

Modeling of Unsaturated Polyester Prepolymer Structures.

II. Hydroxyl and Carboxyl Functionalities

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ABSTRACT: Based on the structural model being derived in Part I, a statistics approach has been used to further estimate separately carboxyl and hydroxyl functionalities of unsaturated polyester (UP) prepolymers directly from their molecular parameters. This extended model shows satisfactory results when comparing with experimental results of hydroxyl functionality. The influence of molecular parameters, such as hydroxyl and carboxyl indexes, Ordelt saturation extent, and molecular mass polydispersity, on the carboxyl and hydroxyl functionalities is discussed. Examples showing the important impact of synthesis deviation on the hydroxyl and carboxyl functionalities, by model estimation, and, finally, on the SMC thickening are also discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 147–156, 1997

INTRODUCTION

Currently, the glass fiber-reinforced unsaturated polyester composites are widely used in a large number of industries, such as transportation, electrics, electronics, and housing, as well as in the manufacture of sport and leisure articles, furniture, and sanitary and domestic appliances. In all the applications, semifinished compounds, such as sheet-molding compounds (SMC) and bulk-molding compounds (BMC), have been developed for high-temperature molding processes. SMC technology always employs chemical thickening of unsaturated polyester (UP) resins during maturation. BMC technology currently is also increasingly employing the same approach. The purpose of the chemical thickening is to provide a tack-free prepreg which is stiff enough to permit easy material handling and also to provide sufficient resin viscosity to carry the glass fibers to the extremities of the mold during the mold-filling stage in a curing process.

The viscosity control of UP semicomponents, to date, is still a state of art rather than a well-controlled technology. The main problem likely comes from an uncertainty of the UP prepolymers' functionality. It is caused mainly by the side reaction of Ordelt saturation. The chain branches introduced by the Ordelt saturation leads to an increase of the number of reactive chain ends of the UP prepolymers. In the past, determination of the number of functional end groups was very difficult due to the complexity of molecular dispersity and competing side reactions.

In Part I of this work,¹ it was demonstrated that a satisfactory estimation on the chain branches and the overall chain ends of UP prepolymers becomes feasible by a structural model. By this model, the average number of chain ends and number- and functionality-average functionalities could be estimated directly from molecular parameters of UP prepolymers such as hydroxyl and acid indexes, Ordelt saturation extent, and molecular polydispersity. Only simple hypothesis concerning the type and length of branches are necessary.

However, the estimation of the number of all

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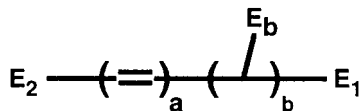
reactive chain ends which contain either hydroxyl or carboxyl groups does not completely meet the requirements of current SMC thickening technologies. In the traditional SMC technology, the most used thickening reaction involves an interaction of carboxyl groups of UP prepolymers with alkaline earth oxides,^{2,3} such as MgO and CaO, or hydroxides to increase the viscosity of uncrosslinked reactive systems during maturation, just after compound mixing. In this technology, an estimation of carboxyl functionality is mostly important for controlling the thickening viscosity. Another important thickening technology is to use an isocyanate as a thickening agent.⁴ This thickening process involves an addition reaction between an alcohol and an isocyanate to form covalent urethane bonds. The reaction between the hydroxyl chain ends and the isocyanate groups of a di- or poly-isocyanate will result in a molar mass increase and, consequently, in a viscosity increase. In this technology, an estimation of hydroxyl functionality is much more concerned than that of carboxyl functionality.

Therefore, a simple model providing reliable estimation of both carboxyl and hydroxyl functionalities of UP prepolymers should be very useful for developing SMC thickening technology. In this part, we try to further estimate, separately, carboxyl and hydroxyl functionalities of UP prepolymers based on the same structural model of Part I by applying a statistics approach. The goal was to propose a reliable estimation of active functionalities of UP prepolymers directly from their molecular parameters.

MODEL DERIVATION

Carboxyl Functionality

In Part I, a generalized molecular structure of unsaturated polyester prepolymers was derived as the form shown in Scheme 1:



Scheme 1 UP prepolymer structure.

where E_1 and E_2 are the main chain end groups, either a hydroxyl group or a carboxyl group; E_b , the branch chain end group, mainly a hydroxyl group; a , the number of constitutive units containing unsaturation points; and b , the number

of constitutive units containing chain branches including short-chain branches and long-chain branches.

For the species i , the overall chain end number is f_i and the number of hydroxyl groups and the number of carboxyl groups at the end of the linear UP molecular chain end are h_i and c_i , respectively. Further, the number of branches, i.e., number of branching chain end groups, of the species i is b_i . As discussed in Part I, the branches are mostly terminated by diol units, so b_i is assumed to be the branched hydroxyl number of species i . Therefore, one has the following relationships:

$$c_i + h_i = 2 \quad (1)$$

$$f_i = c_i + h_i + b_i = 2 + b_i \quad (2)$$

$$(f_{\text{OH}})_i = b_i + h_i = f_i - c_i \quad (3)$$

and

$$(f_{\text{COOH}})_i = c_i \quad (4)$$

where, $(f_{\text{OH}})_i$ is the hydroxyl functionality of species i ; and $(f_{\text{COOH}})_i$, the carboxyl functionality of species i .

One defines the overall number of carboxyl groups (N_c), the overall number of hydroxyl groups on the main chain (N_h), and the overall number of hydroxyl groups on the branching chain (N_b) as follows:

$$N_c = \sum A_i c_i \quad (5)$$

$$N_h = \sum A_i h_i \quad (6)$$

$$N_b = \sum A_i b_i \quad (7)$$

where A_i is the number of molecules i having either c_i or h_i or b_i correspondingly.

