Reactive Processing of Nonmiscible Polymers: Shear Rate Effect

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ABSTRACT: The effect of shearing in a corotating twin-screw extruder on the apparent kinetic rate of model reactions was studied. Oxazoline-terminated oligomers with different molar masses were prepared and used in condensation reactions with carboxylic acid terminated oligomers. A miscibility study of these oligomers allowed the choice of miscible and nonmiscible reactive systems. Reactions were first conducted in a glass reactor and then in the kneading-disc area of a corotating twin-screw extruder modified to neutralize the transport along the screws. For nonmiscible reactive systems, reactions were slower than equivalent reactions with miscible reactants. A shear increase for these nonmiscible reactants resulted in an increase in the apparent kinetic rate, which was in all cases lower than the rate obtained for miscible reactants. For very high shear rates, mechanical degradation was observed. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2357–2362, 2004

Key words: reactive processing; blends; shear; kinetics (polym.)

INTRODUCTION

Reactions of polymers and oligomers can be performed without diluents on a laboratory scale with internal mixers or small extruders with generally low input. On an industrial scale, twin-screw extruders are often used.[1–7]

Because polymers are rarely miscible as a result of their low mixing entropy, grafting and modification reactions, reactive compatibilization, coupling reactions, and so forth can be achieved with nonmiscible reactants.

It is now well established that the morphology of nonmiscible blends obtained by mixing in a corotating twin-screw extruder is generally obtained during the melting of the blend constituents and in the first restriction area, which often contains kneading elements.[8,9] In addition, polymers remain for most of the residence time in the restriction areas, which are composed of kneading elements, left-handed screw elements, the screw die, and the part of the right-handed screw elements necessary to build up the pressure needed to go through these restriction areas.[10–12]

Reactive extrusion results reported in the literature generally concern reactions leading to positive results. These reactions are often qualified as fast and leading to complete reactions in very short residence times.[13–15]

Therefore, if a particular kinetic behavior of the reactants in a corotating twin-screw extrusion is considered, this effect could logically be due to their residence in kneading areas. Does such an effect really exist? What is the effect of the reactant miscibility and the shearing in kneading elements on the conducted reactions?

Because reactions are often performed at relatively high temperatures so that the complete melting of the reactants and the correct viscosity are obtained, can the high reaction rate be only a temperature effect?

This study is a contribution to the analysis of these points with model reactions.

The miscibility effect was analyzed with miscible and nonmiscible reactants that were prepared and used in the same oxazoline/acid condensation reaction.

The shearing effect on these reactions was studied in reactions performed in classical laboratory reactors and in kneading disks of a corotating twin-screw extruder.

EXPERIMENTAL

Materials

The reactants used in this study are listed in Table I. They were used as received without purification.

Condensation reactions

Reactions in glass reactors

Preparation of oxazoline-terminated polymers (OTPs) OTPs were prepared by the condensation reactions of a fatty dicarboxylic acid (FDA; Pripol; Uniqema, Lon-

TABLE I
Characteristics of the Different Reactants

Name	Code	Molar mass (g mol^{-1})	T_m (°C)	T_g (°C)	Origin
2,2′-(1,3-Phenylene)-bis(2-oxazoline)	PBO	216	148		Mikuni Chemical
Fatty dicarboxylic acid (Pripol 1009)	FDA	577		−50	Unichema
Carboxyl-terminated butadiene with 18% acrylonitrile	CTBNx8	3550		−52	BF Goodrich
Carboxyl-terminated butadiene with 26% acrylonitrile	CTBNx13	3150		−39	BF Goodrich

T_m = melting temperature.

don, UK) with a dioxazoline [2,2′-(1,3-phenylene)-bis(2-oxazoline) (PBO)] in a three-necked flask equipped with a mechanical stirring apparatus and a nitrogen inlet. The flask was heated in a regulated oil bath. The dicarboxylic acid was first added to the flask, and it was stirred until the complete stabilization of the temperature (120°C). PBO was then added. The reactions were monitored by size exclusion chromatography (SEC) and stopped when all PBO had reacted and the molar mass of the obtained OTP had leveled off (ca. 6 h).

