Thickening Reaction of Unsaturated Polyester Resins with Inorganic Oxides and the Rubber Elasticity Theory

Sheet molding compounds are increasingly becoming an important class of materials for many technological applications. These materials are expected to grow in the next decade because of the good physical and mechanical properties obtained with these materials, at relatively low cost. For instance, one of the current applications of SMC materials is in automobile body panels where a very good surface quality is a primary goal.[1,2]

A great portion of the SMC materials are based on unsaturated polyester resins. These resins, when combined with fillers and glass fibers, result in composite materials that offer combinations of properties not found in other materials such as high strength, dimensional stability with low weight and thickness, corrosion and chemical resistance, and very good surface quality.[3]

One of the keys for the success of the SMC materials has been the fact that unsaturated polyester resins can be thickened with inorganic oxides and hydroxides to yield a tack-free sheet stiff enough to permit easy handling. These inorganic materials belong to the group IIA metal oxides or hydroxides: MgO, $Mg(OH)_2$, CaO, $Ca(OH)_2$, and ZnO, the most commonly used.[3] Small concentrations of these inorganic oxides are usually enough to achieve high viscosities (10^6 p) being the ratio of 1 mol of inorganic salt to 1 mol of undiluted prepolymer, the most commonly used.

Unsaturated polyester resins are manufactured by several techniques.[3,4] Among them, the two-stage fusion reaction is found to produce polyester resins with a more reproducible thickening reaction. In a two-stage reaction the glycol and the saturated carboxylic acid are heated to 190°C until a low acid value is reached. Then the unsaturated anhydride or carboxylic acid is added. Figure 1 shows an example of a two-stage reaction between an isophthalic acid and propylene glycol, followed by the addition of maleic anhydride. The termination groups in the polymer may be one acidic group in each end, one acidic and one alcohol group, or two alcohol functionalities in the ends of the polymer chain. The nature of the functional group in the terminal points of the polyester chains is very critical to the thickening reaction with inorganic salts. In this regard, Burns et al.[5] have shown that in a series of unsaturated polyester resins prepolymers with terminal acidic groups at the two ends of the chain have shown higher viscosities with magnesium oxide than prepolymers with alcohol functionalities. Additionally, the unsaturated polyester prepolymer is usually diluted with a vinyl monomer, most commonly styrene, that acts as a crosslinkage agent and lowers the viscosity of the prepolymer.

The thickening reaction between an unsaturated polyester resin and magnesium oxide has been discussed by several investigators.[5-8] Two theories have been proposed: the first one postulating a two-stage reaction[6-8] and the second one postulating the formation of chain extension and chain entanglement.[5,9] In the two-stage reaction, it is proposed that a high molecular weight salt is formed by the reaction between magnesium oxide and the carboxylic acid groups on a polyester chain followed by the formation of a complex between the salt and carboxyl groups of the ester linkages (Fig. 2). In the chain extension/chain entanglement theory, it is postulated that the dicarboxylic acid groups on a polyester chain react with magnesium oxide (MgO) yielding very high molecular weight species (via condensation polymerization) and thus giving rise to a large increase in viscosity (Fig. 3).

Recently, Rao and Ghandhi[10] proposed that the thickening reaction is due to the formation of the ionic sites with close resemblance to other polymers containing metal ions or ionomers. Through a slow diffusion process, the metal ions aggregate to form domains that are interconnected by hydrocarbon chains. Since the molecules are held by ionic forces to the domains, the latter act like a strong entanglement point.

After the thickening reaction takes place to achieve the desired viscosity, the unsaturated sites of the polyester resin are then reacted with the styrene monomer (crosslinkage agent) via free radical polymerization to form a dense network structure.