Number-average values for the carboxyl functionality (\bar{c}_n), main-chain hydroxyl functionality (\bar{h}_n), and branching chain hydroxyl functionality (\bar{b}_n) are expressed as follows:

$$\bar{c}_n = \sum A_i c_i / \sum A_i \quad (8)$$

$$\bar{h}_n = \sum A_i h_i / \sum A_i \quad (9)$$

$$\bar{b}_n = \sum A_i b_i / \sum A_i \quad (10)$$

Then, the number-average overall functionality, \bar{f}_n , is

$$\bar{f}_n = \bar{c}_n + \bar{h}_n + \bar{b}_n \quad (11)$$

There is a relationship between numbers of functional groups and experimental hydroxyl I_H and carboxyl I_C indexes (as expressed from standard titration):

$$N_c = N_o(I_C/56,100) = kI_C \quad (12)$$

$$N_h + N_b = N_o(I_H/56,100) = kI_H \quad (13)$$

where N_o is Avogadro's number; I_C , the acid index in mg KOH/g of sample; I_H , hydroxyl index in mg KOH/g of sample; and $k = N_o/56,100$.

Since

$$N_h/N_b = \bar{h}_n/\bar{b}_n = (\bar{f}_n - \bar{c}_n - \bar{b}_n)/\bar{b}_n \quad (14)$$

and

$$\bar{c}_n/\bar{f}_n = I_C/(I_H + I_C) \quad (15)$$

one can solve eqs. (13) and (14) simultaneously to have following solutions:

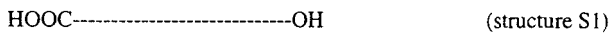
$$N_h = kI_H(\bar{f}_n r_H - \bar{b}_n)/(\bar{f}_n r_H) \quad (16)$$

$$N_b = kI_H \bar{b}_n/(\bar{f}_n r_H) \quad (17)$$

where r_H is the hydroxyl ratio of the UP prepolymer:

$$r_H = I_H/(I_H + I_C) \quad (18)$$

The main-chain end groups, E_1 and E_2 , shown in Scheme 1, may be hydroxyl or carboxyl groups. It means the main chain can be one of the following structures:



The number of molecules having the structure **S1** is the product of N_c and N_h . Similarly, the **S2** molecular number is $N_c(N_c - 1)/2$, and the **S3** molecular number is $N_h(N_h - 1)/2$.

Therefore, the number-average carboxyl functionality $(\bar{f}_{\text{COOH}})_n = \bar{c}_n$ can be derived from eq. (8) into eq. (19) (assuming that no branch is terminated by carboxyl groups, see Scheme 1):

$$\bar{c}_n = 2N_c/[N_c + N_h] \quad (19)$$

Finally, by introducing eqs. (12) and (16) into eq. (19), one obtains

$$\bar{c}_n = \bar{f}_n I_C/(I_H + I_C) = \bar{f}_n r_c \quad (20)$$

where $r_c = I_C/(I_H + I_C) = 1 - r_h =$ acid ratio. It is noticed that eq. (20) is identical to eq. (15).

Furthermore, the functionality-average carboxyl functionality (the second moment of the distribution of functionalities) can be derived as follows:

$$\begin{aligned} (\bar{f}_{\text{COOH}})_w &= \bar{c}_w = \sum A_i c_i^2 / \sum A_i c_i \\ &= 2 - N_h/(N_c + N_h - 1) \end{aligned} \quad (21)$$

In eq. (21), since the sum of N_c and N_h is much larger than 1, the term of $(N_c + N_h - 1)$ can be simplified into $(N_c + N_h)$. Therefore, eq. (21) becomes

$$\bar{c}_w = 2 - N_h/(N_c + N_h) \quad (22)$$

Applying eqs. (12) and (16) into eq. (22), one obtains

$$(\bar{f}_{\text{COOH}})_w = \bar{c}_w = 2 - \frac{\bar{f}_n r_h - \bar{b}_n}{\bar{f}_n - \bar{b}_n}$$

or

$$\bar{c}_w = 2 - \frac{\bar{h}_n}{2} = 1 + \frac{\bar{c}_n}{2} \quad (23)$$

The number-average functionality, \bar{f}_n , was derived in Part I in terms of the index molar mass ($\bar{M}_{n,\text{index}}$ from I_C and I_H), Ordelt saturation degree (X_{Ordelt}), molar mass of unsaturation unit ($M_{c=c}$), and molar mass of branches (m). It is reexpressed in eq. (24):

$$\begin{aligned} \bar{f}_n &= 2 \\ &+ \left[\frac{2\bar{M}_{n,\text{index}}X_{\text{Ordelt}}}{2M_{c=c} + 2mX_{\text{Ordelt}} - \bar{M}_{n,\text{index}}X_{\text{Ordelt}}} \right] \end{aligned} \quad (24)$$

In conclusion, the number- and functionality-average carboxyl functionalities \bar{c}_n and \bar{c}_w can be estimated directly from experimental data such as $\bar{M}_{n,\text{index}}$, I_C , I_H , X_{Ordelt} , $M_{c=c}$, and m by eqs. (20) and (23), taking into account the same assumptions as in Part I concerning the type and length of branches.

