Optimum Temperature Profile for Noncatalytic Reaction to Produce Polyamide Hot Melt Adhesives

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ABSTRACT: Foaming is a general problem in the manufacturing of fatty polyamides. It is mainly affected by the mixing rate and reaction temperature. The effect of the reaction temperature and rate of mixing on foaming are investigated. Time minimization for the polyamidation reaction to prevent foaming is performed. The process constraints are the rate of temperature increase and the rate of the production of water. It is found that with an increase in the mixing rate, foaming starts at lower temperatures and with a decrease in the mixing rate, foaming only starts at high temperatures. For each mixing rate, with an increase in the temperature, the duration of foaming is shorter because the increase in the rate of foaming ends. Temperature profiles with time for different mixing rates are generated, and it is found that the reaction time decreases with increasing mixing rate. The generated temperature profiles are verified experimentally, and no foaming is observed. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1817–1822, 2006

Key words: polyamides; adhesives; polymerization

INTRODUCTION

Hot melt adhesives are solid adhesives heated to a molten liquid state for application to substrates, which are applied hot and then cooled, quickly setting up a bond. The largest uses of hot melt adhesives are in packing, bookbinding, disposable paper products, wood bonding, shoemaking, and textile binding. Manufacturing of fatty polyamides is phasing a foaming problem because of the water formation as a result of the polyamidation reaction. Foaming can be explained as the distribution of a gas throughout a continuous liquid phase in a finely divided form.[1–3] Initially, as the foam is formed, the globular bubbles are discrete with large amounts of liquid separating each bubble. The walls (lamellae) of the bubble are therefore thick within the liquid phase. This type of foam is sometimes called spherical or wet foam. Over time, the individual bubbles congregate more closely together as the liquid begins to drain from the bubbles, so that the walls of the bubbles become thinner. This type of foam in which the bubbles are closely packed together and have little liquid separating them is described as dry foam.[3] As the foam walls get thinner they eventually rupture and the individual bubbles collapse into larger bubbles made up of the gas from the smaller units. These large bubbles then will migrate to the surface.

From the above-mentioned work and other literature,[4–8] it can be concluded that the reaction temperature has a significant effect on foaming and, in order to prevent it, the reaction should be started at the lowest possible temperatures. It should then be gradually increased so that the rate of production of water will be low enough to prevent the onset of foaming. By a gradual increase in the temperature, the evaporation of ethylenediamine is also prevented.[9] As mentioned by several groups,[6–9] the rate of production of water, which is directly related to the rate of the reaction, is an important criteria for the control of foaming. It can be inferred that, to prevent foaming, in addition to a gradual increase in the temperature, the mixing rate should be low, as practiced in industry. This low mixing rate condition should be maintained until the rate of the reaction becomes acceptably low, which subsequently lowers the rate of water production. After foaming is completed, the mixing rate can be increased to increase heat transfer and the temperature can be raised to increase the rate of the reaction.

Although foaming is a general problem in the manufacturing of fatty polyamides,[6–8] there is no substantial work found on the effects of the mixing rate and temperature on foaming, and this includes the generation of a temperature profile to prevent the formation of foam. In our previous work[10] we investigated the effects of the mixing rate and temperature on foaming for fatty polyamides with a catalyst. In the present work we studied the effects of the mixing rate and temperature on foaming without a catalyst. To avoid
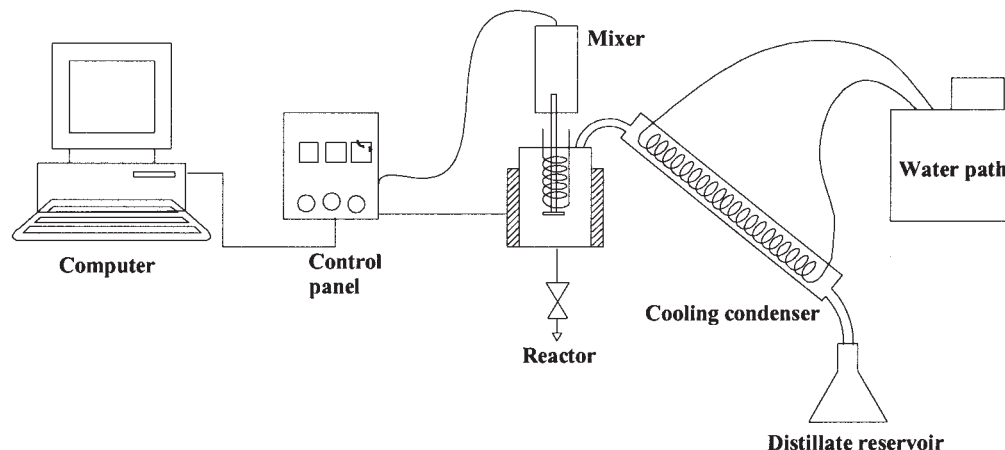
Figure 1 A schematic diagram of the experimental setup.