OTP/carboxyl-terminated butadiene (CTBN) condensation The reactions of OTP and CTBN were processed in a three-necked flask equipped with a mechanical stirring apparatus and a nitrogen inlet in an oil bath. CTBN was first added to the flask and was stirred until the complete stabilization of the temperature. OTP was then added. The samples were removed from the flask after selected time intervals and were rapidly cooled in liquid nitrogen.

Reactions in extruders

A Clextral BC21 modular, intermeshing, corotating twin-screw extruder (Firminy, France) with a screw diameter of 25 mm was used in this study. The screw profile is presented in Figure 1.

This screw profile contained 100-mm kneading disks with 90° staggering angles followed by 50 mm of reversed screw elements. Typically, 10 g of CTBN and 41.04 g of OTP were premixed and directly introduced over the kneading disks. Samples were removed from the kneading-disk area and rapidly cooled in liquid

nitrogen. With this screw profile, the reactants remained in the kneading-disk area. This kneading-disk area was used as an internal mixer; the reactant mixing efficiency was comparable to that obtained in a classical corotating twin-screw extruder.

Apparatus

Infrared spectra were obtained with a Nicolet 550 Fourier transform infrared spectrometer (Madison, WI). When the reactive systems were analyzed at a high temperature, the monomer mixtures were directly placed between KBr cells in a heated device.

The SEC measurements were made with a Waters 510 apparatus with a refractive-index detector (Medford, MA). Gel columns from Polymer Laboratories (Amherst, MA) (500- and 100-Å) were used for the analysis of the small-molar-mass products. Three Millipore (Billerica, MA) Microstyragel columns (HR1, HR2, and HR3) were used for the analysis of the high-molar-mass polymers. The molar masses were calculated with a calibration curve established with polystyrene (PS) standards. The solvent medium was tetrahydrofuran. It was used at a 1 mL/min flow rate and at a pressure of 3×10^3 Pa.

Differential scanning calorimetry (DSC) measurements were carried out with a Mettler TA300 instrument (Viroflay, France) operated at a 10°C/min heating rate. Sample masses of about 10 mg were used for this analysis.

The titration of carboxylic functions was performed in benzyl alcohol solutions with a Tacussel Electronique PHN 850 titrator (Villeurbanne, France) with a
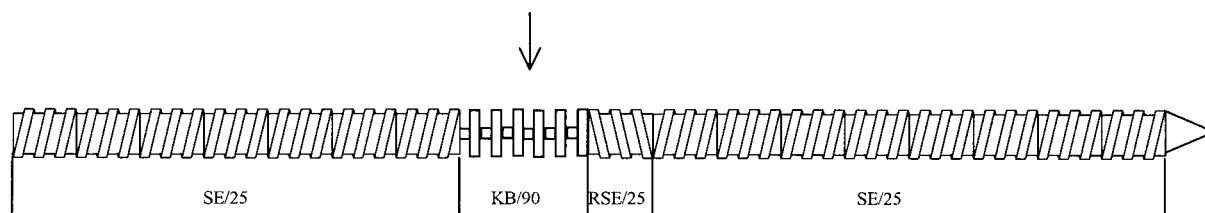

Figure 1   Twin-screw-extruder profile.

0.1N KOH/ethanol solution. A Blanco titration was performed on pure benzyl alcohol

RESULTS AND DISCUSSION

Mixing effects on nonmiscible liquid–liquid reactant kinetics

In a previous article,[16] the oxazoline/acid condensation reaction was studied, and it was shown that, for homogeneous systems, the reaction obeyed a second-order kinetic model. The reaction rate was calculated with the kinetic reaction rate constant, $k = 10.3 \times 10^6 e^{-80600/RT}$ (kg mol^{-1} s^{-1}). (R is the universal gas constant and T is the absolute temperature.)