Hydroxyl Functionality

As shown in Scheme 1, the total hydroxyl number of the species i , $(f_{\text{OH}})_i$, is the sum of the branched hydroxyl number, b_i , and the number of hydroxyl end groups on the main chain, h_i , as shown as eq. (3). The number-average hydroxyl groups on the branches, \bar{b}_n , was derived in Part I and is reexpressed in eq. (25):

$$\bar{b}_n = \frac{2\bar{M}_{n,\text{index}}X_{\text{Ordelt}}}{2M_{c=c} + 2mX_{\text{Ordelt}} - \bar{M}_{n,\text{index}}X_{\text{Ordelt}}} \quad (25)$$

Similar to number-average carboxyl functionality shown in eq. (19), the number-average hydroxyl functionality on the main chain, \bar{h}_n , can be derived as follows:

$$\bar{h}_n = \sum A_i h_i / \sum A_i = 2N_h / [N_c + N_h] \quad (26)$$

Finally, by introducing eqs. (12) and (16) into eq. (26), one obtains

$$\begin{aligned} \bar{h}_n &= \bar{f}_n r_{\text{H}} - \bar{b}_n \\ \bar{h}_n &= 2r_{\text{H}} - \bar{b}_n(1 - r_{\text{H}}) \end{aligned} \quad (27)$$

Similar to the functionality-average carboxyl functionality derived in eq. (21), the functionality-average main-chain hydroxyl functionality can be derived as follows:

$$\begin{aligned} \bar{h}_w &= \sum A_i h_i^2 / \sum A_i h_i \\ &= 2 - N_c / (N_c + N_h - 1) \end{aligned} \quad (28)$$

In eq. (28), since the sum of N_c and N_h is much larger than 1, the term of $(N_c + N_h - 1)$ can be simplified into $(N_c + N_h)$. Therefore, eq. (28) becomes

$$\bar{h}_w = 2 - N_c / (N_c + N_h) \quad (29)$$

Applying eqs. (12) and (16) into eq. (29), one obtains

$$\begin{aligned} \bar{h}_w &= 2 - \frac{\bar{f}_n I_{\text{C}}}{(\bar{f}_n - \bar{b}_n)(I_{\text{C}} + I_{\text{H}})} \\ \bar{h}_w &= 2 - \frac{\bar{f}_n}{2} \left[\frac{I_{\text{C}}}{I_{\text{C}} + I_{\text{H}}} \right] \\ \bar{h}_w &= 2 - \frac{c_n}{2} \\ \bar{h}_w &= 1 + \frac{\bar{h}_n}{2} \end{aligned} \quad (30)$$

Taking the sum of \bar{c}_w and \bar{h}_w from eqs. (23) and (30), one may find an interesting result:

$$\bar{c}_w + \bar{h}_w = 3 \quad (31)$$

It is noticed that the sum of \bar{c}_n and \bar{h}_n is equal to 2 as mentioned before.

The number-average hydroxyl functionality of a UP prepolymer is derived in the following equation:

$$\begin{aligned} (\bar{f}_{\text{OH}})_n &= \frac{\sum A_i (f_{\text{OH}})_i}{\sum A_i} = \frac{\sum A_i (b_i + h_i)}{\sum A_i} = \bar{b}_n + \bar{h}_n \\ (\bar{f}_{\text{OH}})_n &= \bar{f}_n I_{\text{H}} / (I_{\text{H}} + I_{\text{C}}) = \bar{f}_n r_{\text{H}} \end{aligned} \quad (32)$$

Similarly, the functionality-average hydroxyl functionality is derived in the following equations:

$$\begin{aligned} (\bar{f}_{\text{OH}})_w &= \frac{\sum A_i (f_{\text{OH}})_i^2}{\sum A_i (f_{\text{OH}})_i} = \frac{\sum A_i (f_i - c_i)^2}{\sum A_i (f_i - c_i)} \\ (\bar{f}_{\text{OH}})_w &= \frac{\sum A_i f_i^2 - \sum A_i f_i c_i + \sum A_i c_i^2}{\sum A_i f_i - \sum A_i c_i} \end{aligned}$$

also expressed as

$$\begin{aligned} &\left(\frac{\sum A_i f_i^2}{\sum A_i f_i} \right) \left(\frac{\sum A_i f_i}{\sum A_i} \right) \\ &- 2 \left(\frac{\sum A_i f_i c_i}{\sum A_i} \right) \\ &+ \left(\frac{\sum A_i c_i^2}{\sum A_i c_i} \right) \left(\frac{\sum A_i c_i}{\sum A_i} \right) \\ (\bar{f}_{\text{OH}})_w &= \frac{\left(\frac{\sum A_i f_i^2}{\sum A_i f_i} \right) \left(\frac{\sum A_i f_i}{\sum A_i} \right) - 2 \left(\frac{\sum A_i f_i c_i}{\sum A_i} \right) + \left(\frac{\sum A_i c_i^2}{\sum A_i c_i} \right) \left(\frac{\sum A_i c_i}{\sum A_i} \right)}{\left(\frac{\sum A_i f_i}{\sum A_i} \right) - \left(\frac{\sum A_i c_i}{\sum A_i} \right)} \end{aligned} \quad (33)$$

