

Synthesis of Epoxy–Amine Multiacrylic Prepolymers by Reactive Extrusion

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SYNOPSIS

Epoxy-amine multiacrylic prepolymers were prepared by reactive extrusion using a one-step competitive reaction of diglycidyl ether of bisphenol A (DGEBA) and glycidyl methacrylate (GMA) with diamines. The technical and chemical limitations of the process were analyzed through a reactive extrusion diagram. Diphenyl was used as a tracer for residence time distribution (RTD) studies. Extrusion parameter analysis showed that the reactions are kinetically controlled and that an increase in reaction temperature leads to higher residence time and broader distributions. At constant temperature, we found a linear evolution of the average residence time (\bar{t}_m) with kneading disk blocks and left-handed screw element length. The structure of the obtained oligomers was analyzed using a conversion distribution concept. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy–amine multiacrylic prepolymers can lead, by double bond polymerization, to polymer networks that have potential applications in medical, electronic, and composite material fields. Manaka¹ prepared several methacrylated monomers through the reaction of several diamines with epoxy-2,3 propoxymethacrylate (or glycidyl methacrylate, GMA). Following radical polymerization of these monomers, he obtained very brittle compounds due to the high crosslink density of the networks formed. Klee et al.^{2,3} prepared similar prepolymers through the reaction of GMA with diglycidyl ether of bisphenol A (DGEBA)-diamine adduct. DGEBA, included in the oligomer chains, confers a certain flexibility to the final network, increasing its mechanical properties. We recently described a one-step synthesis of epoxy-amine multiacrylic prepolymers through a direct reaction of diamines with DGEBA and GMA.^{4,5}

The increasing popularity of the use of a twin-screw extruder as a reactor is mainly based on the

high level of efficiency obtained for the synthesis and modification of polymers combined with the economic and ecological aspects in the use of this device. Reviews concerning the chemical reactions and different process and technological aspects were made by Brown and Orlando⁶ and Xanthos.⁷

The present article deals with synthesis by reactive extrusion of multiacrylic oligomers. The system is based on a competitive reaction of a diamine with a diepoxy, DGEBA, acting as a chain extender, and a monoepoxy, GMA, acting as a chain termination agent, avoiding the gelation of the system and introducing double bounds in the oligomer formed.

The synthesis of similar prepolymers based on isocyanate/alcohol reactions by reactive extrusion have also been studied.⁸ From a general point of view, the structure of the obtained oligomer, and furthermore the structure and properties of the issued networks by radical polymerization of the double bonds of the oligomers depends on the relative concentrations of the chain extender and the chain termination agent and on the nature of the amine and additives used (fillers, reactive rubber, or diluent). The synthesis of such oligomers can easily be done in a batch reactor if small quantities are to be prepared. For larger quantities, if a batch reaction

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is used without efficient heat extraction, the high exothermy of these reactions increases the temperature of the batch to a level that initiates the polymerization of double bonds and the gelation of the system. The twin-screw extruder used in this study, is equipped with efficient heat extraction. The regulation allows good control of the reaction making the continuous synthesis of these oligomers technically realistic.

Residence Time Distribution (RTD)

RTD describes the history of the product within the extruder. The mixing of reactants, the efficiency of the chemical reactions, the degradation of products, and the quality of the issued material depends to a large extent, on RTD. With the characterization of RTD, a great deal of information is available for the choice of extrusion parameters and the optimization of the process. A tracer must be used for RTD determination. Different tracers are described in the literature: colorant^{9,10} particles,^{10,11} magnetic powder,¹² radioactive elements,¹³ and UV tracers^{11,14-16} were used. It is important that the addition of a tracer does not disturb the transport and rheology of the system. For this reason miscible tracers, having a similar structure than reactants, are preferred.^{11,15,16} In this study, strong evolution of the structure occurs during the reactions, and a tracer having the structure of the material does not exist. For this reason we used a UV tracer, biphenyl. This tracer is miscible with reactants and products, and because we use it in small quantities, we can assume that no evolution of the chemorheology of the system occurs during extrusion.

EXPERIMENTAL

Materials

The DGEBA epoxy prepolymer used in the study was Bakelite 164 with an equivalent weight of epoxy groups equal to 188 g, as determined by acid titration. The main species is pure DGEBA ($M = 376$ g/mol, $\bar{n} = 0.15$), and the ratio of the secondary hydroxyl group to the epoxy group is equal to 0.075. Catalyst and Versamid were supplied by Cray Valley–Total Chimie and 4,4'-diamino dicyclohexyl methane (PACM) was supplied by Anchor. 1-(2-Aminoethyl)piperazine (AEP) and GMA were from Aldrich. Materials were used as received without any special purification.