When a reaction is conducted on nonmiscible reactants, diffusion can occur at the interface.

The exchange surface (S) is a function of the ratio of the matrix viscosity to the dispersed-phase viscosity.

Reagent A diffuses toward reagent B and reacts at the surface. The conversion rate ($\dot{\alpha}$) is[17–21]

$$\dot{\alpha} = \frac{1}{m_A^0} \int \int_S \frac{d\overrightarrow{m_A}}{dt} \vec{n} dS \tag{1}$$

where m_A^0 is the initial mass of component A and $\vec{n}$ is the normal vector of the exchange surface. When the mass flux, $\overrightarrow{\varphi_A} = h_A \rho_A$ (where h_A is the mass-transfer coefficient of A and ρ_A is the mass concentration of A), is constant

$$\dot{\alpha} = \frac{h_A S}{V_A^0} \frac{\rho_A}{\rho_A^0} \tag{2}$$

where V_A^0 is the initial volume of component A. For a constant total volume, $\dot{\alpha}$ becomes

$$\dot{\alpha} = \frac{6 h_A b}{d_B^0} \frac{(1-\alpha)^{5/3}}{1+b\alpha} \tag{3}$$

where α is the conversion and b is a constant. In this case, the reaction is diffusion-limited, d_B^0, the initial diameter of particle B, being a function of the shear rate when the reactive system is mixed. h_A changes with the reaction time and increases with the shear rate.

For a high value of h_A, we obtain

$$\dot{\alpha} = \frac{6 K_B}{d_B^0} \left[\frac{k D_B}{V_0^A} \right]^{1/2} \frac{(1-\alpha)^{7/6}}{(1+b_\alpha)^{1/2}} \tag{4}$$

where K_B is the Henry coefficient and D_B is the diffusion coefficient of B to A. The reaction order is initially equal to 1 and decreases with α. h_B, the mass-transfer

coefficient of B, is a function of the Damköher number:[20]

$$h_B = \frac{(r_B^0)^2}{4 D_B \dfrac{V_B^0}{k}} \tag{5}$$

where V_B^0 is the initial volume of component B and r_B^0 is the initial radius of particle B. For low values of h_A, $\dot{\alpha}$ becomes

$$\dot{\alpha} = \frac{3h}{V_A^0} \left(\frac{1-\alpha}{1+b\alpha} \right)^{4/3} \tag{6}$$

In this case, the reaction order is also lower than 2, even for high shear rates.

For a kinetic homogeneous reaction, $\dot{\alpha}$ is given by

$$\dot{\alpha} = \frac{kb}{V_B^0} \frac{(1-\alpha)^2}{1+b} \tag{7}$$

Unless a favorable orientation of the reactants takes place at the interface or for particular reactions, reactions conducted with nonmiscible reactants are slower than equivalent reactions with miscible reactants. The apparent reaction rate should increase when the interface surface increases (e.g., when the shear rate increases). At a constant temperature and when no secondary reaction occurs, the reaction apparent rate is generally lower than the rate with miscible reactants and should tend, at a high shear rate, to the rate for miscible reactants.

These aspects are verified in the following sections.

Reactive mixture miscibility

Through the condensation reactions of PBO (dioxazoline) and FDA (diacid), with different initial ratios of acid to oxazoline, OTPs with different molar masses were prepared (Table II). The obtained oligomers showed Newtonian rheological behavior or shear rates lower than 100 s^{-1}. Their viscosity (μ) was calculated as follows:[16]

TABLE III
T_g **Values for Blends of OTP with CTBN**

Product	T_{g1} (°C)	T_{g2} (°C)
OTP 0.5/CTBNx8	−56	
OTP 0.5/CTBNx13	−39	
OTP 0.66/CTBNx8	−58	
OTP 0.66/CTBNx13	−45	−17
OTP 0.75/CTBNx8	−62	−16
OTP 0.75/CTBNx13	−43	−16

$$\mu = A \exp\left[\frac{E_a}{RT}\right]\bar{M}^n \qquad (8)$$

where A (frequency factor) is 1.86×10^{-22} Pa S g^n mol^{-n}, E_a (activation energy) is 58 kJ g^{-1} mol^{-1}, and n is 4.