Equation (33) can be transformed into eq. (34) by the definition of number- and functionality-average values:

$$(\bar{f}_{\text{OH}})_w = \frac{\bar{f}_n \bar{f}_w - 2(\bar{f}_c)_n + \bar{c}_w \bar{c}_n}{\bar{f}_n - \bar{c}_n} \quad (34)$$

where

$$(\bar{f}_c)_n = \frac{\sum A_i (f_i c_i)}{\sum A_i} \quad (35)$$

If one consider three structures of UP prepolymers (**S1**, **S2**, and **S3**) having the same branching chain distribution, eq. (35) can be derived by the probabilities of three molecular structures in the following equation:

$$(\bar{f}_c)_n = \left[\frac{N_c N_h}{\frac{N_c(N_c - 1)}{2} + N_c N_h + \frac{N_h(N_h - 1)}{2}} \right] \times \left(\frac{\sum A_i f_i}{\sum A_i} \right) + 2 \times \left[\frac{\frac{N_c(N_c - 1)}{2}}{\frac{N_c(N_c - 1)}{2} + N_c N_h + \frac{N_h(N_h - 1)}{2}} \right] \left(\frac{\sum A_i f_i}{\sum A_i} \right)$$

which can be simplified as

$$(\bar{f}_c)_n = \bar{f}_n \frac{2N_c}{N_c + N_h} \quad (36)$$

By introducing eq. (19) into eq. (36), one obtains

$$(\bar{f}_c)_n = \bar{f}_n \bar{c}_n \quad (37)$$

Therefore, eq. (37) becomes

$$(\bar{f}_{OH})_w = \frac{\bar{f}_n \bar{f}_w - 2\bar{f}_n \bar{c}_n + \bar{c}_w \bar{c}_n}{\bar{f}_n - \bar{c}_n} \quad (38)$$

Since \bar{f}_n , \bar{f}_w , \bar{c}_n , and \bar{c}_w were derived previously, consequently, the functionality-average hydroxyl functionality of a UP prepolymer, $(\bar{f}_{OH})_w$, as well as $(\bar{f}_{COOH})_w$, can be estimated directly from experimental data such as I_C and I_H , molecular mass polydispersity (I_p), Ordelt saturation degree (X_{Ordelt}), molar mass of unsaturation unit ($M_{c=c}$), and molar mass of branches (m). Equation (38) can be further derived into eq. (39) by substitution of \bar{c}_n and \bar{c}_w :

$$(\bar{f}_{OH})_w = \frac{\bar{f}_w - 2\bar{f}_n[(3 + r_H)(1 - r_H)] + (1 - r_H)}{r_H} \quad (39)$$

RESULTS AND DISCUSSION

Hydroxyl Functionality

As mentioned in the previous section, the number- and functionality-average hydroxyl functionalit-

ies of UP prepolymers can be estimated by eqs. (34) and (41) from the prepolymers' experimental parameters. The determination of the hydroxyl functionality of UP prepolymers is a critical point for isocyanate thickening technology in SMC application. Lecoite et al.⁵ experimentally studied effects of molecular structures of different UP prepolymers on the reaction of UP resins with a diisocyanate. UP prepolymers were 1 : 1 copolymers of fumaric acid with a combination of diethylene glycol (DEG) and neopentyl glycol (NPG). The diol composition of F90 is NPG/DEG equal to 90/10 by mol, while that of F80 is 80/20. As they were prepared from fumaric acid, the extent of the Ordelt reaction is rather low, and for isocyanate thickening, the concentration of hydroxyl chain ends is much higher than is the concentration of carboxyl chain ends, $I_H \gg I_C$. The UP prepolymers were dissolved in styrene (53% bw) and reacted with diphenyl methane diisocyanate (MDI). The stoichiometric ratio of —NCO groups to —OH groups was set at 1 : 1 for all experiments. The gel phenomena were measured by the appearance of an insoluble fraction in a polar solvent like tetrahydrofuran and gel conversion determined by FTIR measurements.⁵ The gel conversion of all systems was used to determine the UP prepolymer functionality by the Macosko–Miller equation⁶ shown as follows:

$$\frac{[\text{NCO}]}{[\text{OH}]} x_{\text{gel}}^2 = \frac{1}{(\bar{f}_w - 1)(g - 1)} \quad (40)$$

where $[\text{NCO}]/[\text{OH}] = 1$; x_{gel} = the isocyanate conversion at the gel point; \bar{f}_w = the functionality average functionality of UP prepolymers; and g = functionality of pure MDI, $g = 2$.

With the experimental conditions chosen: room temperature for the reaction temperature, isocyanate-to-hydroxyl ratio equal to 1, and a low concentration of carboxyl groups, the isocyanate–carboxyl reaction is assumed to be negligible. So, the functional-average functionality that we are able to measure is the functionality-average functionality of OH groups, $(\bar{f}_{OH})_{w,\text{exp}}$. The isocyanate–hydroxyl reaction causes a viscosity increase during the thickening process. As gelation occurs for all the UP resins reacted with MDI, it means that $(\bar{f}_{OH})_w$ is always higher than 2. But the time (or NCO conversion) at which gelation occurs depends on the functionality of the UP prepolymer. It has been demonstrated that the gel was a loose chemical gel in styrene. Gelation can

Table I Experimental and Simulated Average Functionalities of UP Prepolymers

Prepolymer	$(\bar{f}_{\text{OH}})_{w,\text{exp}}^a$	$(\bar{f}_{\text{OH}})_n$	$(\bar{f}_{\text{OH}})_w$
F80-1	2.11	1.85	2.09
F80-2	2.35	1.97	2.40
F90-1	2.09	1.83	2.06
F90-3	2.69	2.08	2.87

^a Data from Ref. 5.

be suppressed by using a —NCO to —OH ratio lower or higher than 1, beyond a critical value. But in all cases, the control of the viscosity increase imposes the knowledge of the functionality-average functionality, $(\bar{f}_{\text{OH}})_w$. The results are shown in Table I.