Fig. 1.   Illustration of a two stages synthesis of an unsaturated polyester resin.
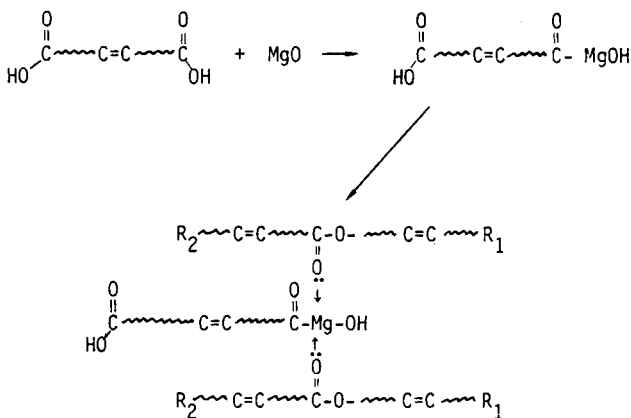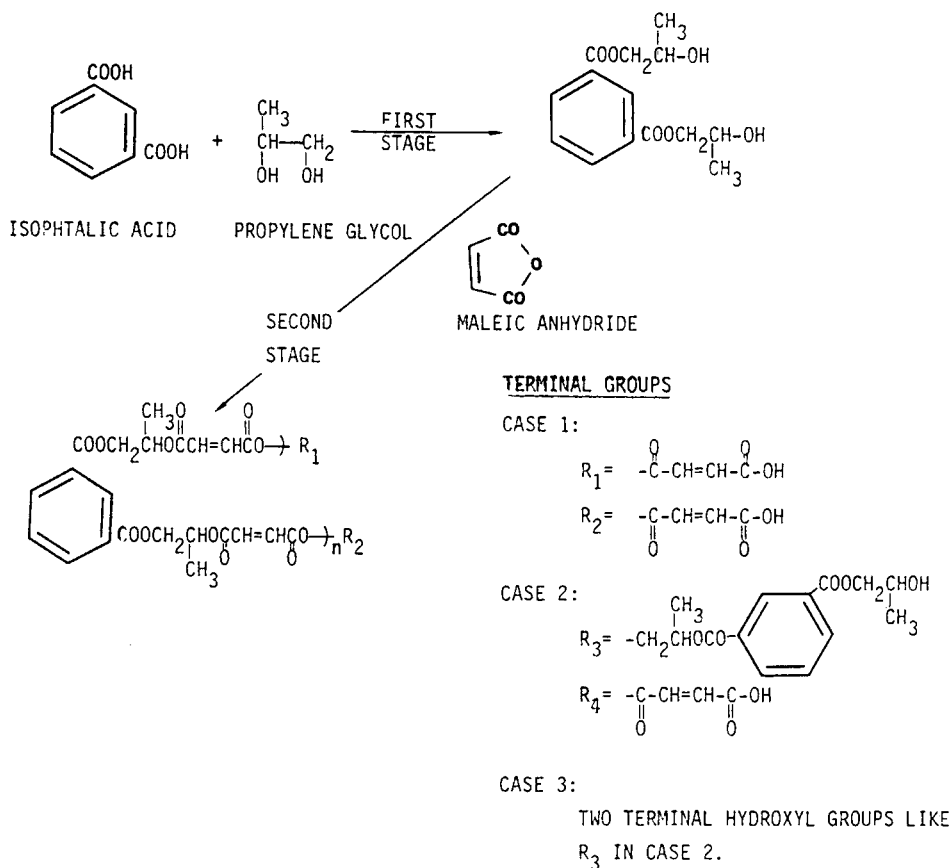

Fig. 2.   Illustration of the magnesium complex.

In this note, the theoretical description of a rigid polyester resin is presented, taking into consideration the existence of both ionic and covalent crosslinks in the final rigid network. The analysis is based on the rubber elasticity theory for soft networks which is here extended to rigid unsaturated polyester resins.
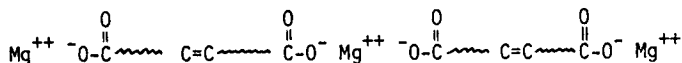
Fig. 3. Illustration of linear molecular weight species formed from terminal carboxyl groups in the unsaturated polyester chain and the inorganic oxide (MgO).

THEORETICAL DESCRIPTION OF A RIGID POLYESTER NETWORK

Unsaturated polyester resins, when cured, usually form rigid networks with glass transition temperatures well above room temperature. This is the opposite of rubber networks which usually show a glass transition temperature well below room temperature, resulting in a relatively flexible network. Thus, the main fundamental thermodynamic difference between these two systems would be in the entropic nature of the network where the rigid network should be less thermodynamically entropic.

In rubber elasticity the quantitative relation between chain extension and entropy reduction have been clarified by the research of Guth and James,[11–15] Treloar,[16,17] Wall,[18] and Flory.[19,20] The idea developed was that the retractive forces of an elastomer arise through the reduction of entropy rather than through the changes in enthalpy. From the rubber elasticity theory, the equation of state for a macroscopic network can be written as[20]

$$\sigma = \left(\frac{\partial F}{\partial \alpha}\right)_{T,V} = nRT\frac{\bar{r}_i^2}{\bar{r}_0^2}\left(\alpha - \frac{1}{\alpha^2}\right) \tag{1}$$

where RT is the ideal gas constant times the absolute temperature. $\bar{r}_i^2$ refers to the mean square end to end distance of the chain in the network and $\bar{r}_0^2$ to the mean square end to end distance of the isolated chain. α is the extension ratio. The quantity $\bar{r}_i^2/\bar{r}_0^2$ is known as the "front factor," usually taken as the unity. The quantity n represents the number of active network chain segments per unit volume. For crosslinks formed from covalent bonds

$$n = \frac{\rho}{M_c}\left(1 - \frac{2M_c}{M}\right) \tag{2}$$

where M_c is the molecular weight between crosslinks and M is the molecular weight of the repeating unit and ρ is the density.