Apparatus

A Nicolet MX-1 spectrometer was used for FTIR absorption. The absorbance of the epoxy band at 915 cm^{-1} was determined by the baseline technique in phenylglycidylether (PGE) or DGEBA + diamine. The phenyl group bands were used as reference bands (1497 or 1180 cm^{-1}), because they are assumed to be unmodified during the reaction. The absorbance values are in the domain of validity of the Lambert–Beer law.

A Mettler TA3000 was used for differential scanning calorimetry (DSC) measurements at a $10^\circ\text{C}/\text{min}$ heating rate, under argon atmosphere.

Size exclusion chromatography (SEC) was performed in a Waters device equipped with UV and refractive index detectors. The solvent was tetrahydrofuran (THF) at a $1.5\text{ mL}/\text{min}$ flow rate and a pressure of 5.10^6 Pa . Columns of PL (Polymer Laboratories) gel of 1000, 500, 100, and 100 \AA were used. Number and mass average molar masses were calculated using a calibration with polystyrene standards.

Extrusion

A modular intermeshing corotating twin-screw extruder (CLEXTRAL BC21) was used in this study. The screw diameter was 25 mm and the total barrel length 900 mm. Screw profiles are presented in Figure 1. The screw rotation rate was 33 rpm. The input was $2.5\text{ kg}/\text{h}$.

In a typical reaction, we use 6 mol GMA, 1 mol DGEBA, 2 mol diamine, 3 wt % catalyst (phenol sulfonic acid), and 1000 ppm hydroquinone. A mixture of DGEBA, GMA, hydroquinone, and the catalyst was injected through one side of barrel 1 and the diamine through the other side of the same bar-

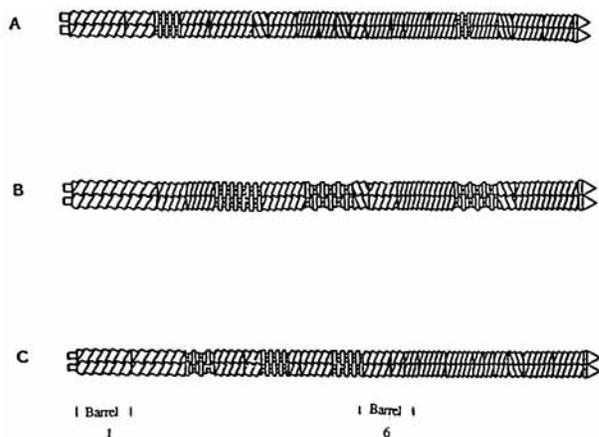


Figure 1 Screw profiles used in reactive extrusion.

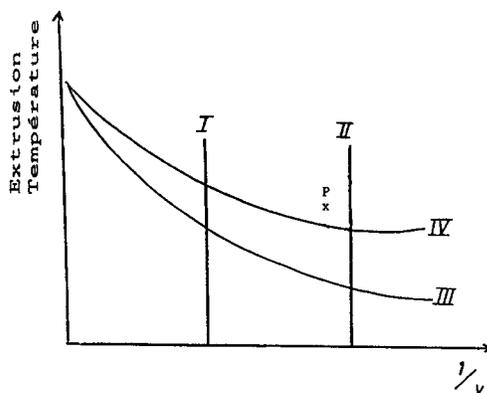


Figure 2 Reactive extrusion diagram.

rel. The stationary state was established in approximately 15 min. Samples of approximately 1 g were then taken from the extruder die, some of them accurately frozen in liquid nitrogen, others kept at room temperature.

RESULTS AND DISCUSSION

Fitting Reaction to Twin-Screw Extrusion Process

Fitting the epoxy-amine reactions chosen for this study to the extrusion process implies taking technical limitations into account, and others related to the different reactions involved in the system. These limitations are summarized in Figure 2. Lines I and II represent the maximum and minimum technically possible extrusion screw speed (v). If the reaction is sensitive to high shear rates, I is shifted to higher $1/v$ values. This is the case, for example when high exothermic reactions are coupled to large viscous dissipation. The temperature can increase up to a level where degradation or secondary reactions can occur. When the used reactants are nonmiscible or when the reaction is diffusion controlled, good mixing is required; and to have enough shearing, II is shifted to lower $1/v$ values.

