

A Study on the Polymer Layer-Forming Phenomena in a Rotating Disk Polycondensation Reactor

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SYNOPSIS

An experimental study is reported on the measurement of polymer melt film thickness in a rotating disk polycondensation reactor. The layer thickness of molten poly(ethylene terephthalate) on a rotating disk was measured at 280°C using an electrical conductivity probe at different radial and angular positions. It was observed that the polymer film thickness was not uniform in both radial and angular positions, particularly for high molecular weight polymers. For the slowly rotating disk system employed in our experimental study, the disk rotational speed and gravity effects on the polymer-layer formation were found to be quite significant. The experimental results were used to develop an empirical correlation for the calculation of polymer film thickness and polymer melt holdup on a rotating disk.

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INTRODUCTION

Many industrially important engineering thermoplastics such as poly(ethylene terephthalate) (PET) are manufactured by multistage melt condensation polymerization processes using either batch or continuous reactors. In a continuous PET process, e.g., low molecular weight prepolymers (degree of polymerization $[X_n] = 10\text{--}30$) are first produced in a train of mechanically stirred tank reactors at about 260–280°C and 10–30 mmHg. As the melt viscosity increases with an increase in polymer molecular weight, prepolymers are transferred to a specially designed finishing polymerization reactor from which ethylene glycol, the main condensation byproduct, is removed at much lower pressure (0.1–1.0 mmHg) until a high molecular weight polymer is obtained. Since the main polymerization reaction is reversible, with ethylene glycol as a main condensation byproduct, the forward reaction (chain growth reaction) should be promoted to obtain high molecular weight polymers. Thus, the design and operation of a finishing-stage reactor is usually focused on how ethylene glycol and other volatile species

can be removed effectively from a highly viscous polymer melt while the formation of unwanted side products is minimized. In a continuous polycondensation process, the finishing reactor usually consists of a high-vacuum horizontal cylindrical vessel with a rotating shaft on which circular disks, cages, or shallow flight screws are mounted in order to facilitate the removal of volatiles from the polymer melt. Various designs of finishing polycondensation reactors are reported in the patent literature.^{1–4}

Recently, it has been reported that demands for thermoplastic polyesters, particularly PET, are expected to grow steadily in the coming years, because, unlike many other polymers or plastics, PET are readily recyclable and considered as one of the environmentally most benign polymers.⁵ With an increasing importance of product quality control, the polymer industry is moving toward the development of more efficient polymerization technology, particularly for existing processes. It is widely recognized that an improved understanding of both chemical and physical phenomena occurring in polymerization reactors is crucial for process improvement or innovation. One of the strategies to improve the understanding of PET polycondensation processes, which will eventually lead to an improved process operation and control, would be to develop and utilize a quantitative reactor model. Such a model

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should be capable of predicting the polymer production rate as well as important polymer properties such as molecular weight, molecular weight distribution, and the concentrations of various side products and functional end groups in the polymer. Although there are many reports on the theoretical modeling of melt polycondensation processes, very few experimental studies have been reported.

It is well known that flow patterns, reactions, and mass-transfer processes in a continuous melt polycondensation reactor are quite complex. As mentioned earlier, one of the key design and operational factors in the finishing polycondensation reactor is to facilitate the removal of volatiles such as ethylene glycol from the highly viscous polymer melt. To do so, it is important to understand relevant physical and chemical phenomena, particularly the formation of polymer layers on an agitator device that provides as large a surface area-to-volume ratio as possible for effective removal of volatiles. Numerous patents describe a variety of agitator and reactor configurations for the finishing polymerization of thermoplastic polyesters.¹⁻⁴

In this article, we consider a rotating disk reactor as a model finishing polycondensation reactor. The main objective of our study was to investigate the polymer film or layer-forming phenomena on a rotating disk using PET melt under realistic reaction conditions. To date, few reports are available in the literature on the polymer melt layer-forming phenomena in finishing polycondensation reactors. In a rotating disk reactor considered in our study, circular disks are mounted on a central shaft in a horizontal cylindrical reactor vessel. The disks are partially immersed (less than 50%) in a bulk polymer melt phase. As the shaft rotates slowly, a small amount of polymer melt is dragged upward, forming a thin layer or film of fluid on the disk surface. Then, volatiles such as ethylene glycol are removed by vacuum from the thin layer on the disk. The polymer layer or film, after being exposed to a vapor phase for a short time, is mixed again with the bulk melt phase as the disk rotates. The bulk polymer melt phase moves toward the outlet of the reactor by a feed pump and the bulk phase is mixed continuously with the polymer film phases on the rotating disks.