The key molecular parameters of F80s and F90s prepolymers used for functionality estimation are listed in Part I (see Table I of Part I¹). The simulated number, $(\bar{f}_{\text{OH}})_n$, and functionality, $(\bar{f}_{\text{OH}})_w$, average functionalities are presented in Table I. The comparison between simulation and experimental values shows that the derived structural model of this study could provide satisfactory estimation results on the hydroxyl functionality, meaning that the hydroxyl functionality of UP prepolymers could be estimated directly from quality control data of the UP prepolymers just after synthesis. An extra manipulation of the gel point to determine the hydroxyl functionality could be avoided. Due to the fact that for these UP prepolymers $I_H \gg I_C$, the chain ends are essentially OH groups and \bar{f}_{OH} functionalities are closed to the overall number of chain ends expressed by \bar{f}_n and \bar{f}_w (cf. Table I of Part I¹).

The simulation results shown in Table I confirm the experimental results that the F80-2 prepolymer has a higher hydroxyl functionality than does F80-1 even though both prepolymers have the same chemical ingredients. The same results are also found for F90-3 and F90-1 prepolymers. The reasons for this functionality deviation between the prepolymers in the same family, according to the model simulation, are explained by the fact that F80-2 has a higher Ordelt extent (X_{Ordelt}) and a higher molar mass polydispersity (I_p) than has F80-1, while F90-3 has a higher molar mass (\bar{M}_n) and a higher molar mass polydispersity (I_p) than has F90-1. To simplify the parameters, one may make X_{Ordelt} and \bar{M}_n into a group, which leads to a simple parameter, i.e., number-average chain branches, \bar{b}_n . The influ-

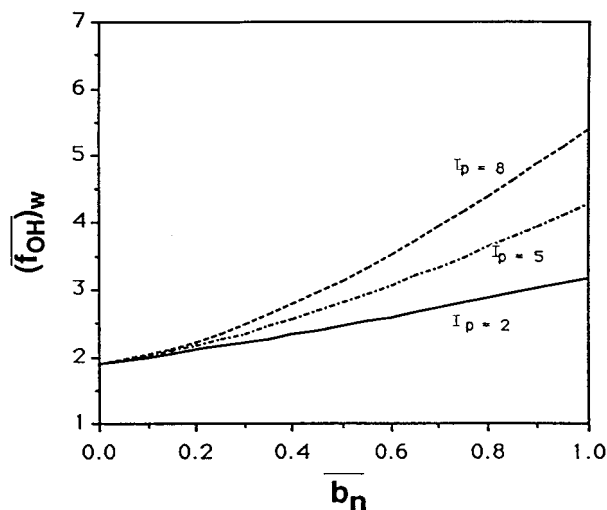


Figure 1 Influences of number-average chain branches (\bar{b}_n) and molar mass polydispersity (I_p) on functionality-average hydroxyl functionality, $(\bar{f}_{\text{OH}})_w$, for UP prepolymers having hydroxyl ratio $r_H = 0.9$.

ences of \bar{b}_n and polydispersity index (I_p) on the hydroxyl functionality are shown by plotting the functionality-average hydroxyl functionality, $(\bar{f}_{\text{OH}})_w$, vs. the number-average chain branches, \bar{b}_n , and for a different polydispersity index, I_p .

Figure 1 shows simulation results for an hydroxyl ratio $r_H = I_H/I_H + I_C = 0.9$, and Figure 2 for $r_H = 0.5$. Since most of the molecular parameters are included in the \bar{b}_n parameter, the results of Figures 1 and 2 are representative for all types

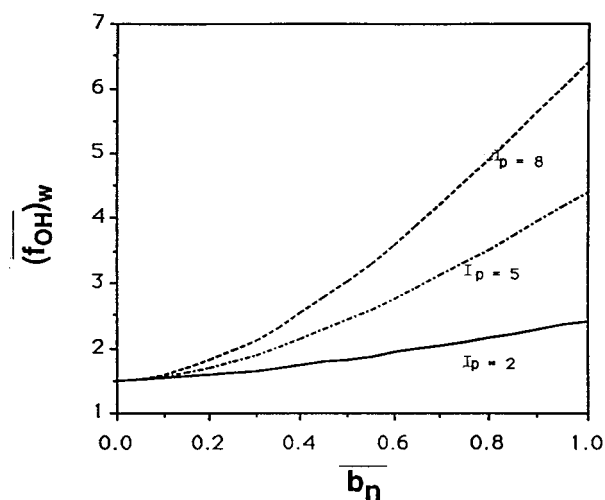


Figure 2 Influences of number-average chain branches (\bar{b}_n) and molar mass polydispersity (I_p) on functionality-average hydroxyl functionality, $(\bar{f}_{\text{OH}})_w$, for UP prepolymers having hydroxyl ratio, $r_H = 0.5$.