For each reactive extrusion we can define, for technical considerations or others related to a specific application, a minimum conversion at the extruder die. This conversion must be obtained for a defined temperature when the reactants are in the extruder. Because \bar{t}_m is a consequence of the $1/v$ value, from kinetic studies, we can set curve III. The good extrusion conditions are in the area above curve III. When reactants or products have limited thermal stability, or when secondary reactions can occur at a high temperature, we add a higher upper reac-

tion temperature limit, curve IV. For the system used, IV represents the temperature of the initiation of the thermal polymerization of the GMA double bonds. This can lead to the gelation of the system. We can take this curve IV up to a higher temperature with the use of a radical inhibitor (hydroquinone). The reaction is only possible if curve III is below curve IV. In our case the epoxy-amine reaction is relatively slow, and an efficient catalyst must be used to lower curve III and achieve this condition. Only the reaction conditions defined by the area between curves I, II, III, and IV lead to good products.

Because \bar{t}_m depends not only on $1/v$ values but also on the screw profile, the extrusion diagram presented in Figure 1 is only valid for one screw profile. Anyhow, the residence time of the reactants within the extruder is reduced, and in the more favorable cases, the expected average residence time is 5 min. Knowing the relatively low reactivity of epoxy-amine reactions and that the temperature (curve IV) must be relatively low to preserve double bonds from radical polymerization, a kinetic study was previously made.⁵

Using these results, we can see, for example, that with the use of phenol sulfonic acid as a catalyst and PACM as the amine, we have epoxy conversions, $x = 0.7, 0.8,$ and 0.9 after 5 min of reaction, respectively, at $90^\circ, 105^\circ,$ and 125°C (Fig. 3). These are reasonable conditions for the reactive extrusion of acrylic oligomers and will be used in this study.

Extrusion Parameter Effect

In this part, the reactive system GMA/DGEBA/PACM was used and, to differentiate this system from those where other amines are used, we note it as a PACM based system. Temperatures between

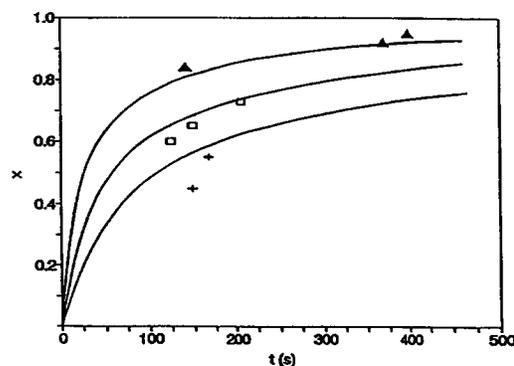


Figure 3 PACM kinetic simulation at $90^\circ, 105^\circ,$ and 125°C . (+), (Δ), and (\square) correspond to reactive extruded oligomers conversion related to \bar{t}_m .

Table I Reactive Extrusion RTD of PACM System

Exp.	Profile	T (°C)	\bar{t}_m (s)	σ_θ^2	σ_t^2 (s ²)	A_s (s ³)	\bar{t}_w (s)	I_t	L_M	L_C	X	T_g (°C)
1	A	105	124	0.026	391	283	127	1.026	75	75	0.6	-32
2		125	140	0.034	670	$5.5 \cdot 10^4$					0.84	-18
3	B	90	166	0.058	1589	$1.9 \cdot 10^5$	175	1.058	225	50	0.55	-40
4		105	205	0.060	2542	$4.4 \cdot 10^5$	218	1.060			0.73	-25
5		125	369	0.065	8869	$2.6 \cdot 10^6$	393	1.065			0.92	-1
6	C	90	145	0.090	1952	681	160	1.090	150	25	0.45	-48
7		105	148	0.072	1583	$2.4 \cdot 10^5$	159	1.072			0.65	-31
8		125	398	0.032	5025	$2.5 \cdot 10^5$	411	1.032			0.95	-3
9	A (Barrel 6)	105	60	0.018	67	1250	61	1.05	25	25		
10	B (Barrel 6)	105	101	0.157	1606	$1.9 \cdot 10^5$	117	1.16	75	25		

Product analysis at the extruder die. The screw speed was 33 rpm for all experiments except exp. 5 where the screw speed was 100 rpm. For exps. 9 and 10 the tracer was injected through barrel 6.

90° and 125°C were selected from kinetic studies.⁵ For each experiment, the epoxy conversion was measured by FTIR and the glass transition temperature (T_g) by DSC. For RTD studies, we used biphenyl as a UV tracer; 0.5 g was injected, as an impulse, in the field hopper to the extruder. Samples were collected from the extruder die, diluted in THF, and analyzed by SEC with a UV detector at 254 nm. The tracer concentrations at time t (C_t) were measured using a calibration curve. The extruder response to the inlet pulse, the residence time distribution E_t , and the cumulative distribution F_t are expressed in eqs. (1) and (2).