foaming for a batch polymerization reaction, the temperature is gradually increased from 405 to 475 K, the temperature profile with time that prevents foaming at each mixing rate is obtained, and the criterion used for controlling foaming is the rate of production of water or the rate of the reaction. At each temperature and mixing rate, the minimum rate of the reaction at which foaming is completed is used as the criterion for controlling foaming.

The temperature range usually employed in the literature and industry is from 405 to 475 K, and a gradual increase of the temperature is carried out to prevent foaming. The purpose of increasing the reaction temperature is to increase the rate of the reaction, thus minimizing the reaction time, and to obtain a temperature profile at which it prevents foaming. This is the aim of this work.

EXPERIMENTAL

The experimental setup shown in Figure 1 consists of a 1.5-L stainless steel reactor (11-cm diameter) equipped with a variable stirrer (with an anchor-type four-blade stirrer with a 5-cm diameter), nitrogen inlet tube, and foam sensor based on electrical conductivity; the reactor is connected to two condensers. A dimer fatty acid (PRIPOL 1013, Uniqema, Gouda, The Netherlands) with 97% purity (0.1% monomer, 97% dimer, and 3% trimer) and an acid value of 195 was used. Ethylenediamine was laboratory reagent grade having purity above 98% as determined by titration with standard acid. All other materials were reagent grade. In a typical operation, 240 g of dimeric fatty acids were charged into the reactor and the mixture was heated to 10 K below the desired operating temperature. An extra molar amount of ethylenediamine (based on moles of dimer fatty acid) was preheated to 391 K and added to the reactor. Extra amine was used to compensate for the amount evaporated during the

preheating process. The stirring speed was set at 75, 200, 300, 400, and 500 rpm. Sufficient free space was provided in anticipation of foaming. The reaction was carried out at five different temperatures in the range of 405–465 K. Within this temperature range, the materials remained in a molten state. The water generated during the reaction and evaporated diamine were purged from the reactor using nitrogen with feed rate of 20 mL min^{-1}. These materials were later condensed and collected in a container prepared for analysis. The temperature of the condenser cooling water was kept at 279 K. The amount of distillate collected with time was measured, and the sample refractometry index was analyzed using a refractometer (model NAR-1T). The foam sensor was placed 1.8 cm above the reaction mass surface. If the volume of the reactants increases by 75% because of foaming, it touches the foam sensor and triggers an alarm. In addition, when the foaming period is over, the alarm goes off. To obtain the rate of the reaction at which the foaming is completed, the time at which foaming ends at each mixing rate and temperature was recorded. At this time, the concentrations of acid, amine, and water were determined from the kinetic model.[11] This also included the kinetic rate constants. These procedures were carried out at all temperatures and mixing rates. For a particular mixing rate, the minimum rate at which foaming ends is known as the minimum rate of foaming.