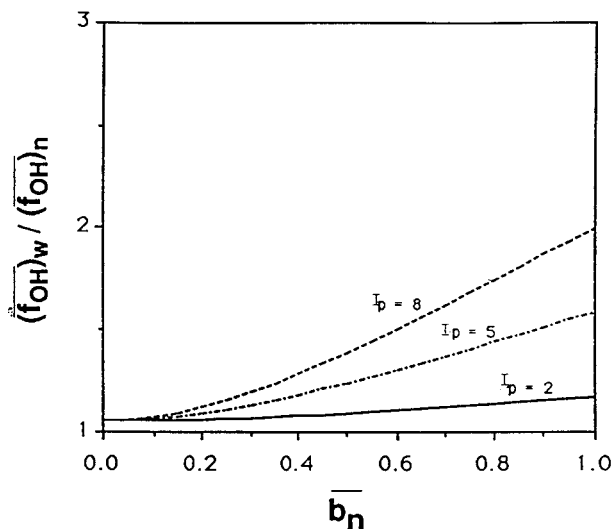


Figure 3 Influences of number-average chain branches (\bar{b}_n) and molar mass polydispersity (I_p) on polydispersity in hydroxyl functionality for UP prepolymers having hydroxyl ratio, $r_H = 0.9$.

of UP prepolymers. The results reveal that higher branching number and/or higher molar mass polydispersity could cause higher functionality-average hydroxyl functionality. However, at a lower branching number region, the effect of polydispersity is suppressed.

Combining eqs. (32) and (39), one can estimate the hydroxyl functionality polydispersity, $(\bar{f}_{OH})_w / (\bar{f}_{OH})_n$, of UP prepolymers from their molecular parameters by eq. (40):

$$\frac{(\bar{f}_{OH})_w}{(\bar{f}_{OH})_n} = \frac{1}{(r_H)^2} \left[1 + \left(\frac{\bar{b}_n}{2 + \bar{b}_n} \right)^2 (I_p - 1) - (1 - r_H) \left(\frac{3 + 2\bar{b}_n}{2 + \bar{b}_n} \right) + \frac{(1 - r_H)^2}{2} \right] \quad (41)$$

Figure 3 shows simulation results of hydroxyl functionality polydispersity, $(\bar{f}_{OH})_w / (\bar{f}_{OH})_n$, as functions of the average branching number (\bar{b}_n) and molar mass polydispersity (I_p) on the condition of r_H equal to 0.9, while Figure 4 shows similar results on the condition of r_H equal to 0.5. The trends are similar to those shown in Figures 1 and 2. The deviation of functionality polydispersity is not significant in the case of low molar mass polydispersity or low branching number. Nevertheless, it should be noticed that a prepolymer having a lower r_H is more sensitive to the changes of molar mass dispersity and branching number on the

functionality polydispersity than one having higher r_H .

Carboxyl Functionality

Based on the structural model derived in this work, one can also estimate the number-average and functionality-average carboxyl functionalities of UP prepolymers. Deriving from eqs. (20) and (23), the number-average and functionality-average carboxyl functionalities can be expressed in eq. (42) and (43), respectively, in terms of chain branches (\bar{b}_n) and acid ratio (r_C):

$$(\bar{f}_{COOH})_n = (2 + \bar{b}_n)r_C \quad (42)$$

or

$$(\bar{f}_{COOH})_w = (2 + r_C) + \frac{r_C \bar{b}_n}{2} \quad (43)$$

Consequently, Figure 5 shows the estimation results of functionality-average carboxyl functionality for UP prepolymers as functions of chain branches (\bar{b}_n) and acid ratio (r_C). It is noticed that there is a criterion for model estimation, i.e., $(\bar{f}_{COOH})_w$ is always larger than or equal to $(\bar{f}_{COOH})_n$. With this criterion, one could finally obtain a relationship between \bar{b}_n and r_C (or r_H) shown as follows:

$$\bar{b}_n \leq \frac{2(1 - r_C)}{r_C} = \frac{2r_H}{(1 - r_H)} \quad (44)$$

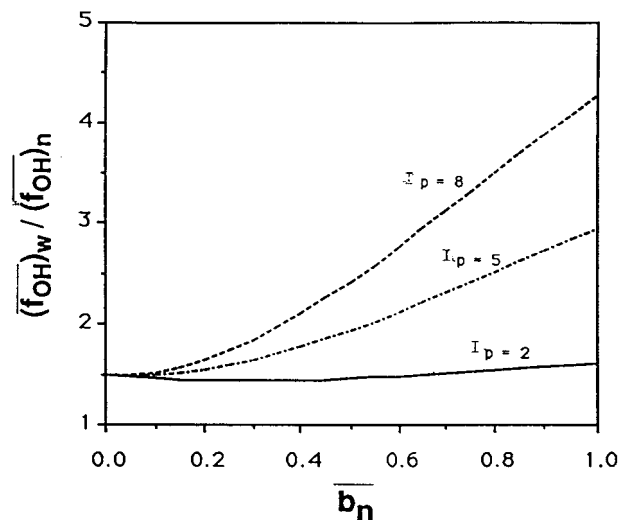


Figure 4 Influences of number-average chain branches (\bar{b}_n) and molar mass polydispersity (I_p) on polydispersity in hydroxyl functionality for UP prepolymers having hydroxyl ratio, $r_H = 0.5$.

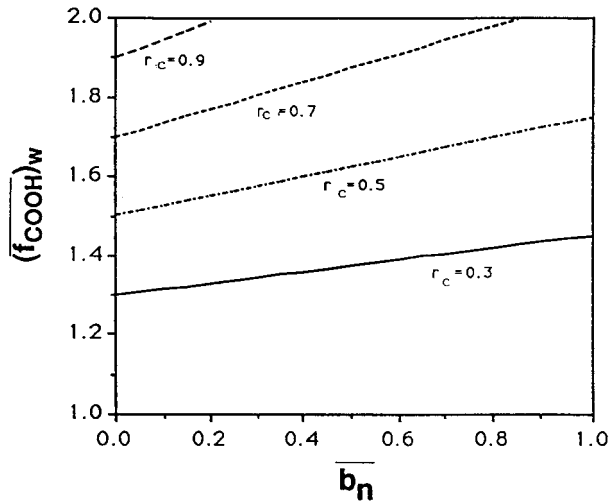


Figure 5 Influences of number-average chain branches (\bar{b}_n) and acid ratio (r_c) on functionality-average carboxyl functionality, $(\bar{f}_{\text{COOH}})_w$, for UP prepolymers.

