On the Thickening Mechanism of Unsaturated Polyesters by Alkaline Earth Oxides and Hydroxides

ERNESTO L. RODRIGUEZ, *The BF Goodrich Company, Avon Lake Technical Center, P.O. Box 122, Avon Lake, Ohio 44012*

Synopsis

The mechanism that describes the thickening process of unsaturated polyester resins with inorganic oxides and hydroxides is presented. This mechanism includes the formation of water, the formation of the ion cluster, the network expansion and the equilibrium, where the viscosity reaches a constant value.

INTRODUCTION

The viscosity of unsaturated polyester resins with acidic groups at the end of the unsaturated polyester increases with the addition of metal oxides or hydroxides belonging to the group IIA such as MgO, $Mg(OH)_2$, CaO, $Ca(OH)_2$, and ZnO.[1,2]

This increase in viscosity or thickening reaction is an important parameter in technological materials such as Sheet Molding Compounds (SMC) where the rate of thickening and the resulting viscosity determine the moldability of the compound and therefore have an influence on the final properties of the SMC.[3,4] Applications of SMC are found in automobile body panels, appliances, and recreational products.[1,2]

The thickening reaction between unsaturated polyesters and magnesium oxide has been discussed by several authors.[4-7] Very little has been reported on the thickening reaction of unsaturated polyesters using other inorganic salts such as $Mg(OH)_2$ CaO, $Ca(OH)_2$, and ZnO. Three theories have been proposed to explain the thickening reaction based on magnesium oxide. The first one postulates a two stage reaction where a high molecular weight salt is formed by the reaction between magnesium oxide and the carboxilic groups on a polyester chain followed by the formation of a complex between the salt and the carboxyl groups of the ester linkages.[5-8] The second one postulates the formation of chain extension and chain entanglement where the dicarboxylic acid groups on a polyester chain react with magnesium oxide yielding very high molecular weight species (via condensation polymerization) and thus giving rise to a large increase in viscosity.[4,7] The third one postulates the formation of ionic sites with close resemblance to other polymer containing metal ions or ionomers.[9-10]

In this note experimental evidences from infrared spectroscopic studies are presented to further explore the thickening mechanisms of unsaturated polyester with inorganic salts.

EXPERIMENTAL

A general purpose unsaturated polyester resin (OCF-E903-1) was used in the study. The acidic value was 20.2 mL of 0.5N KOH/g resin. The water content of the resin was 0.05% obtained by the Karl Fisher titration method. The viscosity of the resin at 60% nonvolatile (40% styrene monomer) was 376 cps determined by a Brookfield viscometer model RVT using the spindle number 3 and 60 rpm. The inorganic oxides and hydroxides, analytical grade, were obtained from Fisher Scientific. The infrared spectra were recorded on a Perking Elmer infrared spectrophotometer model 1330. Sodium chloride cells were used for the infrared analysis. For the mixture preparation, the polyester and the inorganic salt were mixed with an air driven stirrer. The mixtures were stored in sealed containers and under controlled room environment.

RESULTS

The infrared spectra for unsaturated polyester have been described by several authors.[11-13] Figure 1A shows the infrared spectrum for the unsaturated polyester alone. Figures 1B through 1E correspond to the thickened polyester resin with $Mg(OH)_2$, MgO, ZnO, and $Ca(OH)_2$, respectively for a 600 h reaction time at 23C. In Fig. 1 from 2000 cm^{-1} (from 5.0 to 12.5 μm) no significant changes in the location of the absorption bands were observed with the addition of the inorganic oxides. However, in the absorption region from 4000 cm^{-1} to 2500 cm^{-1} (from 2.5 to 4.0 μm) a strong band appeared in the region 3440 to 3540 cm^{-1} for all the inorganic salts. This absorption band is assigned to the appearance of a O—H stretch, an intermolecular hydrogen bond. These results suggest that the thickening reaction of an unsaturated polyester resin is accompanied by the formation of water.