The obtained OTPs were mixed at room temperature with CTBNx8 or CTBNx13. The blend compositions were chosen to obtain a stoichiometric ratio of oxazoline to acid. For example, for the OTP 0.5/CTBNx13 blend, 32.03 g of OTP 0.5 was mixed with 100 g of CTBNx13.

The obtained blends were analyzed with DSC (Table III). When two distinct glass transitions were observed, each close to the glass-transition temperature (T_g) of the corresponding homopolymer, the polymers were not miscible. This was the case for the OTP 0.75/CTBNx8, OTP 0.75/CTBNx13, and OTP 0.66/CTBNx13 blends for the compositions tested.

For the OTP 0.5 blends with CTBNx8 and CTBNx13 and the OTP 0.66 blends with CTBNx13, a single glass transition was obtained in the thermograms, This showed that these polymers were miscible for the tested compositions.

On the basis of these results, we considered the reaction of OTP 0.5 with CTBNx13 and the reaction of OTP 0.75 with CTBNx8 and used them as model reactions for miscible and nonmiscible systems, respectively.

Reactions in the glass reactor: homogeneous and heterogeneous reactive systems

Reactions were conducted at 140°C with a stoichiometric ratio of the oxazoline and acid concentrations. Specimens were taken at different reaction times and were quenched in liquid nitrogen. The different specimens were titrated, and the reaction conversions were calculated. Experiments were performed with and without mixing. For reactions without mixing, homogenization was achieved through the mixing of the reactive system for 2 min before the anchor rotation was stopped. The obtained results are given in Figure 2. These results were also compared with the calculated reaction evolution with results from another study.[16]

For the nonmiscible reactive system (OTP 0.75 with CTBNx8), no reaction or a very low one was obtained. When the nonmiscible reactive system was mixed, a reaction was obtained but at a rate lower than that for
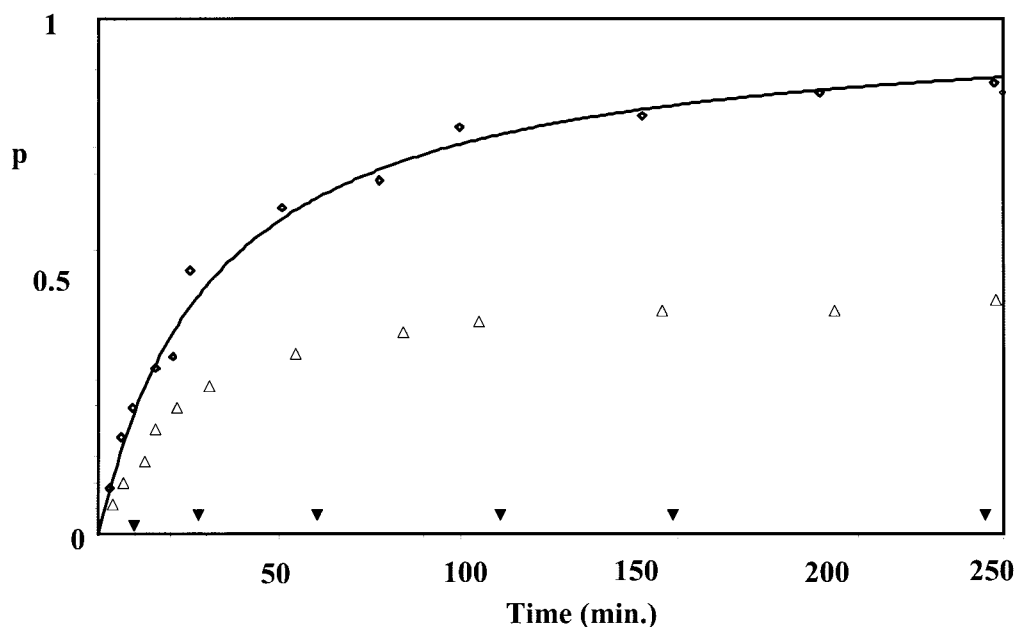

