Transesterification of Ethylene Vinyl Acetate Copolymer in a Modular Intermeshing Corotating Twin Screw Extruder with Different Screw Configurations

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SYNOPSIS

The transesterification of ethylene-vinyl acetate (EVA) copolymer to produce ethylene-vinyl alcohol copolymer (EVAL) was studied in both a batch reactor and in a modular corotating twin screw extruder with various screw configurations. Increasing the number of left-handed screw elements and kneading disc blocks increases the extent of conversion under any set of operating conditions. Conversion is increased by decreasing screw speed and reducing throughput. Reactor design models have been developed to represent the modular twin screw extruders. These use a drag flow reactor for screw elements, a continuous stirred tank reactor (CSTR) to represent kneading disc blocks and a plug flow reactor to represent post screw and die regions. Comparisons are made with experiment. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Twin screw extruders[1,2] are playing an increasingly important role in polymer processing and modification technology. The chemical modification of thermoplastics in a twin screw extruder is an area of great commercial interest. The extensive patent literature on both chemical modification and polymerization in twin screw extruders has recently been reviewed by Brown.[3]

The saponification and transesterification of polyvinyl acetate has been of concern for a long time. In the 1940s, Sakurada and Kurashiki Rayon[4,5] saponified polyvinyl acetate to polyvinyl alcohol and solution spun fibers from the latter. More recently the hydrolysis and transesterification of ethylene vinyl acetate (EVA) copolymer has been investigated.[6-9] Lambla and coworkers[8,9] presented studies in both a Haake Rheocord batch mixer and in a Werner and Pfleiderer modular corotating twin
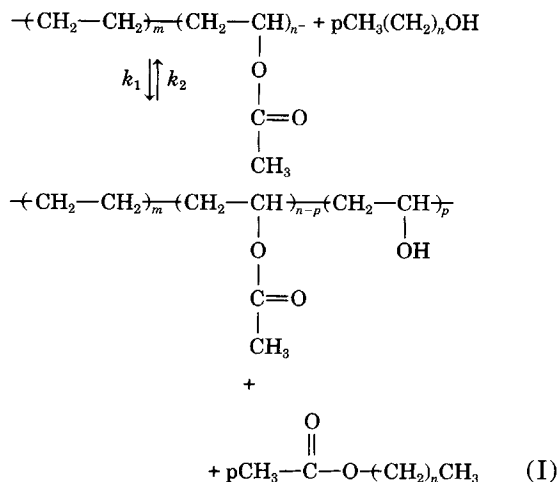
screw extruder. They also investigated the role of the type of alcohol and the type of catalyst used in the transesterification reaction.

It is our purpose in the present article to make a more extensive investigation of transesterification in a modular corotating twin screw extruder especially with regard to the influence of modular screw design and process variables such as throughput and material feed rate. The authors designed[10] a modular twin screw extruder that was used for flow visualization and to measure residence time distributions as a function of process variables. In this study we used a batch reactor and this special twin screw extruder. Our intent was to see the effect of different types of screw and kneading disc mixing elements on the extent of conversion.

TRANSESTERIFICATION OF EVA COPOLYMER

The partial transesterification of EVA copolymer with an aliphatic n-alcohol should be an equilibrium chemical reaction that may be described by

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$$-(CH_2-CH_2)_{\overline{m}}(CH_2-CH)_{n^-} + pCH_3(CH_2)_nOH$$

$$k_1 \Big\Uparrow k_2$$

$$\begin{array}{c} | \\ O \\ | \\ C=O \\ | \\ CH_3 \end{array}$$

$$-(CH_2-CH_2)_{\overline{m}}(CH_2-CH)_{\overline{n-p}}(CH_2-CH)_{\overline{p}}$$

$$\begin{array}{cc} | & | \\ O & OH \\ | \\ C=O \\ | \\ CH_3 \end{array}$$

$$+$$

$$\begin{array}{c} O \\ \| \\ + pCH_3-C-O-(CH_2)_nCH_3 \end{array} \quad \text{(I)}$$

The forward rate of the reaction depends upon the polyvinyl acetate concentration C_{PAc}, the alcohol concentration C_{A1}, and the temperature. Specifically

$$r_F = k_1 C_{PAc} C_{A1}. \quad (1)$$

The reverse reaction depends upon the polymeric alcohol C_{PA1} and the low molecular weight acetate concentration

$$r_R = k_2 C_{PA1} C_{Ac}. \quad (2)$$

This reaction will go to an equilibrium determined by

$$r_F = r_R \quad (3a)$$

$$\frac{C_{PA1} C_{A1}}{C_{PAc} C_{A1}} = K(T) \quad (3b)$$

where the equilibrium constant, $K(T)$, is temperature dependent.

EXPERIMENTAL

Materials

A commercial EVA copolymer obtained from DuPont (Elvax 670) was used as a starting material. It had 12 wt % VA and a melt index of 0.3. Its shear viscosity, η, to shear rate, $\dot{\gamma}$, relationship was obtained at 150, 170, and 190°C using a rotational rheometer (Rheometrics RMS 800) at low shear rates and a capillary rheometer (Instron) at high shear rates. This is shown in Figure 1.