Figure 2 shows the infrared spectra for the unsaturated polyester thickened with $Mg(OH)_2$ as a function of time at 23C. The intensity of two absorption bands increased with time. The first absorption at 3695 cm^{-1} corresponds to the O—H stretch intermolecular hydrogen bonding assigned to water formed during the thickening reaction. These results suggest that more $Mg(OH)_2$ is reacted with the acidic groups of the polyester as a function of time. Figure 3 shows the infrared spectrum for the $Mg(OH)_2$ alone where the band at 3695 cm^{-1} corresponds to the free O—H stretching.[14]

DISCUSSION AND CONCLUSIONS

It is recognized that organic acids exist as dimers in nonpolar solvents.[15] The carboxylic acid functional groups of an unsaturated polyester in styrene monomer may be held together by two hydrogen bonds as follows
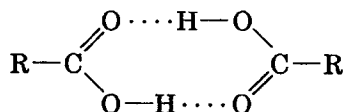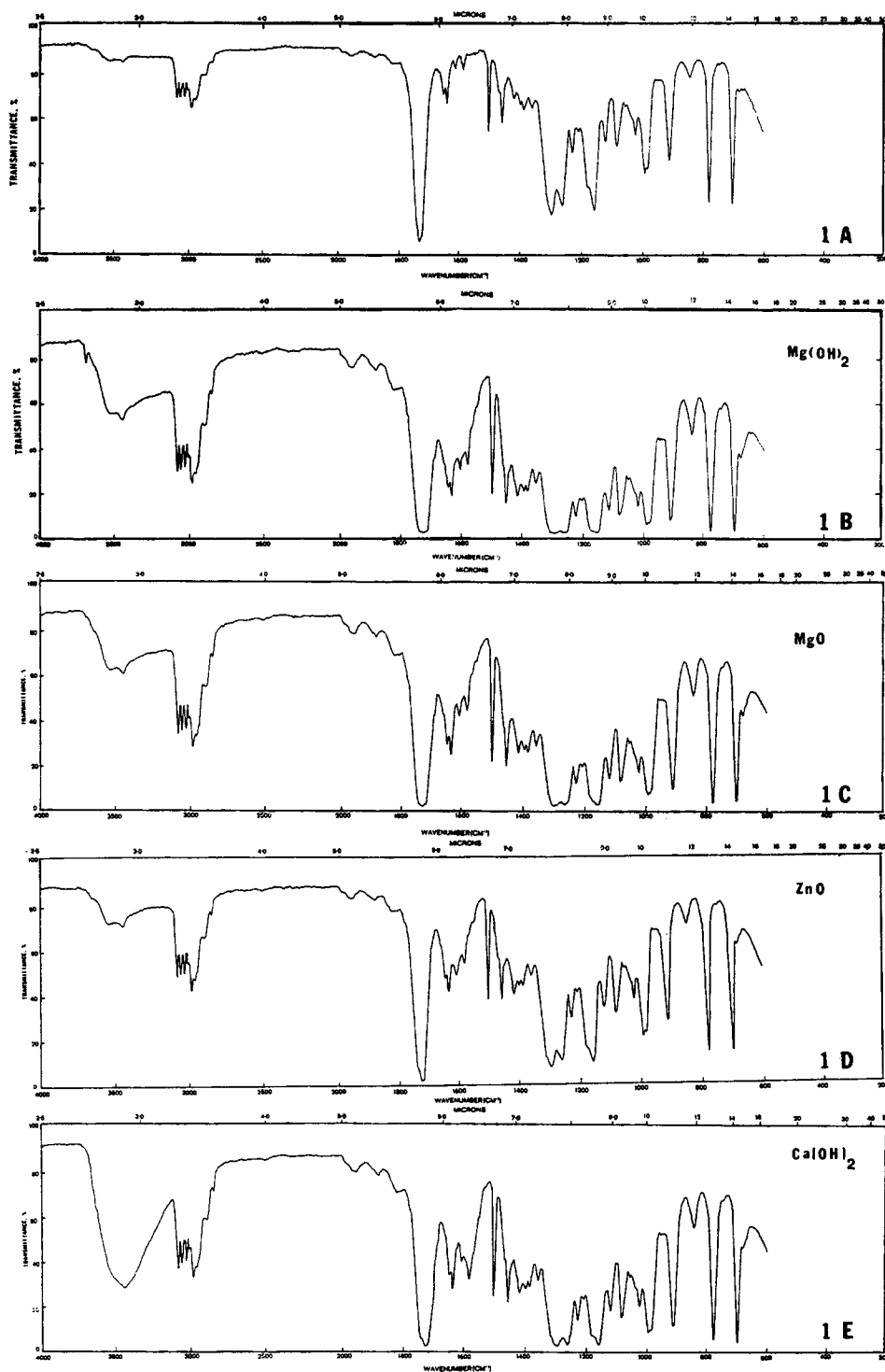
Fig. 1.   Infrared spectra for 4 weight percent of inorganic salt after 600 h reaction time.
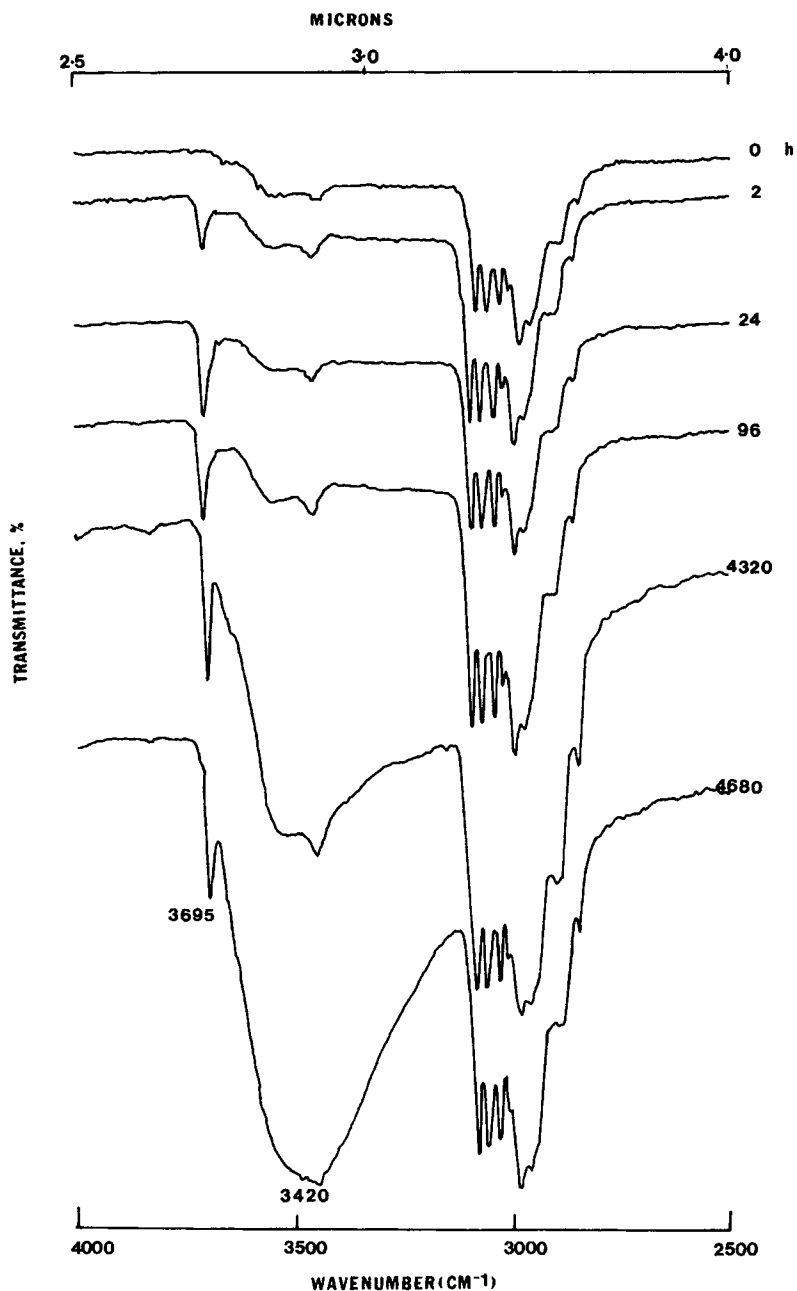
MICRONS