Quite obviously, the polymer holdup affects the rate of mass transfer, which, in turn, affects the rate of molecular weight increase. One can expect that the film thickness or holdup on a disc will be affected by the polymer's molecular weight or melt viscosity. For the development of a quantitative reactor model, it is necessary to know the melt holdup on a rotating disk and the rate of mass transfer in each disk. Al-

though rotating disk devices have been used as gas-liquid contacting devices in other applications such as wastewater treatment, blood oxygenation, and thin-film coating for viscous liquids,⁶⁻¹⁰ low-viscosity fluids and high disk rotating speed are generally employed in these processes. The disk operating conditions in these processes are quite different from those used in a finishing-stage polycondensation reactor where a much higher viscosity polymer melt is handled. In this article, we report an experimental study on the investigation of polymer melt layer-forming phenomena on a rotating disk reactor.

EXPERIMENTAL

For the study of polymer film or layer-forming phenomena, we built a bench scale batch rotating disk reactor device as shown schematically in Figure 1. The reactor (diameter = 14 cm) is made of stainless steel and a disk (diameter = 12.7 cm) is mounted on a central shaft. This reactor can be used as a semibatch polycondensation reactor. The reactor is first charged with dried PET pellets and heated to 280°C by an electrical heating blanket. When the polymer pellets are completely melted, the disk is less than 50% immersed in the polymer melt. The stirrer bearing units that hold the central shaft are cooled by a circulating cold fluid in the seal jacket. On one end of the reactor cover, several holes (diameter = 0.4 cm) are drilled in several radial and angular positions so that a probe can be inserted into it to measure the film thickness at each location on the disk. Figure 2 shows the layout of the holes on the reactor cover.

A schematic diagram of the probe assembly is shown in Figure 3. The probe consists of inner and outer metal tubes which are separated by silicone rubbers. The probe is attached to a micrometer to measure the distance that the probe moves toward the disk surface. After the polymer pellets are completely melted, the disk rotates at a prespecified speed. Then, the probe is inserted into a hole on the reactor cover and pushed slowly toward the rotating disk. As the probe tip reaches the surface of the polymer layer, the annulus near the probe tip is filled with a small amount of polymer melt, causing a large change in voltage across the reference electrical resistance. A small amount of condensable byproducts and transesterification or polymerization catalyst (e.g., Ti, Zn, Mn, Sb) left in the polymer is believed to act as an electric conductor. The voltage signal is monitored by a data acquisition computer and the probe position (z_1) at which the first significant

