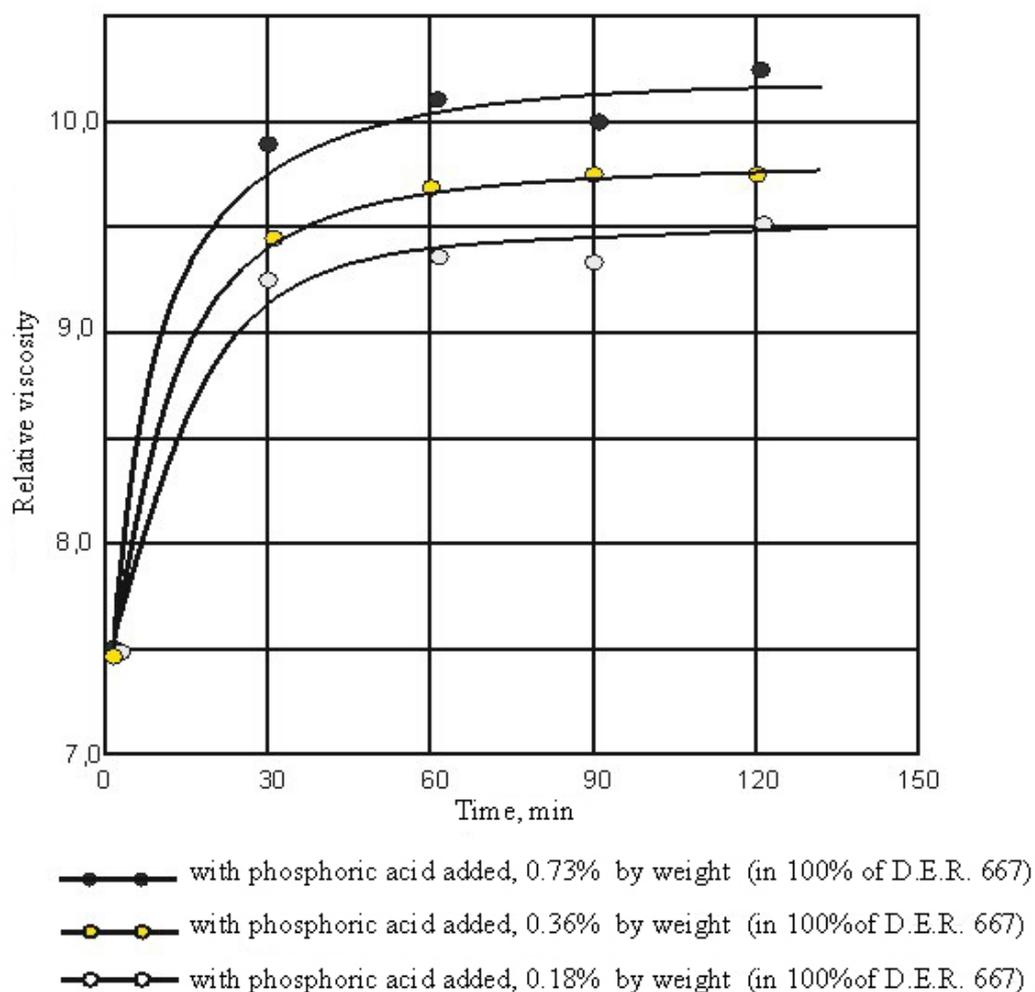


Figure 7. Relative Viscosity Dynamics for Epoxy Oligomer in Relation to Different Amounts of Phosphoric Acid Added, Introduction Temperature 120°C

Note that a change in the composition of the solvent system (replacing of some non-polar xylene with ethyl cellosolve until 90/10 ratio) will give a lower increase in viscosity if takes place in the presence of 0.73% of acid. This fact suggests that not only chemical reactions from [Figure 1](#) take place in the presence of acid, but also the physicochemical processes, such as the formation of hydrogen bonds between the OH groups of the acid and the α -oxide groups of the epoxy oligomer. These processes result in partial association of macromolecules and in structures formed in the solution of this oligomer.

The analysis of the effect of phosphoric acid in different concentrations on the viscosity of phenol-formaldehyde resin being heated revealed that the viscosity increases linearly with time. The absolute increase is not significant compared to that in the case of the epoxy resin ([Figure 8](#)).