$$E_t = \frac{C_t}{\sum_0^\infty C_t \cdot \Delta T} \quad (1)$$

$$F_t = \sum_0^t E_t \cdot \Delta T. \quad (2)$$

We can also calculate the number average residence time \bar{t}_m :

$$\bar{t}_m = \sum_0^\infty t \cdot E(t) \cdot \Delta t. \quad (3)$$

A dimensionless time Θ is

$$\Theta = t/\bar{t}_m. \quad (4)$$

The variance σ_t^2 and a dimensionless variance σ_θ^2 are

$$\sigma_t^2 = \sum_0^\infty (t - \bar{t}_m)^2 \cdot E(t) \cdot \Delta t \quad (5)$$

$$\sigma_\theta^2 = \frac{\sigma_t^2}{\bar{t}_m^2}. \quad (6)$$

The skewness factor A_s is

$$A_s = \sum_0^\infty (t - \bar{t}_m)^3 \cdot E(t) \cdot \Delta t / \sqrt{\sigma_\theta^2}. \quad (7)$$

The weight average residence time is expressed:

$$\bar{t}_w = \frac{\sum_0^\infty t^2 \cdot C_t}{\sum_0^\infty t \cdot C_t} \quad (8)$$

and a dispersity index I

$$I = \bar{t}_w/\bar{t}_m. \quad (9)$$

Results concerning RTD of the reactive extrusion PACM system extrusion are reported in Table I. The determination of the conversion range to be established at the extruder die as well as its T_g are usually directed by technical constraints. For example in the system we use in this study, if the conversion is too low, the reaction can continue outside the extruder; and if large quantities are prepared, the mass effect can lead to the gelation of the system by double bond polymerization and sometimes to the degradation of the product. In other applications, for example when the product is used as a matrix for composite material prepared on line, a low viscosity is needed. In this case, we must avoid high conversions at a low temperature. From preliminary