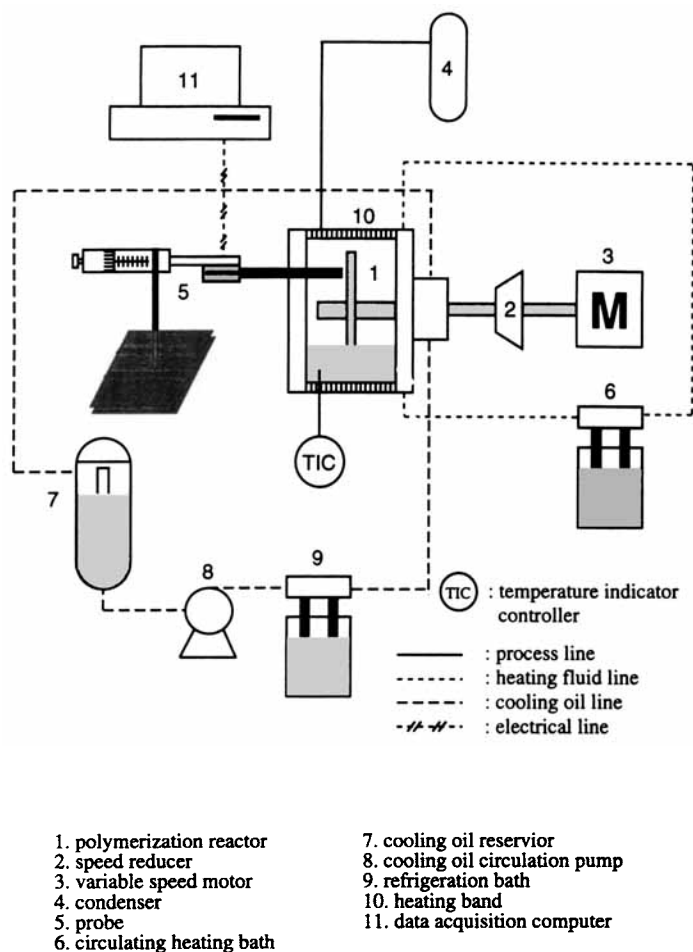


Figure 1 Schematic diagram of a melt polycondensation reactor system used for film-thickness measurement.

change in the voltage signal occurs is marked. Then, the probe is moved further toward the rotating disk by turning the micrometer knob slowly. As the probe tip reaches the metal disk surface, another large voltage change occurs across the reference resistance, and again the probe position (z_2) is marked. Then, the distance the probe travels between the two mark points (i.e., $z_2 - z_1$) corresponds to the polymer film thickness on the disk. In this method, the voltage signal by itself is not correlated to a film thickness. Instead, the locations of the two major voltage signal changes are measured to determine the point of contact between the probe tip and the film surface or the metal disk surface. Repeated measurements of the film thickness showed quite reproducible results. Figure 4 shows a typical example of voltage response observed in our experiments. The oscillatory signals shown in Figure 4 were due to a slight vertical misalignment of the disk or the vibration of the entire experimental

equipment when the motor was running. Since the experiments were carried out at high temperature (280°C), care was taken to complete the film-thickness measurements in minimum possible time in order to avoid any changes in the polymer melt properties.

RESULTS AND DISCUSSION

Using the experimental device shown in Figure 1, we measured the thickness of molten polymer layers for three PET samples of different molecular weight (number-average chain length $X_n = 13, 69, 82$). Figures 5 and 6 show the film-thickness profiles for these polymer melts at various angular and radial positions at the disk rotating speed of 10 and 20 rpm, respectively. First, it is seen that the film thickness is not uniform in both angular and radial positions for the cases studied. At the shaft height

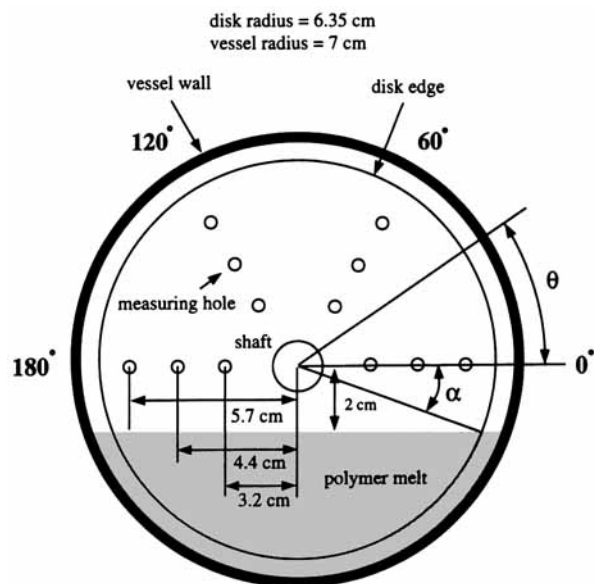


Figure 2 Layout of probe holes on reactor cover.

(i.e., $\theta = 0^\circ$; horizontal position), the film thickness increases in the radial direction and this trend is more pronounced for high molecular weight polymers at high disk rotational speed. When low-viscosity fluids such as water and vacuum pump oil were used, Vijayraghvan and Gupta⁹ reported a similar observation, although they used a much higher disk rotational speed (52–180 rpm). At higher angular positions on the rotating disk, the film-thickness profile changes more noticeably, particularly at 20 rpm. For example, at $\theta = 60^\circ$, the film thickness