Fig. 2.   Infrared spectra for 4 weight percent of Mg(OH)$_2$ as a function of time.

In unsaturated polyester and inorganic oxides systems, the first step in the thickening reaction is the interaction between the inorganic salt and the acidic groups. The solubility of inorganic salts in unsaturated polyester is relatively low.[16] It is believed that a diffusion process controlled by the ionic interaction between the metal of the salt and the acidic groups of the polyester takes place in the first step.
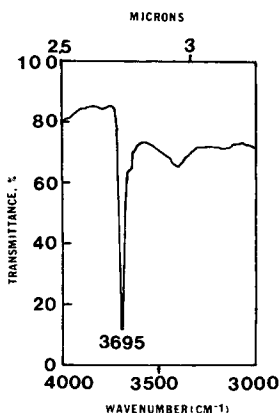
Fig. 3. Infrared spectra for $Mg(OH)_2$.

Among the inorganic oxides, MgO is known to be more reactive than $Mg(OH)_2$, $Ca(OH)_2$, and ZnO in the thickening process of unsaturated poly-esters.[2] It is also known that magnesium oxide reacts with water evolving heat to form hydroxides. On the other hand, magnesium hydroxide is insoluble in water where there is a decided tendency to nonionic behavior despite the high polarizing ability of the Mg^{+2} ion.[17] Therefore, MgO is more reactive with the acidic groups of the unsaturated polyester producing a faster thickening reaction.

F. B. Alve[5] has shown that for MgO the presence of water is necessary for the thickening reaction to take place. The residual from excessively high water levels (a by-product of the polyesterification process which is not completely removable at the completion of the resin synthesis) leads to a considerably increased early rate of viscosity with magnesium oxide.[3]

J. W. Nicholson et al.[18] using infrared spectroscopy have shown that magnesium ions (from magnesium hydroxide) in a partial hydrolized polyacrylate show considerable covalent character resembling more a bridging bidentate structure of the form

$$R-C \begin{array}{c} O \rightarrow M \leftarrow O \\ \\ O \rightarrow M \leftarrow O \end{array} C-R$$
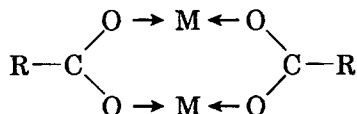
For acidic group functionalities the ionization is demonstrated by the appearance of assymetric and symmetric $C-O$ stretching bands of the COO^- ion at 1547 and 1407 cm^{-1}.[14] These bands were not observed in our infrared measurements, which indicates that the covalent structure discussed by J. W. Nicholson[18] is most likely to take place during the thickening of unsaturated polyester in organic solvents.