Kinetic model and process constraints

The reactor model for the kinetics can be found elsewhere.[11,12] In this model, mass balances for components were applied and empirical equations were introduced for the flow leaving the reactor and the concentration of ethylenediamine and water. The forward and reverse rate constants and empirical parameters were obtained.[11] The process constraints should be considered in order to obtain a feasible operating

TABLE I
Times at Which Foaming Ends and Occurrence of Foaming at Each Mixing Rate and Temperature

	Time at which foaming ends (min)				
T (K)	75 rpm	200 rpm	300 rpm	400 rpm	500 rpm
405	No foaming	No foaming	No foaming	No foaming	2
420	No foaming	No foaming	No foaming	No foaming	22.6
435	No foaming	5	No foaming	11.17	9
450	No foaming	No foaming	4.17	3.17	4
475	No foaming	No foaming	1.5	2.2	1.5

condition. The aim is to minimize the time required to increase the temperature from 405 to 475 K in order to attain an optimum temperature profile without foaming. To obtain this, the temperature should increase as high as possible; however, the increase should be limited such that the reaction rate remains less than the minimum rate for foaming. In addition, the rate of temperature increase is constrained by the heat flux from the reactor jacket: for example, the heater duty has a finite capacity, and the heat transfer may be limited by the overall heat-transfer coefficient; for the laboratory-scale semibatch reactor we used, the maximum rate of temperature increase is 2.5 K min^{-1}. The optimum temperature profile is obtained using a simple computer program developed using MATLAB software. Time discretion is first applied to some steps, and at each step the temperature is increased stepwise. At each step, the rate is checked to see if it remains less than the minimum rate of foaming (r_{min}, which is the minimum rate of reaction above which foaming begins) and the temperature remains as high as possible but less than the maximum rate of the temperature increase (2.5 K min^{-1}). The constraints can be formulated as follows:

$$r \leq r_{min} \tag{1}$$

$$\frac{dT}{dt} \leq \frac{dT}{dt}\Big|_{u} \tag{2}$$

where r is the generation rate of a functional group (mol kg^{-1} min), r_{min} is the minimum rate at which foaming ends (mol kg^{-1} min), t is the time (min), T is the temperature (K), and U is the upper conditions of the rate of the temperature increase. This optimum temperature profile at each time interval will be saved; then, the program will compute the next time step. In this programming, only the temperature is allowed to increase or remain constant. Then, the program will retrieve the saved temperature profile over time that satisfies the process constraints.

RESULTS AND DISCUSSION

In some cases foaming starts to occur at the beginning of the reaction; however, in most of cases, foaming only starts to occur after the reaction has taken place for some time. Table I shows the times at which the foaming ended and the occurrence of foaming at each mixing rate and temperature; at a mixing rate of 75 rpm, foaming does not occur even at high temperatures. For medium mixing rates of 200, 300, and 400 rpm, foaming does not occur at low temperatures; however, foaming starts to take place at high temperatures. At a high mixing rate of 500 rpm, foaming occurs at all temperatures. The occurrence of foaming at high temperatures is attributed to the high rate of water production. Because higher mixing rates will cause nucleation of bubbling, even when the concentration of gas in the polymer is less than a saturated concentration as explained by James and Chang[5] and explained in the Introduction section, excessively high mixing rates will cause more nucleation of bubbling; at high mixing rates. even at low rate of production of water, foaming still exists. At high mixing rates, foaming lasts longer, although the rate of the reaction is sufficiently low, as shown in Table II. With respect to temperature, at a specific mixing rate (e.g., 500 rpm), as the reaction temperature decreases, the duration of foaming becomes longer. This could be attributed to the relatively high concentration of reactants remaining in the reactor as a result of the low rate of the reaction. To obtain a temperature profile with no foaming, first the rate of the reaction at the end of foaming should be obtained. Table II shows the concentration of acid, amine, and water and the rate of the reaction at the time at which foaming ends. The rates are calculated from the following equation:

$$r = k_1 C_{COOH} C_{NH} - k_2 C_{H_2O} C_{CONH} \tag{3}$$

where k_1 and k_2 are the forward and reverse rate constants (kg mol^{-1} min^{-1}), respectively; COOH is carboxylic acid, NH is amine, and CONH is the amide of amine and carboxylic acid.