For a rigid unsaturated polyester network, eq. (1) has to be modified to include the possible semi-ionic weak crosslinks and the physical crosslinks which are permanent loops and entanglements existing in the network structure. Therefore,

$$n = n + n_i + n_p \tag{3}$$

where n, n_i, and n_p are the concentration of chains bound by covalent bonds, ionic interactions, and physical crosslinks, respectively. Then,

$$\sigma = \left[\frac{\rho}{M_c}\left(1 - \frac{2M_c}{M}\right) + n_i + n_p\right]RT\frac{\bar{r}_i^2}{\bar{r}_0^2}\left(\alpha - \frac{1}{\alpha^2}\right) \tag{4}$$

The Young modulus can be written as

$$E = L\left(\frac{\partial \alpha}{\partial L}\right)_{T,V}$$

which yields

$$E = \left[\frac{\rho}{M_c}\left(1 - \frac{2M_c}{M}\right) + n_i + n_p\right]RT\frac{\bar{r}_i^2}{\bar{r}_0^2}\left(2\alpha^2 + \frac{1}{\alpha}\right)$$

which for small strains $2\alpha^2 + 1/\alpha = 3$ and for $\alpha = 1$. Then,

$$E = 3\left[\frac{\rho}{M_c}\left(1 - \frac{2M_c}{M}\right) + n_i + n_p\right]RT\frac{\bar{r}_i^2}{\bar{r}_0^2}$$

and, assuming $\bar{r}_i^2/\bar{r}_0^2 = 1$, then

$$E = 3\left[\frac{\rho}{M_c}\left(1 - \frac{2M_c}{M}\right) + n_i + n_p\right]RT \tag{5}$$

Equation (5) indicates that, in addition to the covalent crosslinks, the semi-ionic and the physical crosslinks should increase the stiffness of a rigid, unsaturated polyester resin.

Ion-containing polymers, more specifically thermoplastic ionomers, have been studied substantially.[21,22] Many studies have suggested that in ionomers the ions are associated in small domains where the size of the grains are about 50–60 Å.[23] Within the ionic domains, the ionic forces, unlike the covalent bonds found in chemical crosslinking, are diffused randomly and act at greater distances because they decay as the square of the distance.

A theoretical treatment of the problem of ion association and clustering in polymers has been made by Eisenberg.[24] Making various assumptions, the electrostatic energy released on the cluster formation was balanced against the net elastic energy necessary to stretch and contract the hydrocarbon chains between ions. The temperature at which these energies balanced, T_c, was identified with the temperature of transition in ionomers, about 50°C.[25] We have assumed that the clustering in ionomers is similar to the ionic interaction in a thickened, unsaturated polyester resin. Thus, from the Eisenberg theory,[24] n_i can be approximately defined by the equation

$$n_i = \rho\frac{N_{AV}}{M_{ci}}\left[\frac{16l^2}{3kT_c}\frac{\bar{r}_i^2}{\bar{r}_0^2}\frac{M_{ci}}{M}\frac{\lambda e^2}{K\epsilon r} + 2\left(\frac{n_0 M_{ci}}{\rho N_{AV}}\right)^{2/3}\right]^{3/2} \tag{6}$$

where N_{AV} is the Avogadros number, M_{ci} is the molecular weight of the repeating unit, l is the length of a C—C bond, ϵ is the dielectric constant, λ is a function of the cluster geometry, n_0 is the number of ions pairs in the multiple, T_c is the cluster decomposition temperature, e is the electron charge, and r is the distance between centers of charge.

Therefore, the theoretical description for a rigid network obtained from a thickened, unsaturated polyester resin followed by the crosslinking reaction with styrene monomer through free radical polymerization can be obtained from eqs. (5) and (6).

The above theoretical description for a rigid network would require experimental testing to confirm its validity. Figure 4 shows a representation of the covalent and ionic crosslinks in the polyester network. One of the issues that remains to be solved is the effect that the inorganic oxides may have on the physical and mechanical properties of a rigid unsaturated polyester network.