The transesterification agent used was 1-hexadecanol, $CH_3(CH_2)_{15}OH$. This material has a melting point of 49°C and a boiling point of 344°C. It was obtained from Aldrich.
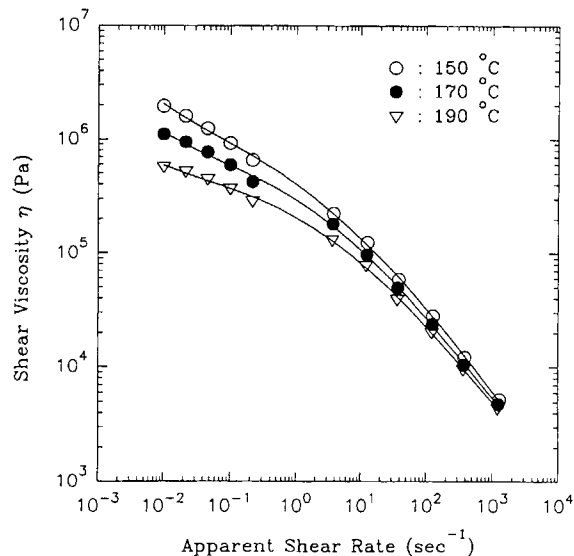

Figure 1   Shear viscosity of ethylene–vinyl acetate copolymer as a function of shear rate.

A catalyst of dibutyl tin dilaurate (DBTDL), $Sn[(CH_2)_3CH_3]_2[OCO(CH_2)_{10}CH_3]_2$, suggested by Lambla et al.[8,9] was used.

Batch Reactor

The transesterification reaction was carried in both batch and continuous twin screw reactors. The batch reactor was a Haake Buchler Rheocord 750 with a chamber volume of 70 cm^3. It contains nonintermeshing counterrotating rotors with double flighted designs. The rotor speed ratio is 7:6.

Twin Screw Extruder

The twin screw extruder was designed and built in our laboratories. Its design is shown in Figure 2. It uses Werner and Pfleiderer ZSK-30 modular screws and kneading disc elements. The modular barrel sections are 101.6 mm long. In some cases these have windows that may be used as viewing ports. In other cases the barrel sections contain vertical downward drilled holes that may be used either for insertion of pressure transducers or for withdrawing samples. This apparatus was described in an earlier article from our laboratories.[10]

Various screw configurations were used for carrying out this reaction. These include all right-handed screws (screw configuration 1), combinations of right- and left-handed screws (screw configuration 2), combinations of right-handed screws and kneading disc blocks (screw configurations 3
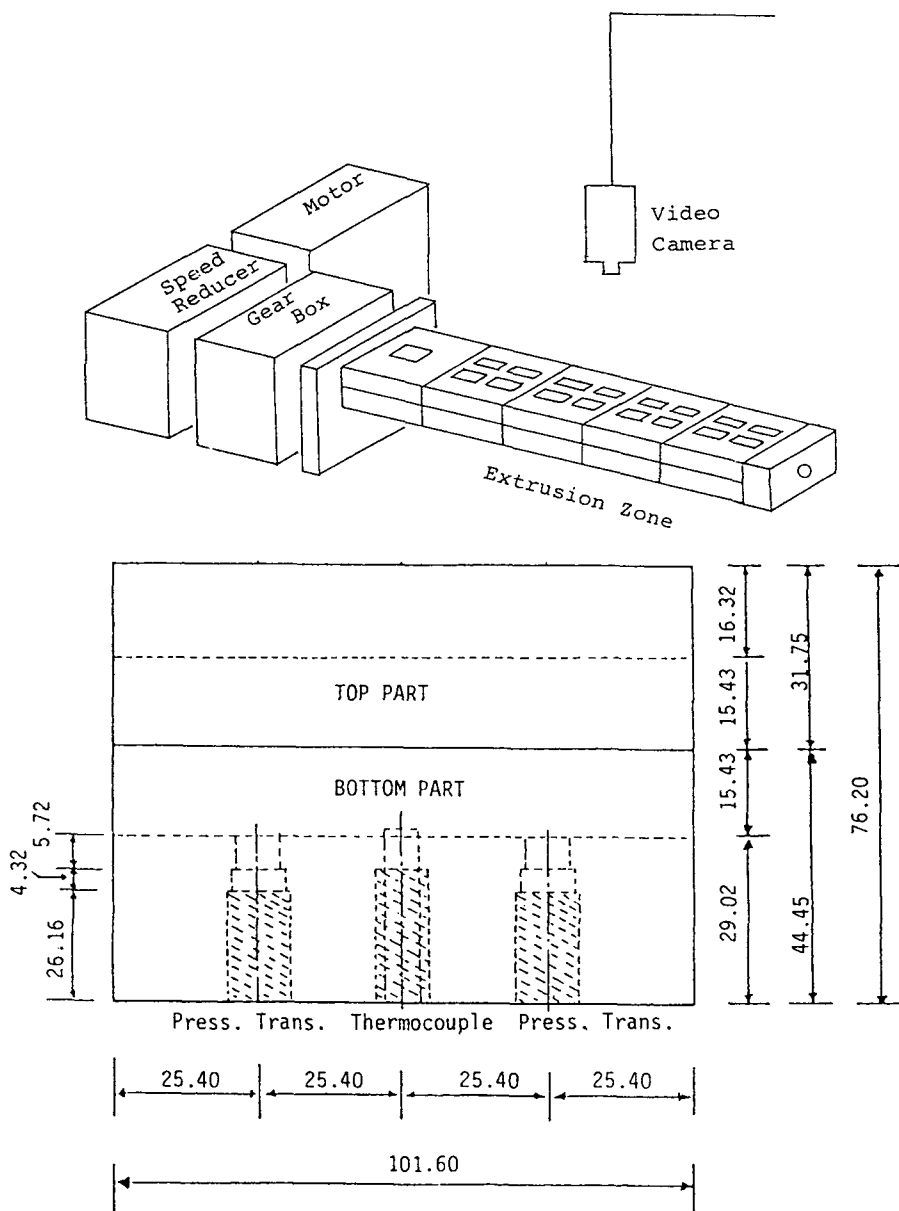
Figure 2 Laboratory twin screw extruder built for research studies: (a) composite extruder; (b) modular barrel section showing exit point.