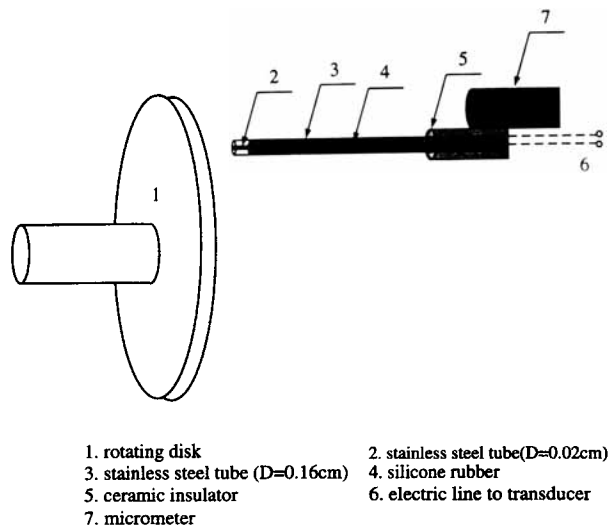


Figure 3 Schematic diagram of a probe assembly.

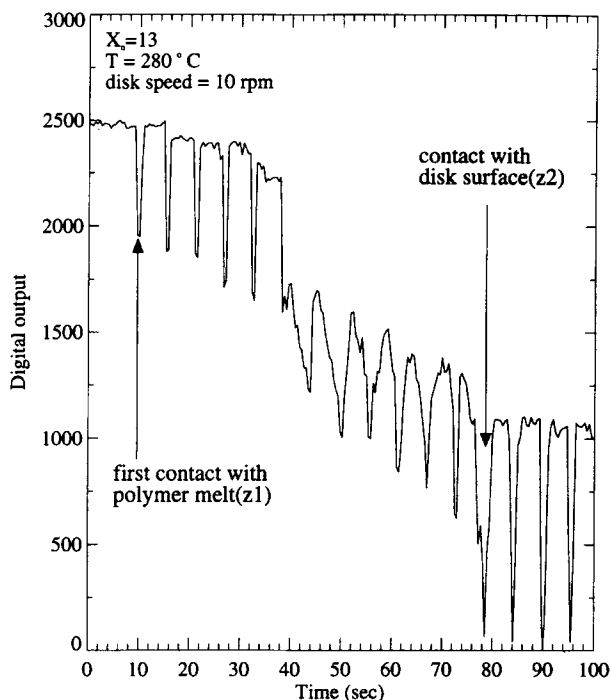


Figure 4 Typical voltage response during the film-thickness measurement.

becomes largest in the middle of the disk radius, whereas at $\theta = 120^\circ$ and 180° , the film thickness is largest near the center of the disk and it decreases monotonically in the radial direction. For low-viscosity fluids and at much higher disk rotational speed, this phenomenon was not observed.⁹ In our system, some “weeping” or draining occurs due to gravity as the disk rotates slowly at high angular positions, making the thin polymer melt near the edge of the disk flow toward the center of the disk.

To examine the relative magnitudes of some forces acting on the polymer film on a rotating disk, we calculated the numerical values of the following dimensionless groups: $D1 = (\mu\omega/r)/\rho g$, $D2 = (\sigma/r^2)/\rho g$. $D1$ represents the ratio of viscous force to gravity force and $D2$ represents the ratio of surface tension force to gravity force. Another dimensionless group, $Fr = r\omega^2/g$ (Froude number) represents the ratio of inertia force to gravity force. For our experimental system, the ranges of these three dimensionless groups are $D1$, 2×10^{-4} – 8×10^{-1} ; $D2$, 7×10^{-4} – 6×10^{-3} ; and Fr , 2×10^{-3} – 3×10^{-2} . For the experiments carried out by Vijayraghvan and Gupta⁹ with water and low-viscosity oil, the ranges of these dimensionless groups are $D1$, 1×10^{-5} – 2×10^{-2} ; $D2$, 2×10^{-4} – 8×10^{-4} ; and Fr , 3×10^{-1} – 5 . In both systems, both viscous force and surface tension force