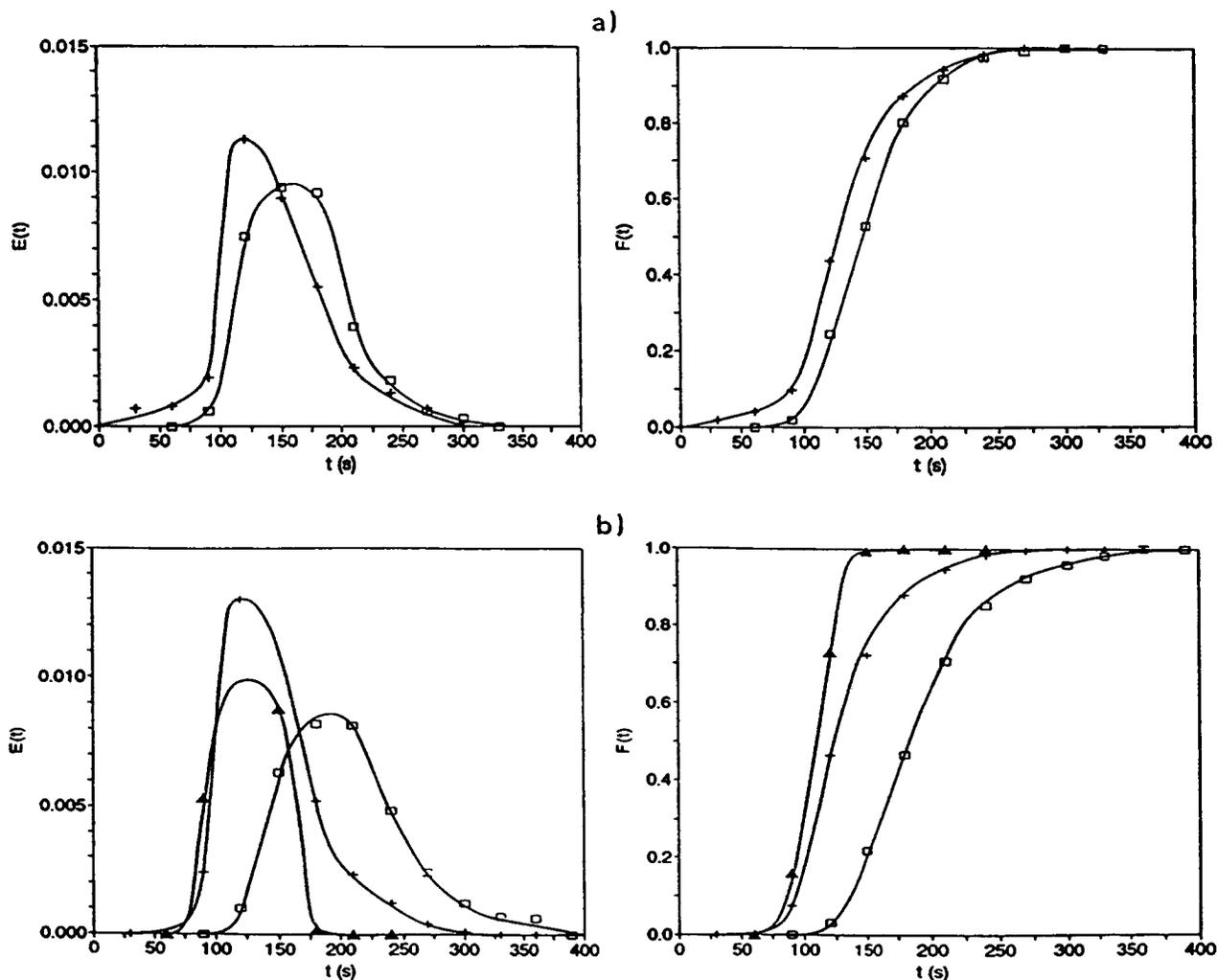


Figure 4 E_t and F_t characteristics of PACM extruded oligomers using profiles (\blacktriangle) A, (\square) B, and ($+$) C at (a) 90°C and (b) 105°C.

experiments and taking into account these points, we chose to obtain a minimum conversion at the die exit not lower than 0.7. We can see (Table I) that with profiles A and C, only the experiments at 125°C lead to the desired product. The other experiments with these profiles lead to points below curve III of the extrusion diagram (Fig. 2). With screw profile B, when operating at 33 rpm only the experiment at 105°C gives the desired product. In the experiment at 125°C, a large increase of viscosity was observed leading to inadequate transport. The reactants remained within the extruder too long and gelation was observed. This experiment is presented as point P in the extrusion diagram. We can obtain the good extrusion conditions either by decreasing the reaction temperature (exp. 4) or by increasing the screw speed (exp. 5).

Analyzing data concerning RTD (Table I), we note that an increase in the reaction temperature leads to higher \bar{t}_m values and broader distributions. This effect is visualized in Figures 4 and 5. The temperature has two opposite effects on the chemorheology of this system: an increase in the reaction rate leading to higher conversions and higher viscosity; and at the same time an increase in temperature leading, at constant conversion, to lower viscosities. In this case, we observed that the kinetic factor is predominant and that a large increase of viscosity is obtained when the reaction temperature increases; and in this process this leads to an increase in \bar{t}_m . Another important extrusion parameter is the screw geometry. We analyzed its effect on \bar{t}_m for experiments at 105°C using profiles A, B, C and also when the tracer is injected in barrel 6. The pre-

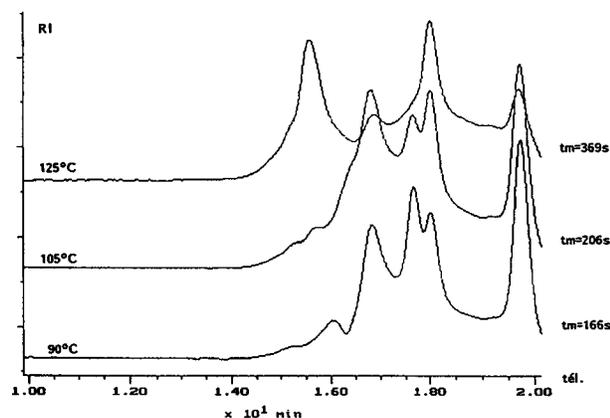


Figure 5 SEC of PACM systems extruded at 90°, 105°, and 125°C using profile B.

dominant factor is represented by the kneading disks and left-handed screw element length, respectively L_M and L_C . As shown in Figure 6 we have a linear evolution of \bar{t}_m with $L_M + L_C$. Examining A_s values, we also note that distribution width increases with $L_M + L_C$. This \bar{t}_m increase leads to an increase in the reaction conversion and the molar mass of the prepared prepolymer as reported in Figure 7. The \bar{t}_m linearity with $L_M + L_C$ is of important practical use, directly giving the possibilities and limits of screw profile design on \bar{t}_m gives indications on the efficiency of the process and its influence on the structure of these reactive extrusion prepared oligomers.