and 4), and combinations of all three elements (screw configuration 5). These are shown in Figure 3.

Batch Reactor

A mixture of EVA copolymer and DBTDL was first fed into the reactor that was heated to 150, 170, and 190°C. The rotor speed was 50 rpm. When the EVA copolymer was completely melted, 1-hexadecanol was fed into the reactor. The torque and reaction time were measured from this point to various spec-

ified reaction times (5, 10, 20, 30, and 40 min). A sample of reacting material was removed from the batch reactor, quenched in liquid nitrogen, and subsequently analyzed.

Twin Screw Extruder

A dry mix of EVA and 1-hexadecanol (MP = 49°C) was fed into the hopper from a solids feeder. The DBTDL, which is a liquid at room temperature, was separately fed into this hopper from a metering pump. All barrel sections were heated to 170°C.
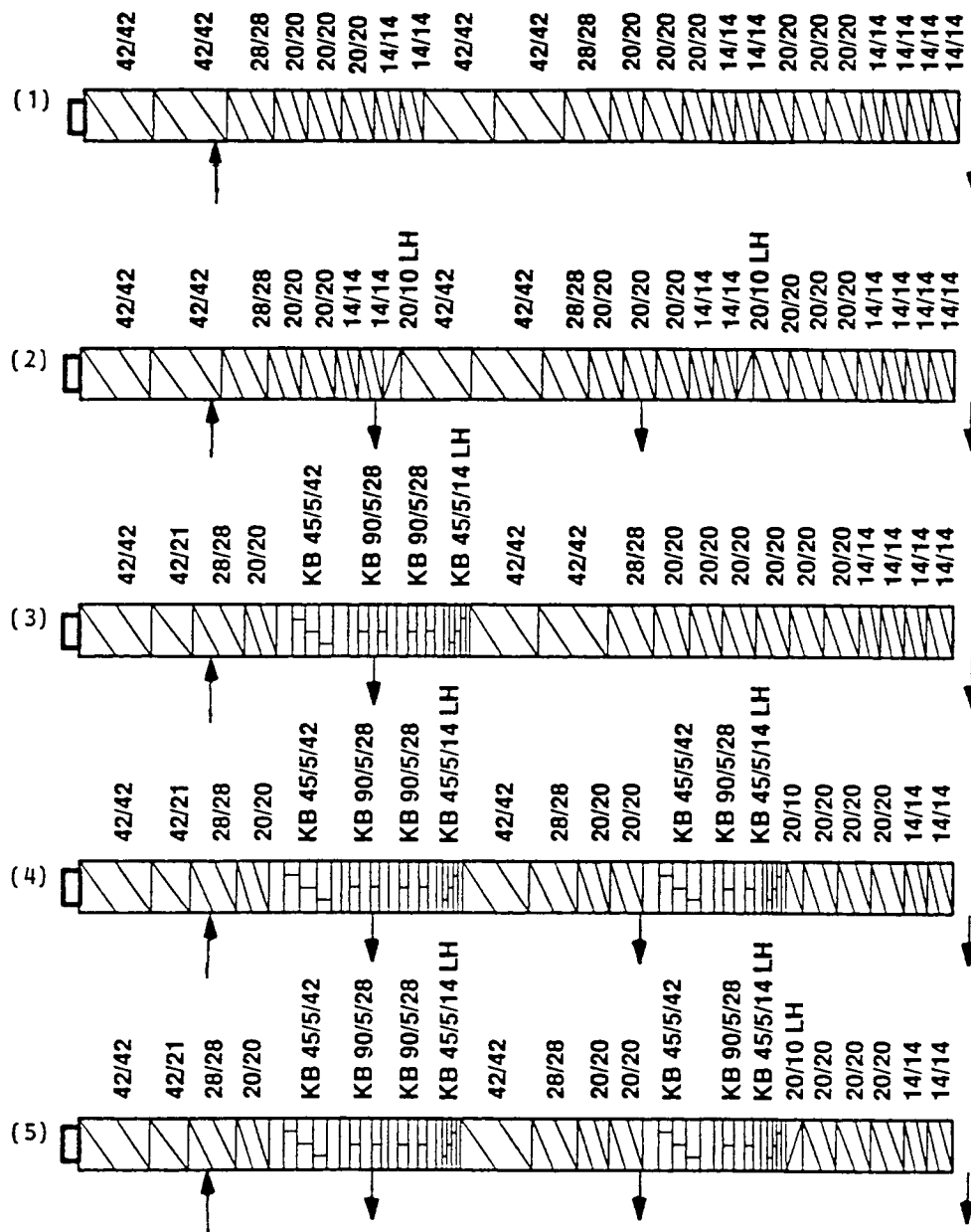
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(1) 42/42 42/42 28/28 20/20 20/20 20/20 14/14 14/14 42/42 42/42 28/28 20/20 20/20 20/20 14/14 14/14 20/20 20/20 20/20 14/14 14/14 14/14 14/14