From the above discussion and the infrared studies, it appears that a thickening reaction may follow the mechanism for an oxide and hydroxide as shown in Figure 4. In the mechanisms illustrated in Fig. 4, the differences between MgO and $Mg(OH)_2$ are in the character of the $COO-Mg$ bond where for MgO the bond is slightly more ionic than for $Mg(OH)_2$ but both still showing some
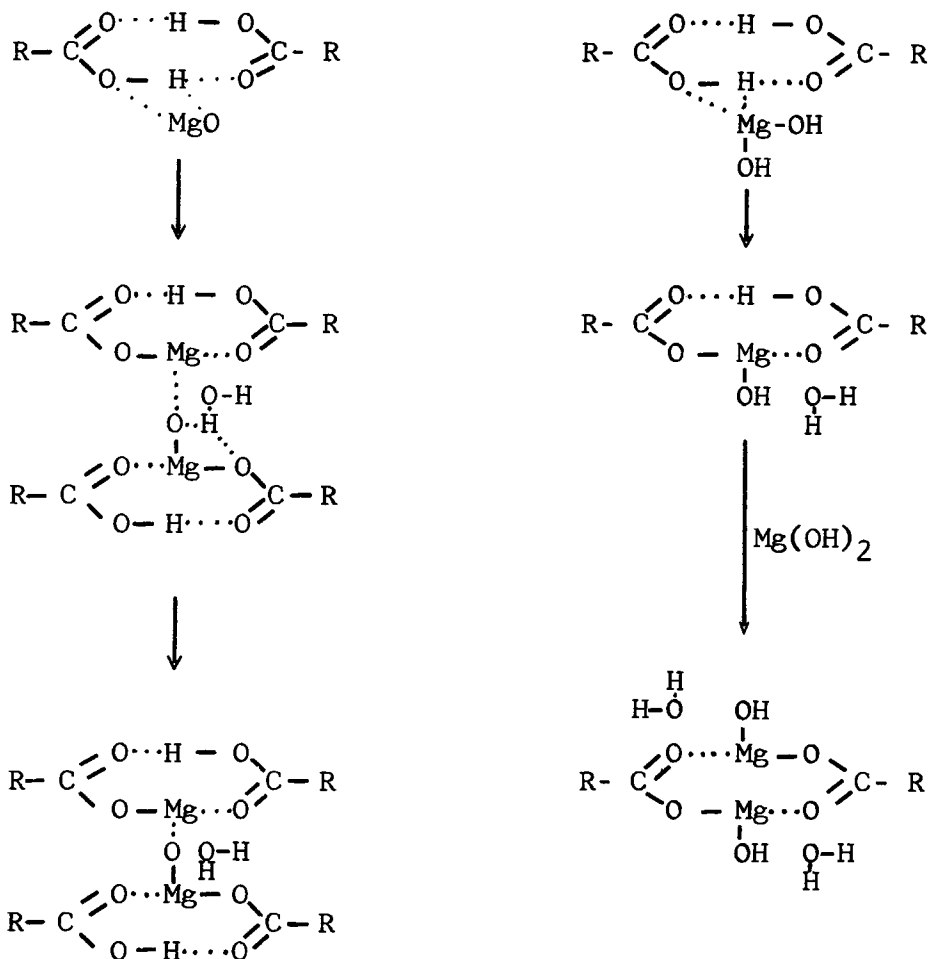
Fig. 4. Proposed mechanisms for the initial step in the thickening reaction of an unsaturated polyester.

covalent character. The water formation detected by infrared can be explained using the proposed thickening mechanisms showing in Fig. 4.

These mechanisms take into account the formation of water and the semi-covalent character of the Mg—O bond in the chemical complexes shown in Fig. 4. Of course, the experimental evidences for the proposed mechanism are mainly based on infrared spectroscopy. Perhaps other different analytical techniques such as carbon and proton NMR may be necessary to further improve our understanding of the thickening process of unsaturated polyester with inorganic salts in an organic medium.