From eqs. (42) and (43), the polydispersity in carboxyl functionality can be calculated by the following equation:

$$\frac{(\bar{f}_{\text{COOH}})_w}{(\bar{f}_{\text{COOH}})_n} = \frac{2 + (2 + \bar{b}_n)r_c}{2(2 + \bar{b}_n)r_c} \quad (45)$$

Figure 6 shows the estimation results of carboxyl functionality polydispersity as functions of chain branches (\bar{b}_n) and acid ratio (r_c). The results

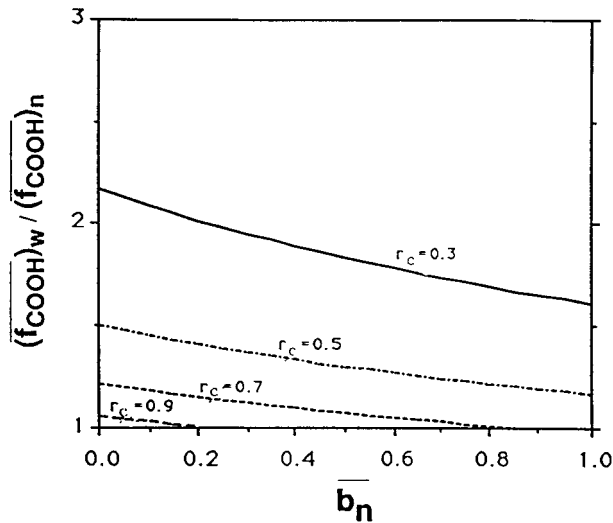


Figure 6 Influences of number-average chain branches (\bar{b}_n) and acid ratio (r_c) on polydispersity in carboxyl functionality for UP prepolymers.

Table II Molecular Parameters and Model Estimation Results for MA-PG Prepolymers ($M_{c=c} = 156$ and $m = 145$)

	Prepolymer		
	P1	P2	P3
<u>Molecular parameters</u>			
\bar{I}_C	30	30	35
\bar{I}_H	50	45	45
$(\bar{M}_n)_{\text{index}}$	1403	1496	1403
r_c	0.375	0.400	0.438
X_{Ordelt}	0.03	0.04	0.05
<u>Model estimation</u>			
\bar{b}_n	0.302	0.453	0.547
\bar{M}_n	1614	1832	1786
$(\bar{f}_{\text{COOH}})_n$	0.863	0.981	1.116
$(\bar{f}_{\text{COOH}})_w$	1.432	1.491	1.678
<u>Magnesium carboxylate polymer</u>			
$(\bar{M}_w)_{\text{Mg-UP}}$	5744	7270	11,220
\bar{n}	3.51	3.92	6.20

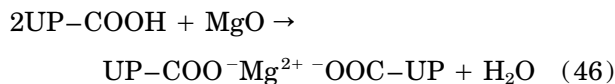
show that the carboxyl functionality polydispersity decreases with an increase of chain branches or acid ratio.

It is well known that the reaction between the carboxyl groups of UP prepolymers and magnesium oxide is a basic key factor on controlling the thickening mechanism in classical SMC technology. It is no doubt that the change of carboxyl functionality of UP prepolymers would cause a strong variation on thickening viscosity. The simulation results of Figure 5 have shown that the functionality-average carboxyl functionality may be significantly varied from 1.3 to 2, depending on the molecular parameters. However, from Figure 5, one still cannot realize well the real impact of the carboxyl functionality variation in SMC application. Hereafter, several examples will be raised to discuss the effect of carboxyl functionality on the SMC thickening.

UPs based on propylene glycol (PG) and maleic anhydride (MA) have been widely used in the SMC industry for automotive application. Typical molecular parameters of an MA-PG polyester for SMC application are listed in Table II under the reference of the P1 prepolymer. Table II also presents molecular parameters of other MA-PG prepolymers: P2 and P3. The P2 prepolymer has a different hydroxyl index and Ordelt extent than has the P1 prepolymer even in both cases when the Ordelt extent is low. In fact, the P2 prepolymer meets the quality control specifications of most of resin suppliers and SMC molders for SMC

application. P3 shows more differences in molecular parameters from the P1 than from the P2 prepolymer. However, the P3 prepolymer could also be easily found in the SMC industry. Since P1, P2, and P3 prepolymers are all based on PG and MA, they have two common molecular parameters, i.e., $M_{C=C} = 156$ and $m = 145$ (definitions see Part I). The estimation results in terms of branching number, real molar mass, and number- and functionality-average carboxyl functionalities for P1, P2, and P3 prepolymers are given in Table II. It is clearly shown that the carboxyl functionalities (number or functionality averages) are increased from the P1 prepolymer through P2 toward the P3 prepolymer.