Increasing Conversion at Screw Dye

In the preceding part, we analyzed the effect of processing conditions on the epoxy-amine reaction in the case of the PACM system, with the conclusion being that in many cases conversion is relatively low. This is a consequence of the low reactivity of PACM. More reactive amines can also be used. However we preferred PACM for two reasons: first with the PACM system we did not observe any amine addition on the methacrylate double bonds⁵ (Michael addition), and second the network issued from the PACM prepolymer is expected to have higher T_g than those issued from other more reactive diamines. For these reasons, and in order to have a compromise between reactivity and T_g , amine mixtures of PACM/AEP and PACM/Versamid were used. In another approach, a DGEBA/PACM adduct was used as reactant instead of PACM. In this case, some of the epoxy amine reactions were made before reactive extrusion. The epoxy conversion of this adduct is $x = 0.09$ and, using it a higher conversion at

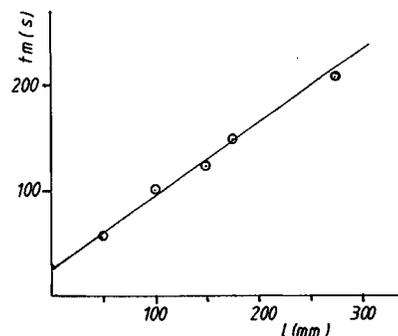


Figure 6 Influence of kneading disks blocks and left-handed screw element length ($L_M + L_C$) on mean residence time (\bar{t}_m) of PACM reactions at 105°C.

the extruder die can be expected. The results are very conclusive (Table II) and a high conversion is obtained when the PACM/AEP amine mixture is used at 105° and 125°C. Not so interesting is the use of the PACM/Versamid mixture with the screw profiles A and C; sufficient conversions were not obtained (exp. 15, 16). The use of the DGEBA-PACM adduct leads also to a high conversion (exp. 14, $x = 0.96$). We note that in experiment 8 (Table II), we also have a high conversion 0.95. However the T_g of the prepolymers is different.

Kinetically Controlled Reactions

In many reactive extrusion experiments, high molar mass reactants are used.⁷ These reactions are often controlled by the reactant mobility and the quality of dispersion when nonmiscible reactants are used, and are consequently controlled by the screw structure and speed. With the system used in this study, it was important to know if processing conditions

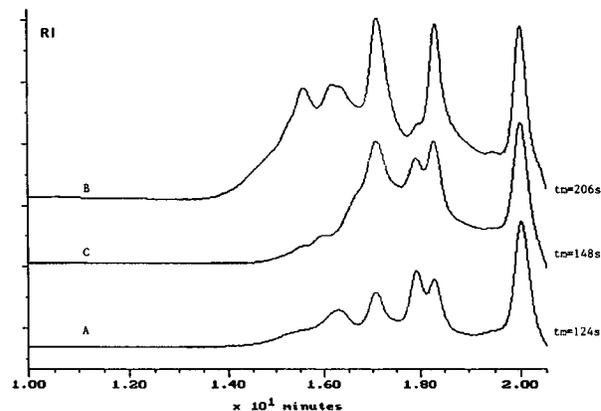


Figure 7 SEC of PACM systems extruded at 105°C using profiles A, B, and C.

Table II Reactive Extrusion Using Systems with Amines Other Than PACM

Exp.	Samples	Profile	T_{ext} (°C)	t_m (s)	x_{ep} IR-TF	$x_{\text{C=C}}$ IR-TF	T (°C)
11	PACM/EP	C	90	—	0.70	0	-18
12		C	105	—	0.97	0	-12
13		C	125	328	1	0.02	-7
14	Adduct DGEBA/PACM	C	125	360	0.96	0	-9
15	PACM/Versamid	C	105	—	0.55	0	-53
16		A	105	187	0.68	0.01	-38

had any influence on the kinetics of the reaction or if the reactions were only kinetically controlled. For this, we associated the epoxy conversion x_{ep} at the extruder die to the measured average residence time and compared them with the kinetic modeling of the batch reaction. As it can be seen in Figure 3, x_{ep}/\bar{t}_m data are very close to kinetic batch curves, meaning that under these conditions, the reactions are simply kinetically controlled. This is an expected result showing that the reactants and products are miscible, and that the reaction temperatures are much higher than the T_g of the final products.

Conversion Distribution

We found that even when a narrow RTD is obtained, all reactants do not remain in the extruder for the same amount of time (Fig. 4). This means that the obtained product is the result of the accumulation of different amounts of products having different conversions. Here is an important difference with a batch reaction where all reactants are allowed to react for the same time providing a good mixing, the conversion distribution is relatively narrow, and a reactive extrusion where the conversion distribution is the consequence of the RTD.

Cassagnau et al.¹⁶ defined a distribution function of a reactive extrusion process (G_x).

$$G_x = \frac{C(x)}{\sum_0^{\infty} C(x)\Delta x} \quad (10)$$

(G_x) is the fraction of modified polymer that has a chemical modification between $C(x)$ and $C(x)\Delta x$.

In this relation, the temporal parameter is substituted by the extent of the reaction. Because these reactions are kinetically controlled, we can use the kinetic modeling for the calculation of x_i .