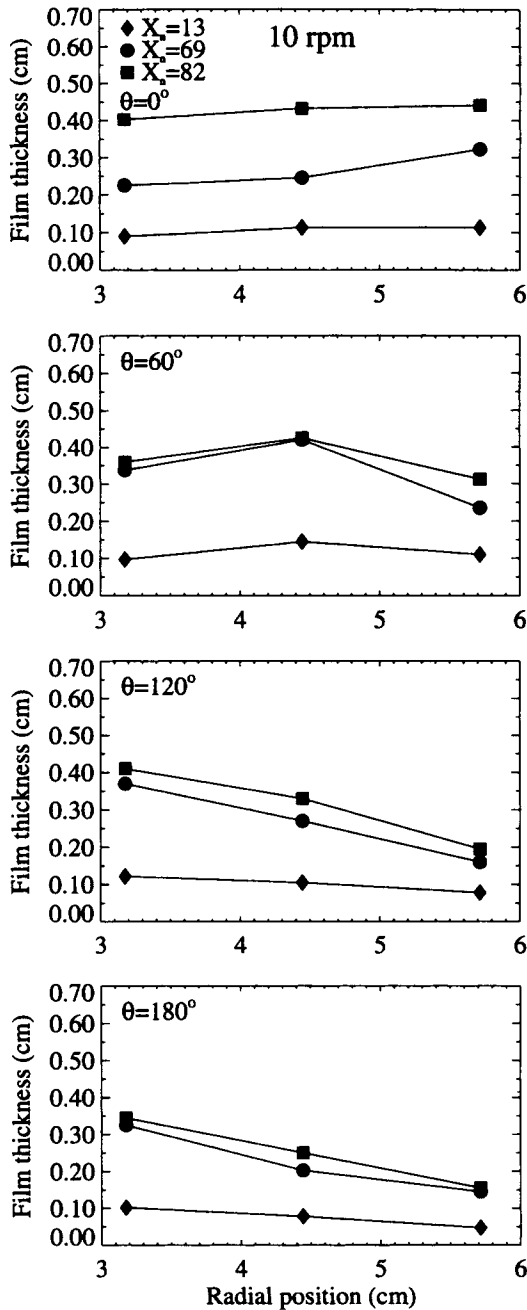


Figure 5 Polymer-layer thickness profiles at 10 rpm.

are much smaller than is the gravity force; however, the ratio of inertial force to gravity force is significantly smaller in our system than in the system used by Vijayraghvan and Gupta. Thus, this analysis indicates that the gravity force is a dominant force that makes the polymer melt move toward the center direction of the disk as it turns. We have also carried out an experiment using a reactor cover equipped with a Pyrex viewing window for visual observation.

It was observed that the whole disk surface was wet during the experiment although the immersion angle (α) was 18.4° . Quite obviously, this was due to the gravitational flow of polymer melt on the slowly rotating disk surface.

Figures 5 and 6 also show that the polymer layer or film thickness is strongly dependent on the polymer's molecular weight or melt viscosity. The melt viscosities of polymer samples calculated using the

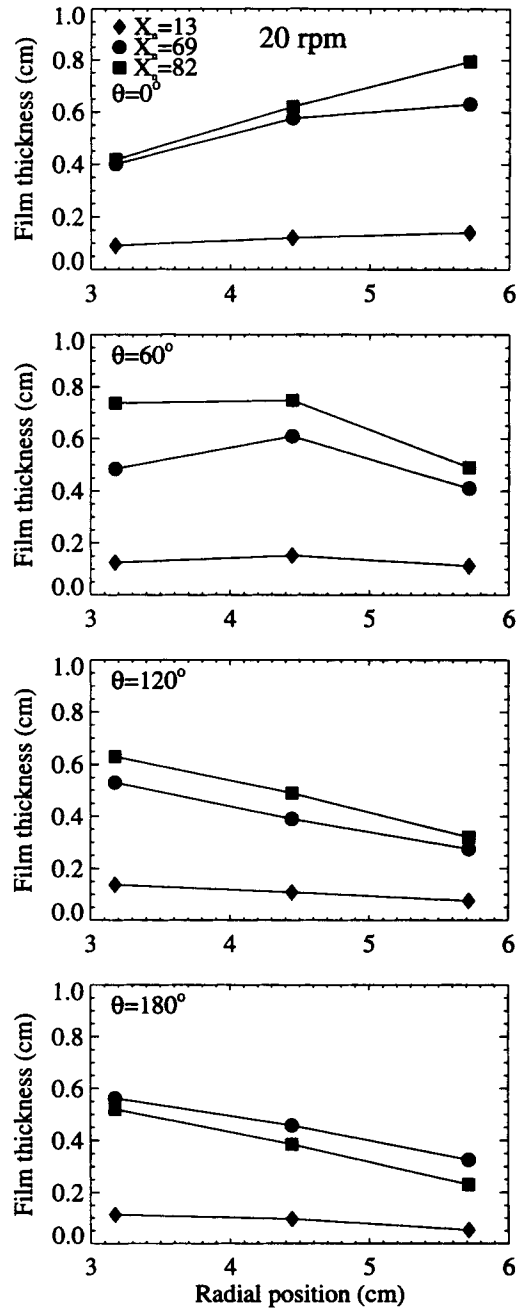


Figure 6 Polymer-layer thickness profiles at 20 rpm.