For a classical SMC thickening process, magnesium oxide is widely used as a thickening agent and is directly added in UP resin with fillers. The amount of magnesium oxide is stoichiometrically calculated with a Mg/COOH molar ratio at 0.5. The initial reaction occurring during the thickening process is the formation of basic or neutral salts from carboxyl end groups and metal oxide. This reaction leads to the formation of a high molar mass, linear chain magnesium carboxylate polymer (Mg-UP):



If one considers this reaction as a stepwise polymerization, the molar mass of the magnesium carboxylate polymer could be estimated by Macosko-Miller's recursive method.⁶ In this work, a stoichiometric ratio (based on I_C determination) was used and a complete reaction [eq. (46)] was assumed. Consequently, the Macosko-Miller equation [eq. (23), Ref. 6] is simplified as follows:

$$(\overline{M}_w)_{\text{Mg-UP}} = (2\overline{M}_{\text{UP}} + \overline{f}M_{\text{Mg}})/(2 - \overline{f}) \quad (47)$$

where $(\overline{M}_w)_{\text{Mg-UP}}$ is the molar mass of the magnesium carboxylate polymer; \overline{M}_{UP} is the molar mass of the UP prepolymer, shown as \overline{M}_n in Table II; $M_{\text{Mg}} = 24.3$; and $\overline{f} = (\overline{f}_{\text{COOH}})_w$ as shown in Table II. The estimated molar mass of magnesium carboxylate polymers are presented in Table II. The results show that the variation of carboxyl functionality has been emphasized and is reflected in the molar mass of the magnesium carboxylate polymer. The magnesium carboxylate-P2 polymer has a ca. 27% higher molar mass than that of the magnesium carboxylate-P1 polymer, while

the magnesium carboxylate-P3 polymer shows nearly a double molar mass. Since the magnesium carboxylate polymer is a basic element for the following physical crosslinking process, the molar mass of the magnesium carboxylate polymer would play an important role in the final viscosity.

The second step in the thickening process is "complexation-reticulation"⁷⁻⁹ or "ionomer aggregation."^{3,10,11} This step causes a viscosity increase during the thickening process. In the mechanism of "complexation reticulation," the magnesium salts form coordination complexes with the ester groups in the chain and/or the hydroxyl end groups, while the mechanism of "ionomer aggregation" states that there is a formation of ionic clusters which contains several $\text{COO}^- \text{Mg}^{2+} \text{-OOC}$ groups. The formation of ionic clusters is caused by the incompatibility of magnesium carboxylate groups with the organic backbones. This results in the formation of highly branched structures exhibiting high viscosity. In both mechanisms, the number of the magnesium carboxylate groups per polymer is a determinant factor for the viscosity increase. The number of the magnesium carboxylate groups (\overline{n}) per polymer chain could be simply estimated by dividing $(\overline{M}_w)_{\text{Mg-UP}}$ by the sum of \overline{M}_{UP} and \overline{M}_{Mg} . Here, \overline{n} is a functionality-average value rather than a number-average one. The estimation results are also shown in Table II. One may consider the magnesium carboxylate groups as the crosslinking points which are responsible for the following molar mass increases and viscosity increases. The results show that the magnesium carboxylate-P2 polymer has 12% more crosslinks than does the magnesium carboxylate-P1 polymer, while the magnesium carboxylate-P3 polymer shows 77% more.

Although one can explain the viscosity increase during the thickening process either by the "complexation-reticulation" mechanism or by the "ionomer aggregation" mechanism, to date, no one can well correlate the final SMC plateau viscosity to molecular characteristics. However, without any other side effect, like water complexation, it should be no doubt that the plateau viscosity must have a strong dependence on the molar mass of magnesium carboxylate polymer, $(\overline{M}_w)_{\text{Mg-UP}}$, and the number of the magnesium carboxylate groups (\overline{n}) per polymer chain. Roughly speaking, if one assumes that the two parameters discussed above show a product effect on the viscosity plateau, the P2 prepolymer may, at least, show a plateau viscosity ca. 40% higher than that of the P1 prepolymer, while the plateau viscosity of the P3 prepoly-

mer system may be at least three to four times of that of the P1 system.

CONCLUSION

This work has provided a possible way to estimate carboxyl and hydroxyl functionalities of UP prepolymers. This estimation can help one to better understand the influence of molecular parameters after UP prepolymer synthesis on the SMC thickening behavior. However, there are still efforts to be made for achieving a well-controlled SMC thickening technology. An estimation of SMC plateau viscosity directly from the molecular parameters of UP prepolymers should be the following challenging issue for the researchers in this area.

REFERENCES

1. Y. S. Yang and J. P. Pascault, *J. Appl. Polym. Sci.*, **64**, 133 (1997).
2. V. J. Frilette, U.S. Pat. 2,568,331 (1951).
3. D. Judas, A. Fradet, and E. Marechal, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 3309 (1984).
4. The General Tire and Rubber Co., U.S. Pat. 3,824,201 (1974).
5. J. P. Lecointe, Y. S. Yang, J. P. Pascault, and L. Suspene, to appear.
6. C. W. Macosko and D. R. Miller, *Macromolecules*, **9**, 199 (1976).
7. I. Vancso-Szmercsanyi and E. Noo, *Kunststoffe*, **58**, 907 (1968).
8. I. Vancso-Szmercsanyi and A. Szilagyi, *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 2155 (1974).
9. A. Szilagyi, V. Izvekov, and I. Vancso-Szmercsanyi, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 2803 (1980).
10. M. Laleg, F. Blanchard, B. Chabert, and J. P. Pascault, *Eur. Polym. J.*, **21**(6), 591 (1985).
11. C. Habassi, M. Brigodiot, A. Fradet, and E. Maréchal, *Makromol. Chem.*, **191**, 639 (1990).