(2) 42/42 42/42 28/28 20/20 20/20 14/14 14/14 20/10 LH 42/42 42/42 28/28 20/20 20/20 20/20 14/14 14/14 20/10 LH 20/20 20/20 20/20 14/14 14/14 14/14 14/14

(3) 42/42 42/21 28/28 20/20 KB 45/5/42 KB 90/5/28 KB 90/5/28 KB 45/5/14 LH 42/42 42/42 28/28 20/20 20/20 20/20 20/20 20/20 14/14 14/14 14/14 14/14

(4) 42/42 42/21 28/28 20/20 KB 45/5/42 KB 90/5/28 KB 90/5/28 KB 45/5/14 LH 42/42 28/28 20/20 20/20 KB 45/5/42 KB 90/5/28 KB 45/5/14 LH 20/10 20/20 20/20 20/20 14/14 14/14

(5) 42/42 42/21 28/28 20/20 KB 45/5/42 KB 90/5/28 KB 90/5/28 KB 45/5/14 LH 42/42 28/28 20/20 20/20 KB 45/5/42 KB 90/5/28 KB 45/5/14 LH 20/10 LH 20/20 20/20 20/20 14/14 14/14

Figure 3 Modular screw configurations.

Various screw speeds were investigated. These were in the range of 10–40 rpm. The feed rate was varied systematically from 0.66 to 1.77 kg/min.

Reacted material was not only collected from the die exit, but from exit points in barrel sections 2 and 4. These ports are shown in Figure 2(b). They can only be used when the fluid inside this barrel section is pressurized. The reacting fluid removed

was immediately placed in liquid nitrogen to freeze the state of reaction for subsequent analysis.

Product Analysis

The transesterified product was characterized using a Perkin–Elmer Fourier Transform Spectrometer. The ester group of the acetate is represented by a

band at 610 cm^{-1} and the CH_2 group by a band at 2680 cm^{-1}. The change in relative absorption at the two bands allows calculation of the change of acetate content. This is essentially the procedure of Bouilloux et al.[8]

RESULTS

Batch Reactor

The torque and conversion were determined as a function of time in the batch reactor. The torque generally rose rapidly, went through a maximum and decreased. The torque levels were highest at the lowest temperatures (150°C) and then decreased with increasing temperatures to 170 and 190°C as shown in Figure 4.

The conversion increased monotonically with respect to time. The conversion rates were rather low at 150°C (below 20%) but were much higher and similar at 170° and 190°C as shown in Figure 5.

Twin Screw Extruder

The extent of conversion using the various screw configurations as a function of position along the screw and screw speed is shown in Figure 6(a–e). It can be seen in each case that increasing screw speed reduces conversion. We first consider screw configuration 1. As the screw speed for screw con-
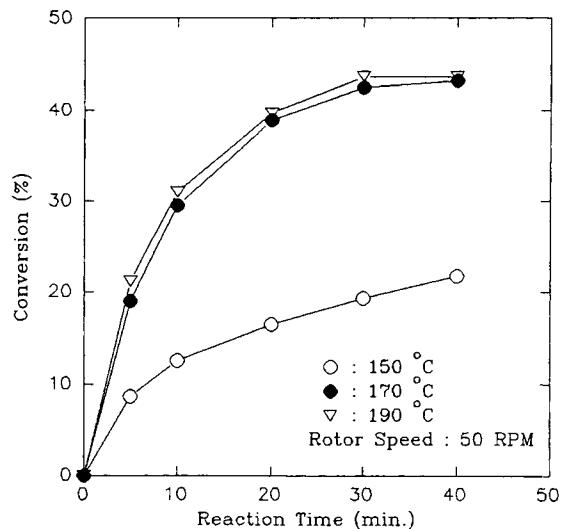
Figure 5   Conversion of EVA to EVAL as a function of time in the Haake–Buchlor Rheocord at 150, 170, and 190°C.

figuration 1 increases from 10 to 20, 30, and 40 rpm, the conversion decreases from 23.2 to 22.0, 19.0, and 17.6% conversion. From another point of view, reducing screw speed from 40 to 10 rpm increases conversion by almost one-third, from 17.67 to 23.2%. More detailed information on the conversion as a function of position along the twin screw machine could not be obtained as the machine was only pressurized in the neighborhood of the machine exit, and one could not remove reacting fluid from intermediate positions.

In screw configurations 2, 3, 4, and 5, one was able to obtain, to varying extents, considerable additional information about the progress of the reaction along the screw axis. This may be seen in Figures 6(b–e). Conversion generally increases monotonically with position along the screw axis. Again conversion increases with decreasing screw speed.

Experiments were carried out at various feed rates. In Figure 7(a–c) we show conversion as a function of feed rate at various positions along the screw axis. Generally increasing feed rate decreases levels of conversion.