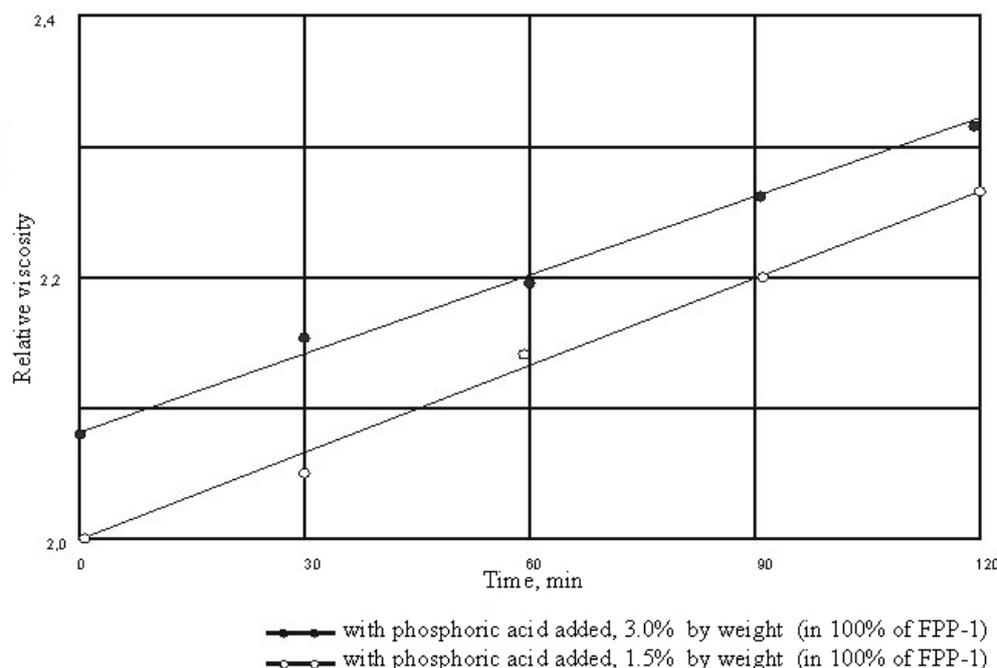


Figure 8. Relative Viscosity Dynamics for Phenol Para-Tertiary Butylphenol Formaldehyde Oligomer in Relation to Different Amounts of Phosphoric Acid Added, Introduction Temperature 120°C

Thus, the main contribution to the increase in molecular weight of epoxy-phenolic compositions is made by the reaction of epoxy resin with phosphoric acid during storage.

CONCLUSIONS

This paper investigated the process of combining epoxy and phenol-formaldehyde resins by heating, performed to make epoxy-phenol composition with an epoxy oligomer with a molecular mass of 4.500–5.000 and a phenol para-tertiary butylphenol formaldehyde oligomer with a molecular weight of 300–400. The optimal timing parameters were established for this process. Trials show that first 100 days are the period of jumps in viscosity, induced probably by the rapid spontaneous occurrence of physical side processes. At a 150-day follow-up, growth curves end plateaued, due to probable relaxation of these side processes.

The contribution of a curing catalyst, which was the phosphoric acid, was revealed regarding the process of making a composition and the behavior of these compositions at storage. As established, this acid should be eliminated from the composition at the stage of production (combination of resins by heating), but added back at subsequent stages.

The analysis of the effect of phosphoric acid on the epoxy resin revealed that it acts as a booster to the viscosity of solutions, especially when those are heated to 120°C. Even in amounts smaller than in the formula, phosphoric acid still leads to a significant increase in viscosity, when added.

Turbidimetric titration curves show that with phosphoric acid added to the solution of the epoxy resin in ethyl cellosolve, the molecular weight of epoxy resin oligomer increases, probably because of the reaction with the α -oxide groups.

In the case of the phenol-formaldehyde component, phosphoric acid leads to an increase in viscosity as well, but this contribution is not significant if taking it in the overall picture of structuring.

Thus, this paper gave some practical recommendations for manufacturing epoxy-phenolic compositions.

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