Figure 2 Kinetic study in a glass reactor at 140°C with a stoichiometric ratio of the oxazoline and acid concentrations: (△,▼) the nonmiscible reactive system with and without mixing, respectively; (◇) the miscible reactive system; and (—) the calculated evolution.
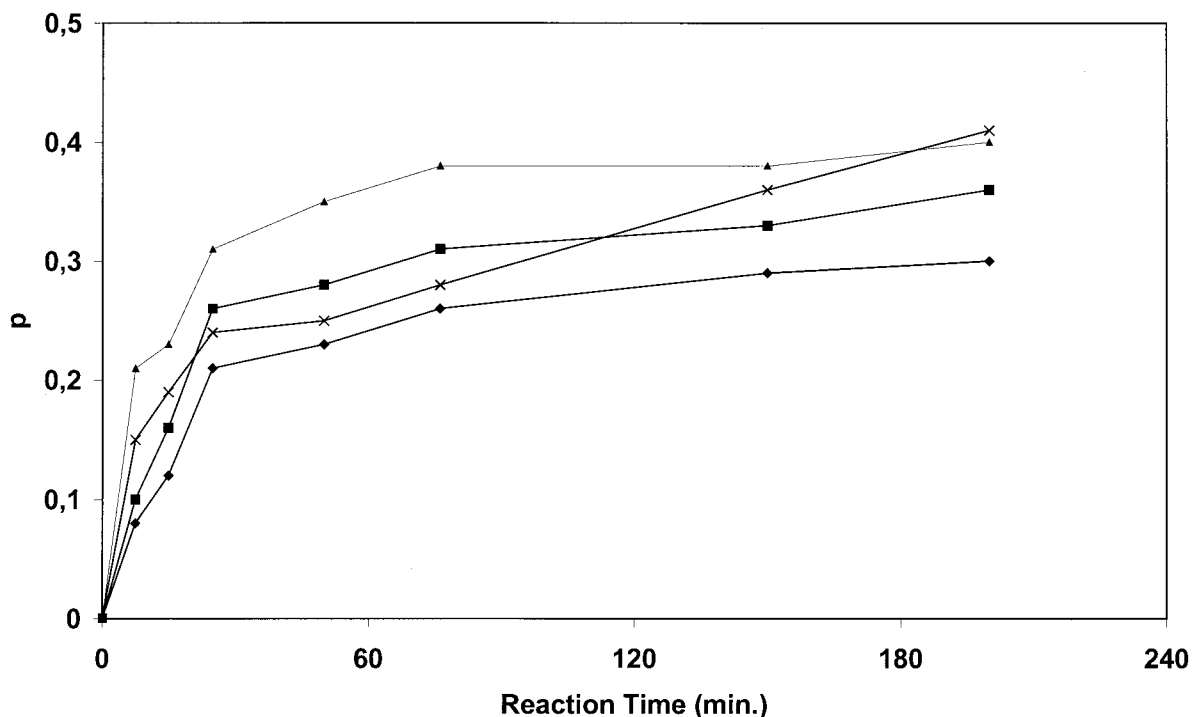
Figure 3 Kinetic study in an extruder at 140°C with a stoichiometric ratio of the oxazoline and acid concentrations: (◆) 20, (■) 60, (▲) 100, and (×) 250 rpm.

the miscible system. The miscible system reacted as predicted by the modeling.[16]

The effect of the mixing on the reactivity of the nonmiscible system was clear: the apparent reaction rate increased with shearing, but the rate remained lower than that for the homogeneous reactive system.