We summarize the conversions achieved under equivalent conditions for the various screw configurations in Figure 8 and Table I. Adding a left-handed screw element to make screw 2 increases the conversion from 19.0 to 21.7%; Screw 3 with a kneading disc block has a conversion of 26.7%; screw 4 with two kneading disc blocks has a conversion of 30.6%; Screw 5 with an assortment of special elements has a conversion of 31.8%.
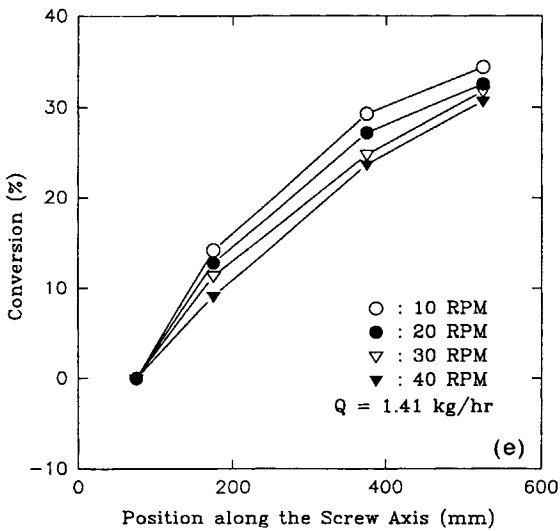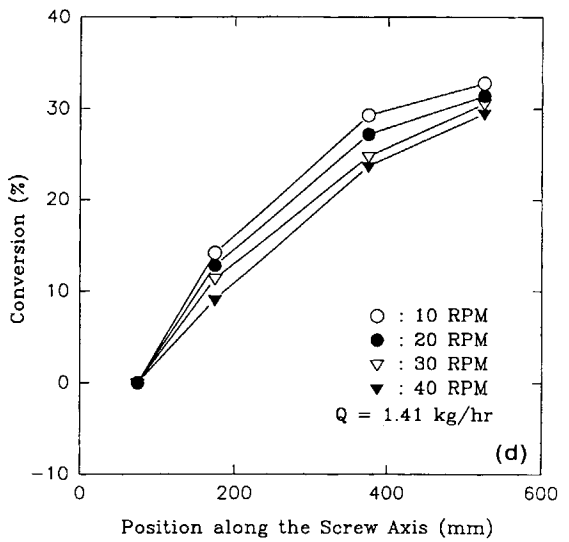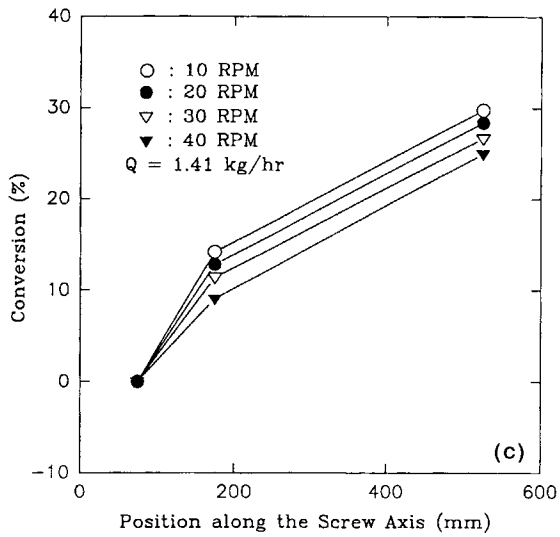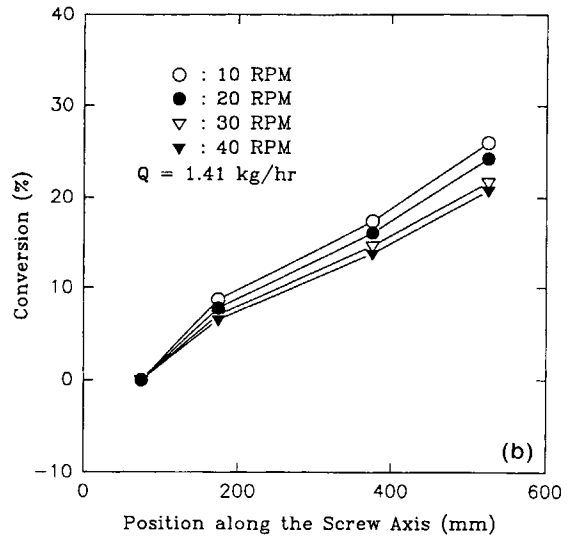
Figure 4   Torque as a function of reactive time in the conversion of EVA to EVAL in a Haake–Buchle Rheocord 750.