Figure 2 shows the rate of the reaction versus time at different mixing rates for the optimum temperature profiles. The results indicate that, for 500 and 400 rpm, the rate at the beginning is higher than the minimum rate of foaming shown in Table II. For the rate profile, the fluctuation in the rate of the reaction is due to the increase in the temperature and decrease in the con-

TABLE II
Concentrations of Acid, Amine, and Water and Rate of Reaction When Foaming Ends

Mixing rate (rpm)	T (K)	Acid concn (mol kg^{-1})	Amine concn (mol kg^{-1})	Water concn (mol/kg^{-1})	Rate (mol kg^{-1} min^{-1})
200	435	1.452	2.498	1.4803	−0.159
300	475	1.525	2.775	1.393	−0.515
	450	1.373	2.376	1.443	−0.190
400	475	1.257	2.341	1.578	−0.342
	450	1.587	2.667	1.304	−0.252
	435	0.885	1.844	1.801	−0.053
500	475	1.474	2.275	1.465	−0.599
	450	1.864	2.976	1.098	−0.185
	435	1.412	2.140	1.265	−0.086
	420	1.162	1.921	1.656	−0.031
	405	2.944	3.552	0.146	−0.067

centration with time, as depicted in Figure 2. At 500 and 400 rpm the rate is higher at first than the minimum rate of foaming whereas the temperature during this interval is constant (Figs. 3, 4); after that, the rate is almost constant and nearly to the 95% minimum rate of foaming (i.e., the minimum rate of the reaction above which foaming starts to take place). The generated temperature profiles can be used to prevent foaming and at the same time to satisfy the minimum time required to reach 475 K. From these results it is also found that for 200 and 300 rpm the rate is less than the minimum rate for foaming, even though the rate of temperature rise is set at the highest possible rate (2.5 K min^{-1}). At 75, 200, and 300 rpm the reaction rate profiles are almost the same and this is attributable to the same temperature profile and the same initial conditions. For optimization purposes, at each mixing rate, the minimum value of the reaction rate is chosen. To ascertain that foaming will not take place, 95% of that minimum value is used for optimization. For example, at 500 rpm the minimum rate that is used for optimization is 0.031 mol kg^{-1} min^{-1}, which is
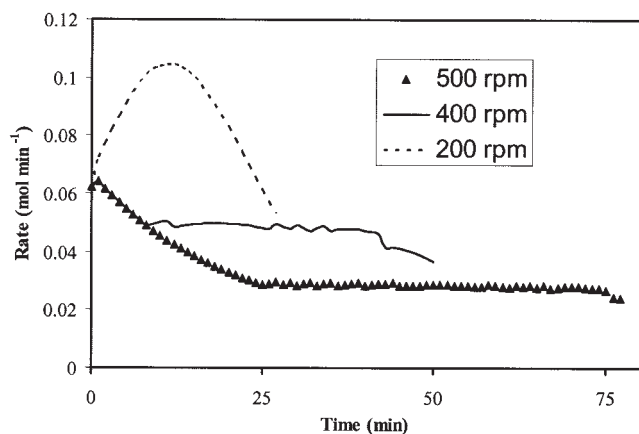
known as the minimum rate of foaming. As can be seen from Table II, as the mixing rate increases, the minimum rate for foaming decreases; this is attributed to the increase in shear rates at higher mixing rates.[5] At each mixing rate we found that, when the temperature is decreased, the rate at which foaming ends also decreases. This is attributed to the different conditions that exist such as the temperature, viscosity, and vapor pressure of water. The minimum rate for foaming at 500 rpm is at 420 K. Although the rate of the reaction at the beginning of the reaction at 405 K is higher than this rate, as can be seen from the Table II, at 405 K there is foaming only for 2 min; this is due to different conditions existing at these two temperatures, such as the viscosity and vapor pressure of water.