The rise in the glass transition of a polymer due to crosslinks has been studied by several authors. Gibss and DiMarzio[26] described a theory to account for the increase in the glass transition with crosslinks. Crosslinking decreases the configurational entropy and, therefore, raises the glass temperature. Gibbs and DiMarzio found that the increase in glass transition with crosslinks density follows the equation

$$\frac{T_g - T_g^0}{T_g} = \frac{BX}{1 - BX} \tag{7}$$

where T_g is the glass transition temperature of the crosslinked polymer, T_g^0 is the glass temperature of the uncrosslinked material, X is the crosslink density, and B is a constant independent of the material.

For our case, eq. (7) takes the form

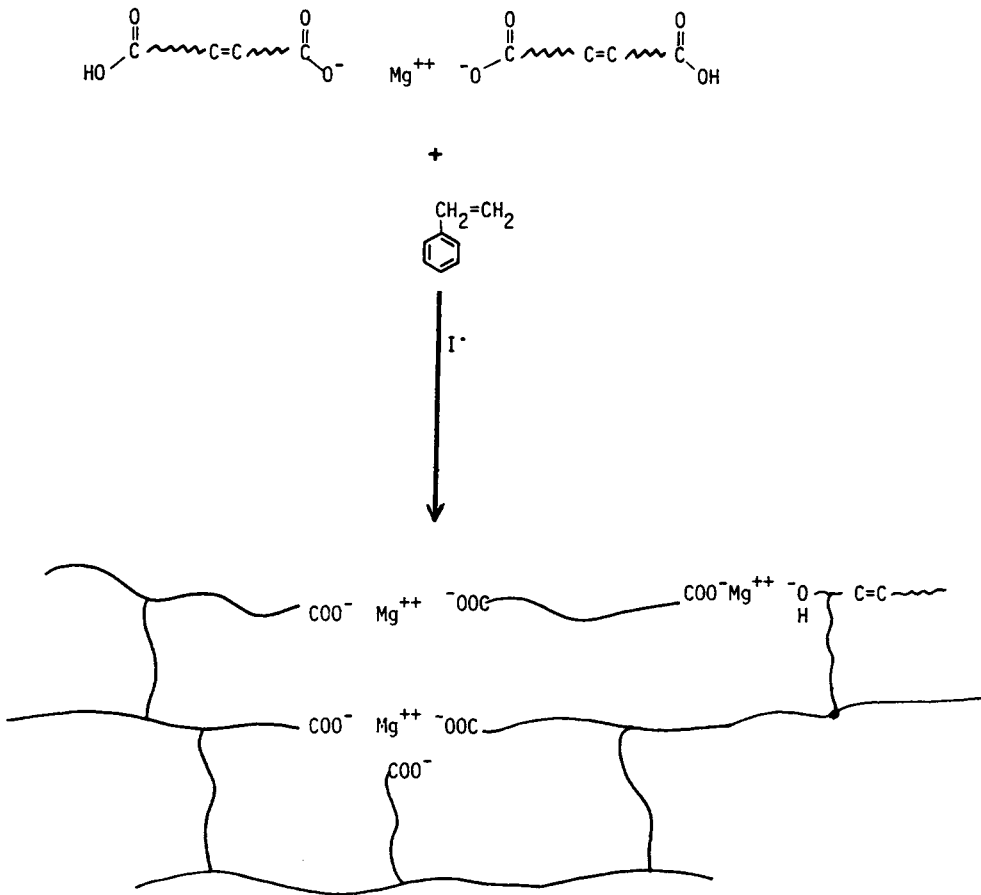$$\frac{T_g - T_g^0}{T_g} = \frac{B(X_c + X_i)}{1 - B(X_c + X_i)} \tag{8}$$

Fig. 4. Representation of a rigid polyester network showing ionic and covalent crosslinks.

to account for the covalent crosslink density X_c and the ionic crosslink density X_i. As for ionomers, it is expected that the introduction of semi-ionic crosslinks would raise the glass transition temperature of the polyester network.[27]

Thus, mechanical characterization and glass transition determination are recommended in order to understand how the ionic crosslinks change the physical properties of the rigid network. Analytical techniques such as infrared spectroscopy, proton and carbon-13 NMR are also suggested to identify the possible mechanism that control the thickening reaction of an unsaturated polyester resin with inorganic oxides.

To conclude, a theoretical model based on the rubber elasticity theory is proposed to describe a rigid unsaturated polyester network where ionic and covalent crosslinks are present. Some experimental work is required and is proposed to confirm the validity of the model.

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