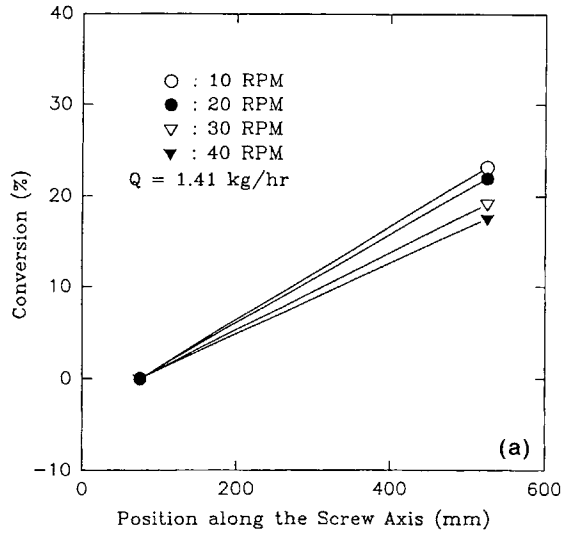
Figure 6   Conversion of EVA to EVAL as a function of position along the screw axis for different screw speeds: (a) screw configuration 1 (all RHS); (b) screw configuration 2 (RHS + 2LHS); (c) screw configuration 3 (RHS + 1KB); (d) screw configuration 4 (RHS + 2KB); (e) screw configuration 5 (RHS + 2KB + LHS).
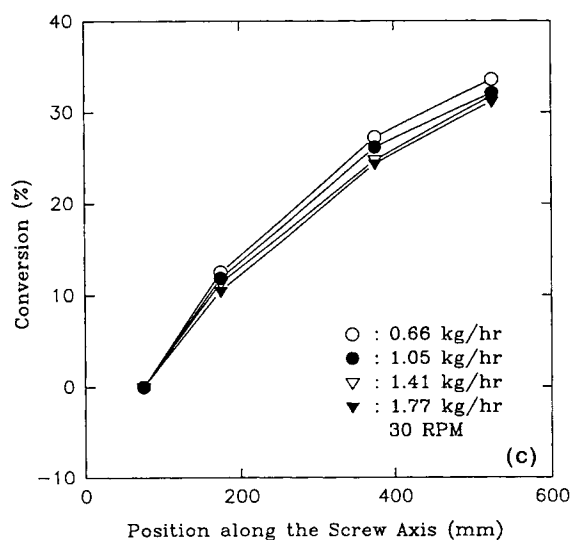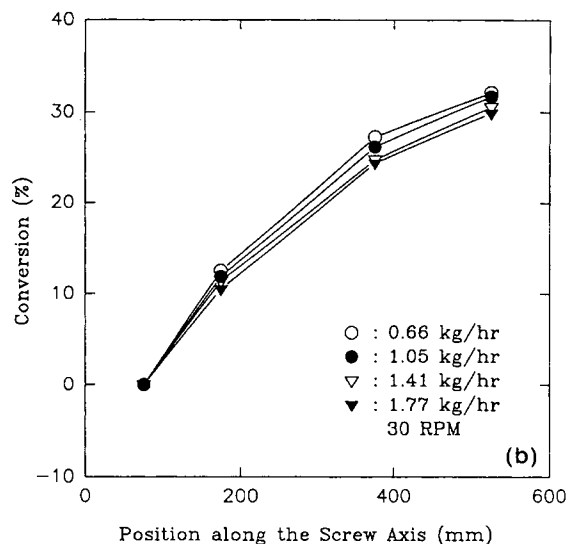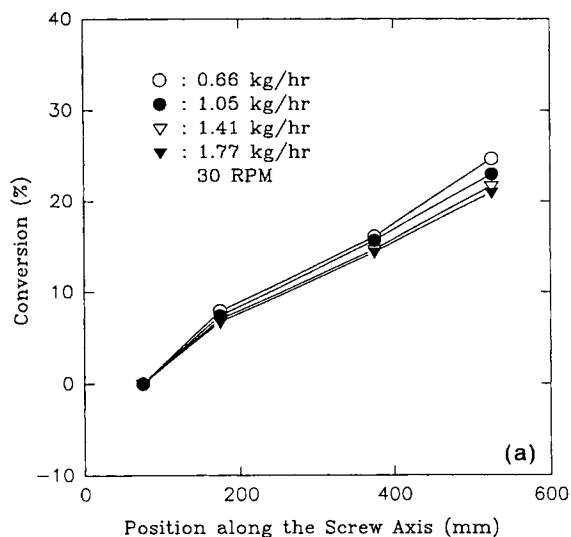
Figure 7 Conversion EVA to EVAL as a function of position along the screw axis for different feed rates: (a) screw configuration 2 (RHS + 2LHS); (b) screw configuration 4 (RHS + 2KB); (c) screw configuration 5 (RHS + 2KB + LHS).