Reaction with corotating twin-screw-extruder kneading disks

Mixing in corotating twin-screw-extruder kneading disks is different from mixing in a classical reactor. For a kinetic study in kneading disks, we neutralized the transport with the screw profile described in Figure 1. Only the quantity of the reactant needed to fill the kneading-disk area was added above the disks. Therefore, the reactions were conducted with an extruder kneading-disk area as an internal mixer. The mixing mechanism and the development of the interfacial area were not exactly the same as those obtained during a classical reactive extrusion because little or no elongational flow was obtained, but we can reasonably conclude that the results obtained are representative of what is really obtained in kneading-disk elements of a corotating twin-screw extruder.

The kinetics were studied for a nonmiscible reactive system (OTP 0.75 with CTBNx8) as the screw rotation rate was increased. As expected, from 20 to 100 rpm, the apparent reaction rate increased regularly. At 100 rpm, the reaction produced results approximately

equivalent to those obtained with the same system in a glass reactor (Figs. 2 and 3).

The reaction performed in the extruder at 250 rpm led to a 0.4 conversion after 200 min of reaction, but the kinetic evolution was different from that obtained at 100 rpm. SEC curves of the products obtained after 200 min of reaction, corresponding to experiments conducted at 20, 100, and 250 rpm in the extruder, are given in Figure 4. As expected, the molar mass of the product prepared at 100 rpm was higher than the molar mass of the product prepared at 20 rpm. The product prepared at 250 rpm showed a binodal distribution.
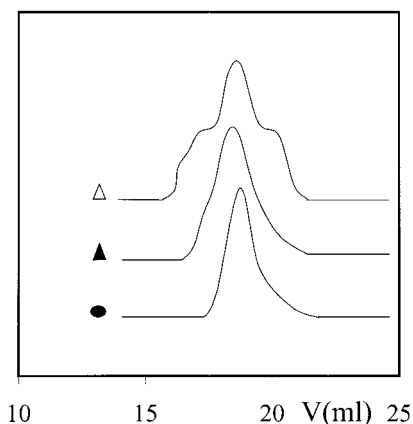

Figure 4 SEC curves of the products obtained after 200 min of reaction in an extruder: (●) 20, (▲) 100, and (△) 250 rpm.

For all these experiments, the reactant temperature was directly measured. All these reactions were performed at 140°C, and the obtained effects could not be attributed to a thermal effect.

The kinetic evolution and molecular distribution in the experiment conducted at 250 rpm could reasonably be attributed to simultaneous polymerization and degradation reactions, the degradation in this case being due to mechanical shear strain. An equivalent mechanical degradation effect was also suspected in a previous study concerning ester amide synthesis by acid oxazoline reactions.[22,23]

CONCLUSIONS

An increase in the apparent reaction rate with mixing during the reactions of nonmiscible polymers has clearly been demonstrated. Even for high shear rates, the reactivity of nonmiscible polymers remains lower than that of equivalent miscible reactants. Generally, the reactive extrusion of nonmiscible polymers is conducted at a relatively high temperature, and the good conversion obtained is due partly to good mixing but often principally to the temperature.

During the reactive extrusion of sensitive polymers, an increase in mixing results in two opposite effects: an increase in the apparent reaction rate and an increase in the progressive degradation effect, especially at high temperatures.

NOMENCLATURE

d_B^0	initial diameter of particle B
D_B	diffusion coefficient of B to A
h_A	mass-transfer coefficient of A
h_B	mass-transfer coefficient of B
k	kinetic reaction rate constant
K_B	Henry coefficient
m_A^0	initial mass of component A
$\vec{n}$	normal vector of the exchange surface
S	exchange surface
V_A^0	initial volume of component A
V_B^0	initial volume of component B

α	conversion
μ	viscosity
$\dot{\alpha} = \dfrac{d\alpha}{dt}$	conversion rate
ρ_A	mass concentration of A
$\varphi_i = \dfrac{1}{S}\dfrac{dm_i}{dt}$	mass flux
R	universal gas constant
T	absolute temperature

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