correlation by Gregory¹¹ are 473 and 866 poise for $X_n = 69$ and 82, respectively.

As mentioned earlier, knowing the polymer holdup on each disk in a finishing-stage polymerization reactor is important for the calculation of the mass-transfer rate and polymerization rate. Since the film thickness is not uniform in both radial and angular locations, the calculation of polymer holdup on a disk can be quite complicated. A number of studies have been reported concerning the thickness of liquid film on a vertical disk rotating at high speed.⁶⁻¹⁰ Vijayraghvan and Gupta⁹ performed a dimensional analysis to construct a correlation for film thickness on a rotating disk using the data obtained for water and low-viscosity vacuum pump oil. The correlation they obtained is

$$T = \frac{7.99Ca^{2.93}\eta^{0.15}R^{5.23}}{Cas^{3.09}\chi^{0.024}} \quad (1)$$

The dimensionless groups used in the above correlation are $T = h(\rho g/\mu r \omega)^{0.5}$ (dimensionless film thickness), $Ca = \mu \omega r/\sigma$ (capillary number), $Fr = r\omega^2/g$ (Froude number), $Re = \rho \omega r^2/\mu$ (Reynolds number), $\eta = \sigma(g\mu^4)^{-1/3}/\rho$, and $\chi = \omega^2 r_0/g - \sin \theta$, where μ = viscosity, ω = angular velocity, r = radial distance, σ = surface tension, ρ = density, g = acceleration of gravity, and r_0 = disk radius. This correlation was tested on our film-thickness data shown in Figures 5 and 6, but a very poor fit was obtained. According to the above correlation, the film thickness increases with the radial distance (r), which is not always the case in our system. We have also tested the correlation proposed by Soroka and Tallmadge,¹² but the agreement between the experimentally measured film-thickness data and the predicted values was not quite satisfactory.

Since one of the main objectives of measuring the film thickness on a rotating disk is to calculate the total polymer melt holdup on the disk, it is necessary to devise a method to do so, albeit approximate, using the data as shown in Figures 5 and 6. We note that at $\theta = 0^\circ$ the draining effect is quite small. Then, the total polymer holdup on a disk can be calculated by multiplying the polymer uptake rate and the total exposure time. Thus, a correlation for the calculation of the film thickness at this angle ($\theta = 0^\circ$) has been developed:

$$h \left(\frac{\rho g}{\mu r \omega} \right)^{0.5} = 2.4 \times 10^{-5} Ca^{1.267} Re^{-1.362} Fr^{1.554} (r/r_0)^{-2.839} \quad (2)$$

For the disk size and operating conditions employed in our experiments, the ranges of three dimension-

less groups are Ca (capillary number) = 0.08–400, Re (Reynolds number) = 0.006–100, and Fr (Froude number) = 0.002–0.03. Figure 7 shows the comparison of experimentally measured film thickness and the film-thickness values estimated according to the above correlation. It is seen that for the three polymer samples of different molecular weight the correlation yields reasonable estimates of the film thickness. As mentioned earlier, the melt viscosity of the polymer was estimated using the correlation by Gregory.¹¹ It should be noted that small amounts of water adsorbed in PET may cause hydrolysis that may change the polymer molecular weight and viscosity. In our experiment, this effect was not investigated and thus there is a possibility that some errors may have occurred in the polymer viscosity values in correlation (2). In Figure 8, the film-thickness profiles predicted by eq. (2) and the correlations