Examining kinetic curves (Fig. 3), it is evident that an equivalent evolution of residence time will have a higher effect on conversion for low than for

high residence times. These evolutions are also very different when the reaction temperatures are different. For example, for the reaction with the PACM system and using the screw profile B at 90° and 105°C, E_t and G_x are reported in Figure 8. First we see that the E_t of these two experiments are in the same range, and that $G(x)$ are very different. Second, $E(t)$ and $G(x)$ curves are dissymmetric. For $E(x)$ we have a slow decrease for the high residence time.

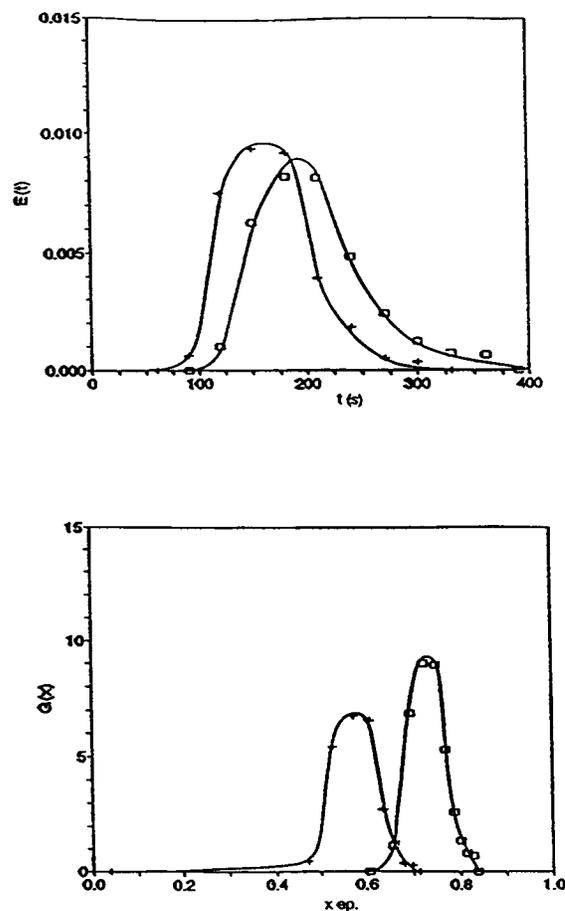


Figure 8 E_t and G_x of PACM systems extruded at (+) 90°C and (□) 105°C using profile B.

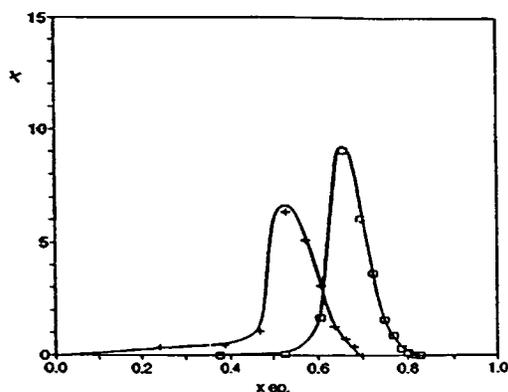
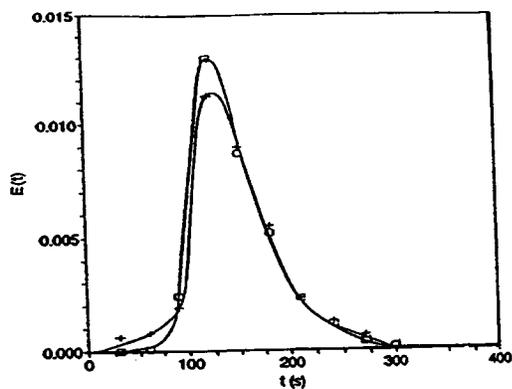


Figure 9 E_t and G_x of PACM systems extruded at (+) 90°C and (□) 105°C using profile C.

This slow decrease has little influence on the reaction conversion because it occurs for high conversion and when the kinetic is very slow. This is reflected by a sharp decrease in the $G(x)$ curve for the higher conversions. For low residence time, a limited evolution of $E(t)$ will have a great influence on conversion, because for these conversions, the kinetic of the reaction is fast and we see that the sharp increase in $E(t)$ for a small residence time leads to a slower increase in $G(x)$.

The example given in Figure 9 clearly shows the effect of temperature on the reactive extrusion. In these two experiments, we have approximately the same RTD and \bar{t}_m values are 147 and 148 s. However, because the kinetics are very different at the two reaction temperatures, the $G(x)$ are very different. As we can see, the information given by $E(t)$ and $G(x)$ values are quite different. Conversion distribution represents the overall reaction, and RTD is more representative of the transport and degree of mixing of the process.