DISCUSSION

Batch Reactor

The kinetic scheme discussed in Eqs. (1)–(3) may be used to determine rate constants k and k_2 from the variation of conversion with time. The rate of reaction is

$$\frac{dC_A}{dt} = k_1 C_{PAc} C_{A1} - k_2 C_{PA1} C_{Ac} \qquad (4a)$$

or

$$\frac{dx}{dt} = k_1 (C_{PAc} - x)(C_{A1} - x) - k_2 x^2 \qquad (4b)$$

where x is the product concentration produced. Equation (4) is equivalent to the expression:

Table I   Comparison of Mean Residence Time and Conversion of EVA to EVAL with Varying Screw Configurations

Screw Configuration (Reactor Type)	Mean Residence Time (s)	Conversion (%)
1 RHS only	179	19.0
2 RHS + 2LHS	208	21.7
3 RHS + 1KB	252	26.7
4 RHS + 2KB	320	30.6
5 RHS + 2KB + 1LHS	349	31.8
Batch reactor	300	19.0

Die exit for screw speed 30 rpm and material feed rate 1.41 kg/h and a batch reactor at 170°C. RHS, right-hand side; LHS, left-hand side; KB, kneading block.

$$\frac{dx}{x^2 - \left(\dfrac{k_1}{k_1 - k_2}\right)(C^{\cdot}_{PAc} + C^{\cdot}_{A1})x + \left(\dfrac{k_1}{k_1 - k_2}\right)C_{PAc}C_{A1}} = (k_1 - k_2)dt. \quad (5)$$

Equation (5) may be integrated to give:

$$\frac{1}{X_1 - X_2} \ln \frac{X_2(X_1 - x)}{X_1(X_2 - x)} = (k_1 - k_2)t \quad (6)$$

where X_1 and X_2 are the roots of the equations

$$x^2 - \left(\frac{k_1}{k_1 - k_2}\right)(C_{PAc} + C_{A1})x$$

$$+ \left(\frac{k_1}{k_1 - k_2}\right)C_{PAc}C_{A1} = 0. \quad (7)$$

Equation (6) was fit to the batch reactor data. The values of k_1 and k_2 determined are listed in Table II.

Twin Screw Extrusion: Qualitative

One would expect the extent of conversion to vary with the residence time in the twin screw extruder. As shown in our earlier study[10] on this apparatus as well as the studies of others,[11,12] increasing screw speed and extrusion rate decrease residence time in a twin screw extruder. This agrees qualitatively with our observations (see Table III).

The above interpretation can be developed further. The mean residence time is the ratio of the occupied volume, V_{occ}, to the throughput Q

$$\bar{t} = \frac{V_{occ}}{Q}. \quad (8)$$

It is well known that twin screw extruders contain both fully filled and starved regions. The values of V_{occ} and $\bar{t}$ are primarily determined by the extent of the fully filled regions. Many of the experiments in

Table II Kinetic Rate Constants Determined from Batch Reactor Data

Temperature (°C)	k_1 (mol^{-1} min^{-1})	k_2 (mol^{-1} min^{-1})
150°	0.012	0.02
170°	0.042	0.07
190°	0.047	0.08

Table III Mean Residence Time and Conversion of EVA to EVAL for Screw Configuration 1

Screw Speed (rpm)	Feed Rate (kg/h)	Mean Residence Time (s)	Conversion (%)
10	1.41	289	23.2
20	1.41	226	22.0
30	1.41	179	19.0
40	1.41	131	17.6
30	0.66	206	22.3
30	1.01	189	20.2
30	1.41	179	19.0
30	1.77	167	18.1

this paper including those in Table III were for a screw configuration of all right handed screws (screw configuration 1). Under such conditions, the screw will only be fully filled in the region near the die.[10,13] The flow in this region may be expressed as[2]

$$Q = \tfrac{1}{2}\pi DN\cos\phi A - k\frac{H^2 A}{\eta}\frac{\Delta p}{L_f} \quad (9)$$

where A is the channel cross section, D screw diameter, H channel depth, η the viscosity, and L_f the fully filled channel length. The die extrusion rate-pressure drop characteristics may be expressed
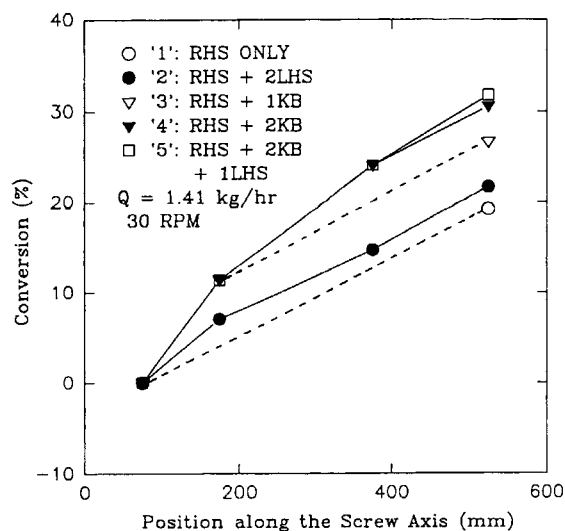
$$Q = \frac{k\Delta p}{\eta}. \quad (10)$$

Figure 8 Conversion of EVA to EVAL along the screw axis with various screw configurations in a modular corotating twin screw extruder.
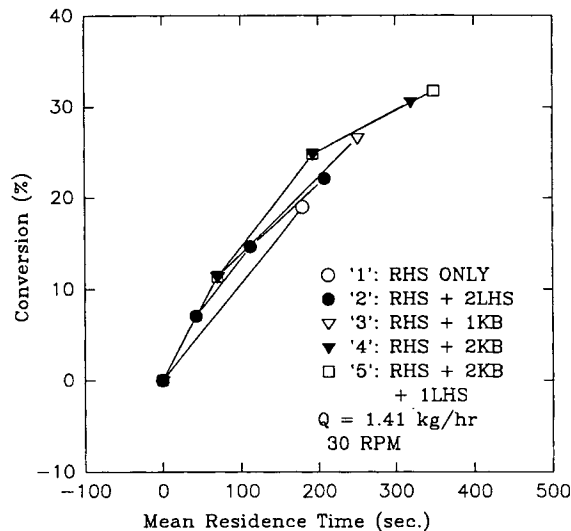
Figure 9 Conversion of EVA to EVAL versus mean residence time with various screw configurations in a modular corotating twin screw extruder.