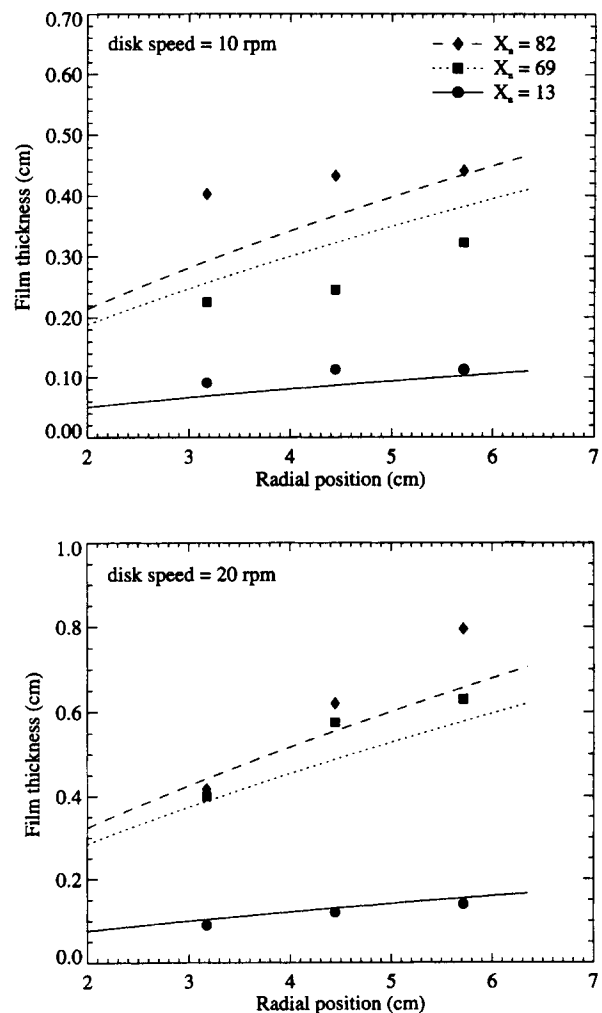


Figure 7 Film-thickness profiles predicted by eq. (1) at $\theta = 0^\circ$; symbols, experimental data.

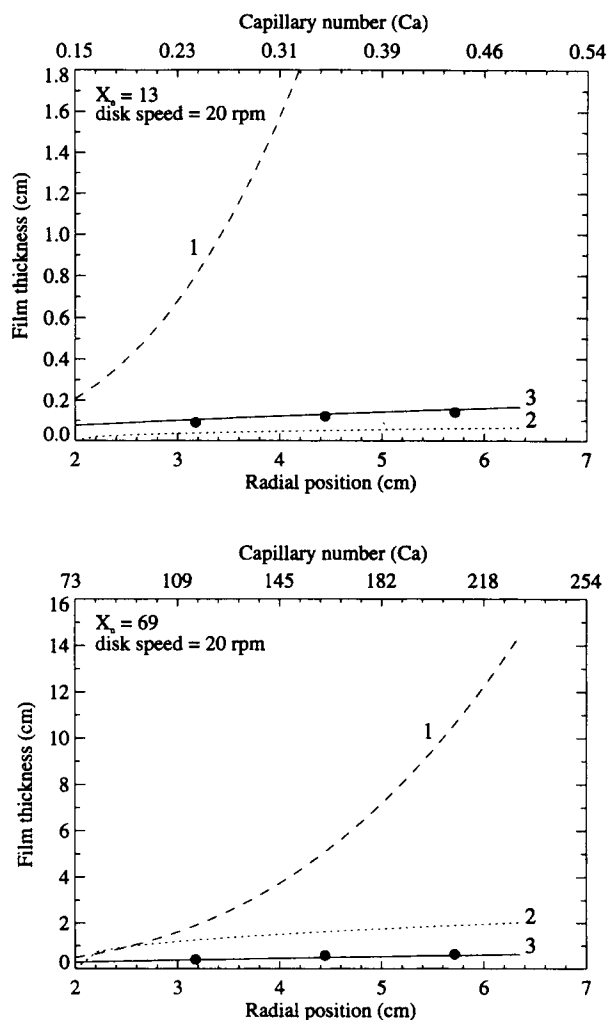


Figure 8 Comparison of predicted film-thickness profiles: (1) Vijayraghvan and Gupta⁶; (2) Soroka and Tallmadge¹²; (3) eqn. (2); (●) experimental data.

suggested by Vijayraghvan and Gupta⁹ and Soroka and Tallmadge¹² are shown with the experimental data. It is seen that the correlation by Soroka and Tallmadge gives either underestimated or overestimated film thickness values, whereas the correlation by Vijayraghvan and Gupta yields quite large deviations.