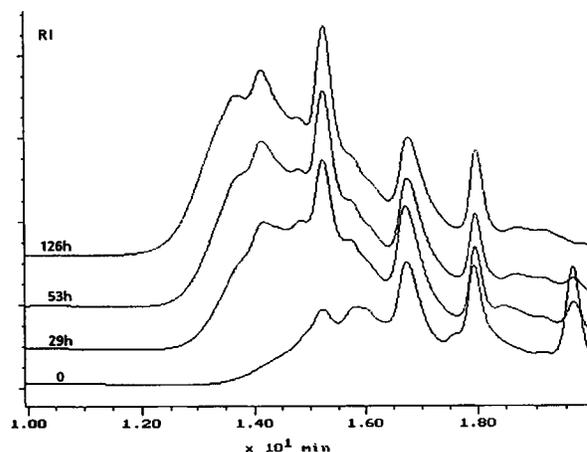


Figure 10 Evolution of SEC at room temperature of PACM systems extruded at 105°C using profile A.

Evolution of Products after Reactive Extrusions

In most cases, the characterization of the products taken from the extruder die showed that the epoxy-amine reactions are not achieved. When aged at room temperature, an evolution of these prepolymers occurs. Because the structure of the issued network by polymerization of double bonds depends on the structure of these prepolymers, it is important to study this evolution. Figure 10 shows the SEC evolution, at room temperatures, of the PACM products obtained by extrusion at 105°C. Reactions evidently continue at room temperature, and the T_g of prepolymers increases and levels off at 10°C. With similar thickening at 50°C, a faster evolution is obtained and the T_g maximum obtained after 1 week is approximately 20°C (Fig. 11). This difference on T_g is due to a different thickening kinetic and initial structural difference of the extruded prepolymers.

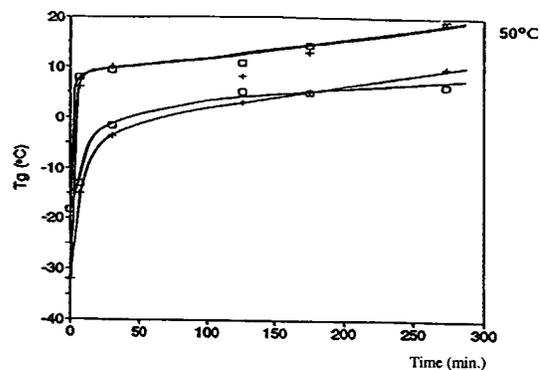


Figure 11 T_g evolution of PACM systems extruded with profile A at (+) 105°C and (□) 125°C. Maturation at room temperature and 50°C.

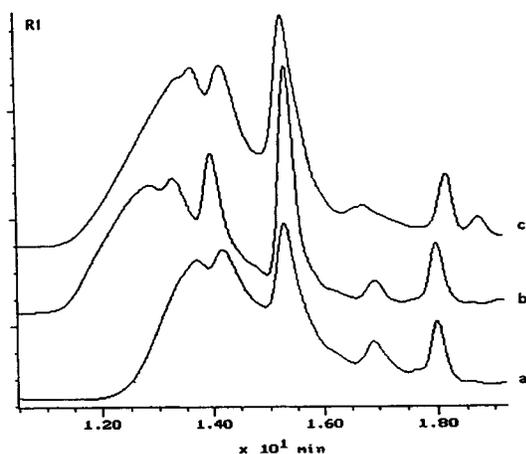


Figure 12 SEC of PACM prepolymers after complete maturation. (a) extruded at 105°C using profile A; (b) extruded at 90°C using profile B; (c) prepared by batch reaction at 50°C for 4 h.

Supposing that a thickening of 30 days at room temperature leads to the end of the chemical reactions and that the obtained structure of the oligomer is definitive, we examined the SEC of the products from different reaction conditions (Fig. 12). We saw that even if an equivalent epoxy conversion is obtained for higher thickening time, the structures are quite different.

CONCLUSION

Epoxy-amine multiacrylic prepolymers can be prepared by reactive extrusion. The appropriate extrusion conditions are defined using an extrusion diagram. The reaction is controlled by extrusion parameters (temperature, screw structure, and speed) and the amine reactivity. The residence time distribution characterizes the extrusion transport; the conversion distribution is more representative of the structure of the issued product. The reaction conversion is not total at the screw exit. The evolution

of the product outside the extruder is controlled during the thickening step. Our next studies with these systems concern the total formulation of the product with the addition of fillers and reactive rubbers and also the modeling of the extrusion process.

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