The second step of the thickening reaction is the rapid increase in viscosity. The causes of the second step reaction are not obvious. In the SMC industry it is known that the thickening is accelerated by elevated temperatures and by a good initial mixing of the components.[1,2] This may suggest that the reactions responsible for the second stage thickening are diffusion dependent. From the structures shown in Fig. 4, it is possible that a network formation takes place.
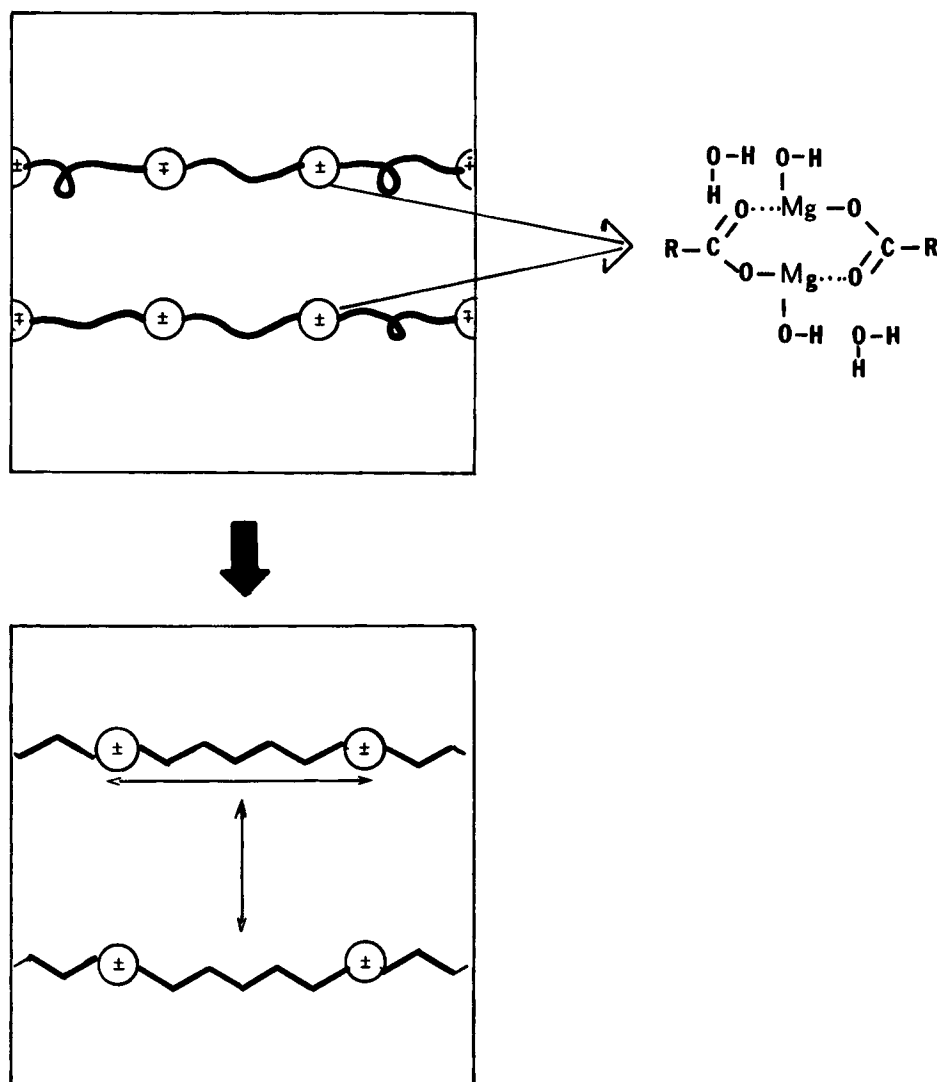
Fig. 5. Illustration of the network expansion responsible for the rapid rise in viscosity.

The bridging between adjacent units shown in Fig. 4 through hydrogen bonding and ionic interactions between the metal ion of the salt and oxygen groups (from carboxilic and alcohol groups) can lead to a significant rise in viscosity.[9,10] Again, for this process to occur, a diffusion of the polymer chains through a viscous medium is required which is driven by the ionic interactions between the polar groups of the polymer chains and the metal ion of the inorganic salt.