With the film-thickness value (h) known, the polymer-uptake rate onto a rotating disk can be calculated by using the following equation:

$$Q = \int_{r_i}^{r_0} r \omega h \left(1 - \frac{\rho g h^2}{3 \mu r \omega} \right) dr \quad (3)$$

where r_i is the inner radius of the wetted area; r_0 , the disk radius; ω , the angular rotational speed, and ρ , the polymer melt density. The total polymer

holdup is then calculated by multiplying the uptake rate (Q) and the total exposure time.

Figure 9 shows the polymer holdup and the maximum film thickness on a disk at $\theta = 0^\circ$ as a function of zero shear melt viscosity for three different disk rotational speeds. Notice that both the melt holdup and film thickness are strongly dependent on the disk speed and polymer melt viscosity or molecular weight. Figures 5, 6, and 9 suggest that the two adjacent disks in a finishing polymerization reactor may have to be properly spaced.

CONCLUDING REMARKS

In this article, film-thickness profiles of PET melt on a rotating disk have been reported for three PET samples of different molecular weight. The film thickness was measured at different radial and angular positions at 10 and 20 rpm. The experimental results indicate that the film thickness is not uniform in both radial and angular positions. The grav-

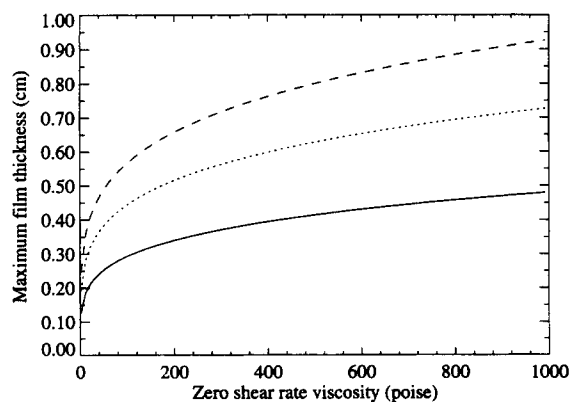
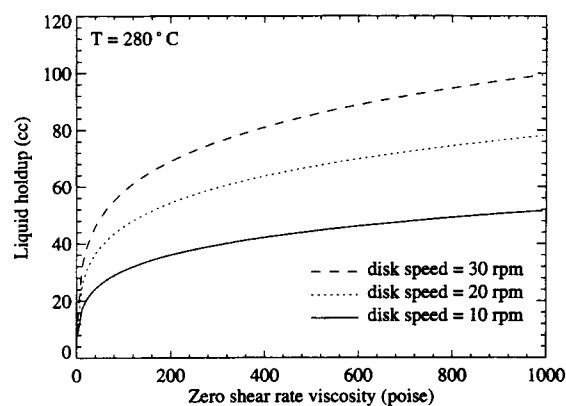


Figure 9 Effect of disk rotating speed and zero shear viscosity on polymer melt holdup and maximum polymer film thickness at $\theta = 0^\circ$.

ity effect was quite significant and the film thickness increased with the polymer's molecular weight. In our experiments, vacuum was not applied to prevent polymerization. In a real polycondensation reactor operating at low pressure (e.g., < 1.0 mmHg), the liquid layer may be filled with bubbles of volatiles formed as byproducts from various reactions, affecting the film-layer-thickness profiles. In a continuous rotating disk reactor where a multitude of disks are used, the experimental results observed in our study suggest that a spacing between the two neighboring disks may have to be optimally determined to avoid a complete saturation of the space, particularly near the outlet of the reactor where high molecular weight polymer is formed. If the space between the two neighboring disks is filled with molten polymer, the efficiency of mass transfer (e.g., ethylene glycol removal rate) will decrease. In modeling a finishing-stage polycondensation reactor, it is crucial to know the melt holdup on disk surfaces for the calculation of the overall mass-transfer rate and, thus, the polymerization rate. Our experimental results, with real PET melt at high temperature, suggest that the rate of ethylene glycol removal from each disk may be quite different in the finishing reactor because the film thickness is strongly dependent on the polymer molecular weight.

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