Figure 3 shows the temperature profile for 500 rpm with no foaming, and the results show that the temperature should be kept constant in the first 25 min constrained by foaming. After that, the temperature should be increased; and, as can be seen from Figure 3, the slope is less than 2.5 K min^{-1}, so it is not constrained by the duty capacity of the heater. Because the minimum rate of foaming increases with the tem-

Figure 2 The rate of the reaction versus time for different mixing rates for the optimum temperature profiles.
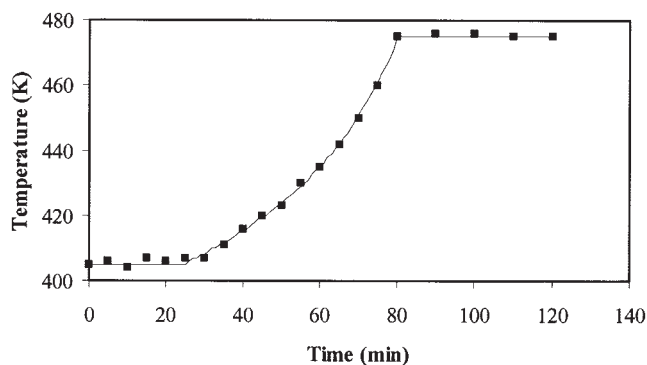

Figure 3 Optimum temperature profiles at 500 rpm for no foaming: (■) experimental data.

Figure 4 Optimum temperature profiles at 400 rpm for no foaming: (■) experimental data.
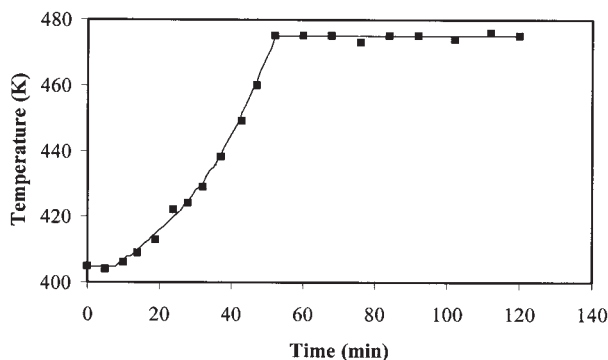

Figure 5 Optimum temperature profiles at 200 rpm for no foaming: (■) experimental data.

perature, although in the first 25 min the rate of the reaction[11] is higher than the minimum rate of foaming, no foaming exists, because at this time interval the temperature is between 405 and 435 K (the temperature at which the minimum rate of foaming is obtained). The reasons for this were already explained. As shown in Figure 3, after 25 min the maximum allowable temperature is constrained by foaming and the plot can be divided into two smaller subregions. The first region has a slope of 0.857 K min^{-1} from 405 to 435 K (25 min), and the second region has a slope of 2 K min^{-1} from 435 to 475 K (80 min). After 80 min the temperature reaches 475 K and the reaction can proceed at this temperature without any foaming occurring. It can be concluded that for 500 rpm, in order to prevent foaming, the temperature should first be set at 405 K for 25 min, then it must be at 435 K for 35 min (0.857 K min^{-1}), and then it must be increased to 475 K for 20 min (2 K min^{-1}). After that, the reaction can be continued at 475 K until the desired conversion is achieved. A common procedure in industry to increase the temperature from 405 to 475 K (52 min) is by linearly increasing it over 2 h,[13] which is equivalent to a heating rate of 0.583 K min^{-1}. The temperature profile generated in Figure 3 reduces the time required by 40 min. Figure 4 shows the temperature profile for 400 rpm with no foaming. The results show that the temperature must be kept constant for the first 8 min because it is constrained by foaming. It takes 44 min to increase the temperature from 405 to 475 K with a heating rate of less than 2.5 K min^{-1}. Moreover, the region can be divided into two smaller subregions. The first one is with a slope of 1.11 K min^{-1} from 405 to 435 K (27 min), and the second region is with a slope of 2.353 K min^{-1} from 430 to 475 K (17 min). In comparison with the time taken for 500 rpm, the total time to reach 475 K is shorter, because of the higher minimum rate of foaming at this mixing rate.