Notice that the multiplication of ionic clusters (regions where the metal ions of the salt and the carboxylic groups of the polyester are located) may cause another phenomenon, which is the network expansion. This is similar to the coil expansion process found upon the neutralization of the acidic groups in polyacrylic acid with a strong base such as KOH. The neutralization of the acidic groups in polyacrylic acid generates negative charges along the backbone
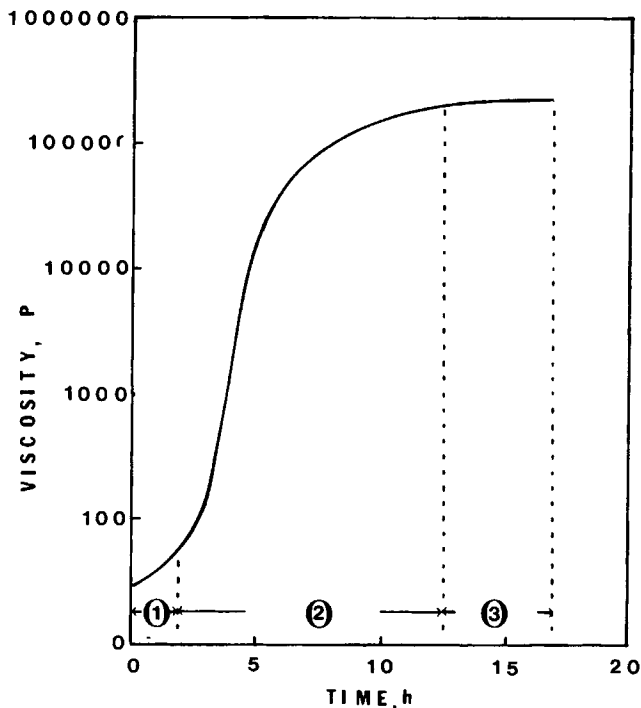
Fig. 6. Typical viscosity/time curve for a chemically thickened system (from reference 1, p. 60). The three steps in the thickening process are illustrated by the circled numbers (see text).

of the polymer. Repulsion of like charges causes uncoiling of the chain into an extended configuration which then results in an increase in viscosity or a thickening effect.[19,20]

It is proposed here that as the number of ionic domains increases with time in the unsaturated polyester/inorganic salt system, the repulsion between the ionic clusters causes an overall network expansion which results in a rapid rise in viscosity. This network expansion is the sum of contributions from individual and collective coil expansion between the ionic domains. This concept is illustrated in Figure 5.

Experimental evidences for the formation of the ionic network and the network expansion can be indirectly found in experimental work reported by other authors. For example, Han et al.[21] have shown that polar solvents such as N,N-dimethylformamide (DMF) nullified the thickening process. This suggests that in the second step of the thickening process the ionic association is disrupted due to the presence of other ionic species (DMF). Rao and Gandhi[9] have also shown the formation of ionic aggregates of magnesium ions much like those observed in other ionomers by means of small angle x-ray scattering (SAXS) and the transmission electron microscopy (TEM).

Experimental support for the network expansion is also found in viscosity measurements as a function of time.[1-4,9,21-22] The viscosity increase with time follows three steps. In step one a relatively slow increase in viscosity (from 10^3 cps to 10^5 cps) is observed. In step two a rapid increase in viscosity from approximately 10×10^6 cps to 80×10^6 cps takes place, which is attributed to

the network formation and network expansion (proposed mechanism in Fig. 5). In step three the viscosity reaches a constant value. This step is a follow up of step two, where the ionic interactions and the network expansion have reached an equilibrium. Figure 6 shows a typical viscosity increase with time for a thickening process.

To conclude, the thickening process of unsaturated resins with inorganic salts is a complex problem. The proposed models in this report are supported by experimental evidences obtained from different sources and based on infrared spectroscopy and viscosity measurements. Further work is required using other analytical techniques that may further contribute to the understanding of the thickening phenomenon.

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