Figure 5 shows the temperature profile for 200 rpm with no foaming; the temperature profile is a straight line with a slope of 2.5 K min^{-1}. This shows that at this
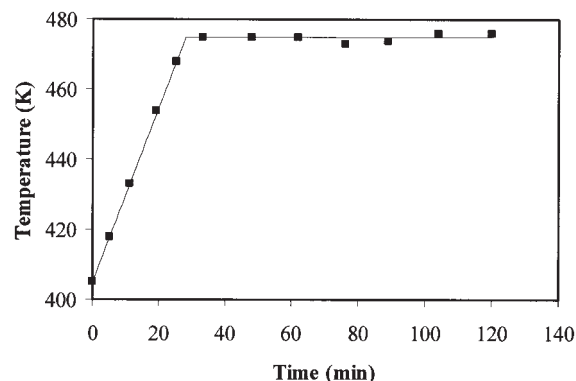
mixing rate the temperature is constrained by the heater capacity and it is not constrained by foaming. This is due to the higher minimum rate of foaming at this mixing rate. Therefore, the heating rate can be increased to the maximum capacity of the heater. For 75 rpm, because there is no foaming at all temperatures, the duty capacity of the heater is the only constraint and the temperature profile will be the same as that of Figure 5. Although at a low mixing rate the time to increase the temperature is shorter, one must consider that a higher mixing rate is better than a lower mixing rate in terms of heat transfer.

Figure 6 provides the concentrations of acid or amine at different mixing rates at the optimum temperature profile. The figure shows that the concentrations are decrease almost linearly with time. The concentration for 500 rpm is higher than those at other mixing rates, and this is attributable to a low minimum rate of foaming. For the same reason as that at 400 rpm, the concentration is higher than that at 75, 200, and 300 rpm. At 75, 200, and 300 rpm the profile of the concentration is the same because of the same
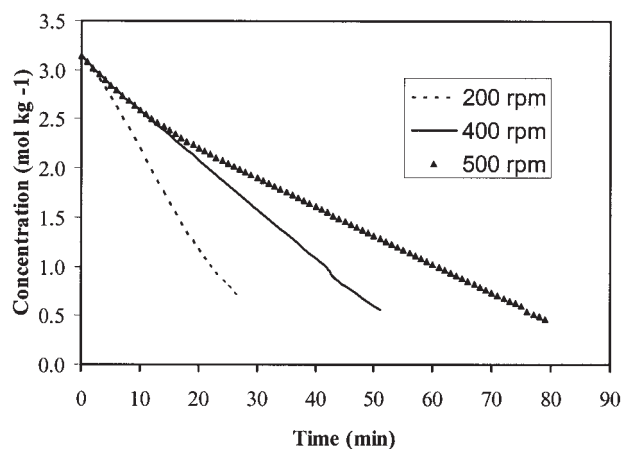

Figure 6 The concentration of acid or amine over time at different mixing rates for optimum temperature profiles.

temperature profile and the same initial conditions. The optimum temperature profiles were verified experimentally. No foaming occurred within the temperature profiles except for the first 2 min at 500 rpm, as expected, because at 405 K (see Table I) and 500 rpm foaming does take place. The start of the temperature profile from 405 K is from industrial practice.

CONCLUSION

The optimum temperature profiles at different mixing rates for optimum operating conditions without foaming in a semibatch polymerization reactor were generated. The process constraints (foaming and heating rate) were considered in the optimization study. We found that an increase in the mixing rate causes foaming to start at lower temperatures and a decrease in the mixing rate causes foaming to occur only at high temperatures. The minimum rate of foaming obtained for different temperatures at a fixed mixing rate decreased with an increase in the mixing rate. This minimum rate was used to obtain the optimum temperature profile for a variable-temperature reaction. The obtained temperature profiles were verified experi-

mentally, and the results showed that no foaming took place.

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