Elimination of Δp between Eqs. (8) and (9) gives

$$Q = \tfrac{1}{2} \frac{\pi DNA}{1 + \dfrac{k}{K} \dfrac{H^2 A}{L_f}} \cos\phi. \tag{11}$$

The value of V_{occ} and $\bar{t}$ in Eq. (7) is primarily determined by L_f. Clearly decreasing N at fixed Q results in increased L_f. Further decreasing Q at fixed N increases L_f.

It is to be noted that introducing left-handed screws and kneading disc blocks increases the extent of fill and V_{occ} in a twin screw extruder.[10,13] This leads as we have found[10] to higher residence times and higher conversions (see the comparison in Figure 9). Table I contrasts residence times and conversions for modular screws with different screw configurations. A more detailed comparison is given in Figure 9. Screw configurations with extensive combinations of kneading discs would seem to pro-

duce higher levels of conversion at equivalent residence times with only screw elements.

Batch Reactor vs. Twin Screw Extruder

The simplest treatment of a twin screw extruder as a reactor would be as a plug flow reactor. The conversion vs. time characteristics of a batch reactor were found to be similar to a twin screw extruder with only right-handed screw elements (see Table I). Conversion in twin screw extruders with kneading disc blocks is noticeably higher.

Reactive Modelling

There is more than a half century of history in simulation of flow in continuous chemical reactors such as tubular reactors and continuous stirred tank reactors.[14] The first effort at simulating conversion in a chemical reactor in a screw extruder was given by Meyuhas et al.[15] in 1973. They envisaged flow in a "flood fed" fully filled uniform screw and calculated polymerization conversions and molecular weight distributions for different kinetic schemes. This approach was rediscovered by Siadet et al.,[16] who sought also to introduce the effect of viscous heating on the reaction kinetics. Drag flow reactors are also described in the book of Biesenberger and Sebastian[17] on polymerization reactor engineering.

The twin screw reactors described in this article are more complex than the simple plug flow reactor models described above. Our reactors consist of the five screw configurations of Figure 3 and include a post screw and die section as well as kneading disc blocks. Our procedure has been to take screw sections as drag flow reactors (DFR), kneading disc blocks as continuous stirred tank reactors (CSTR) and post screw and die sections as plug flow reactors (Table IV). We must also distinguish between starved flow and fully filled flow.

To carry out calculations we must determine in what regions of the twin screw extruders that fully

Table IV   Reactor Models Used in Simulations

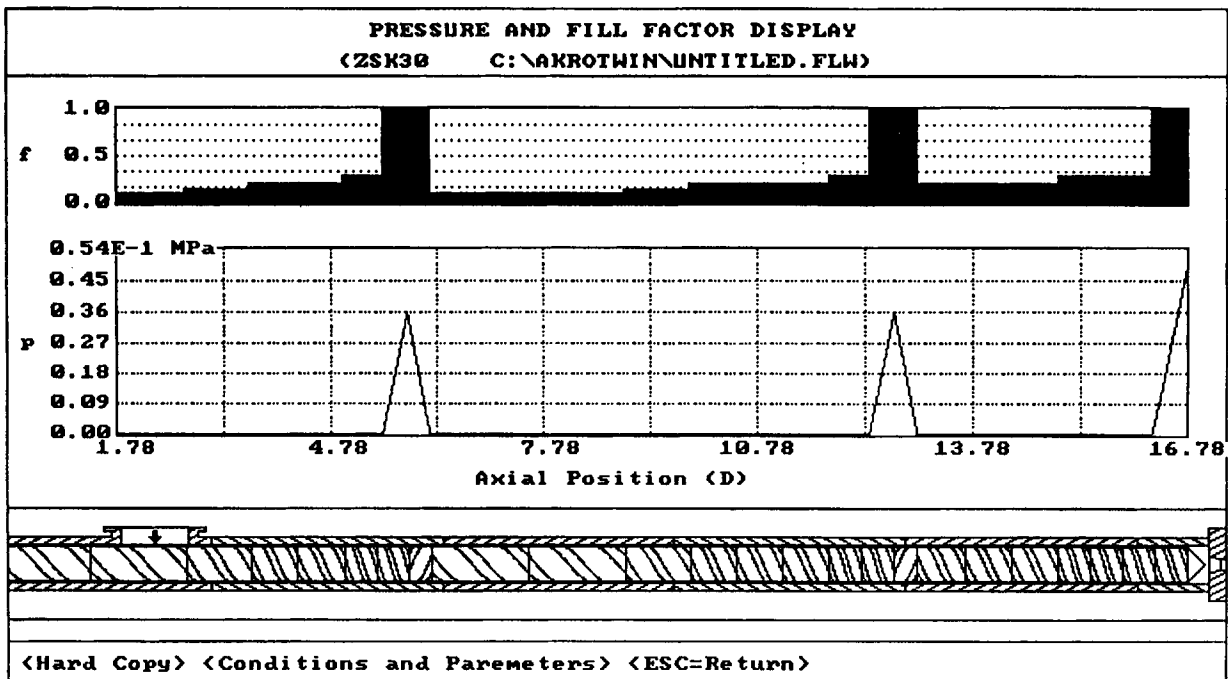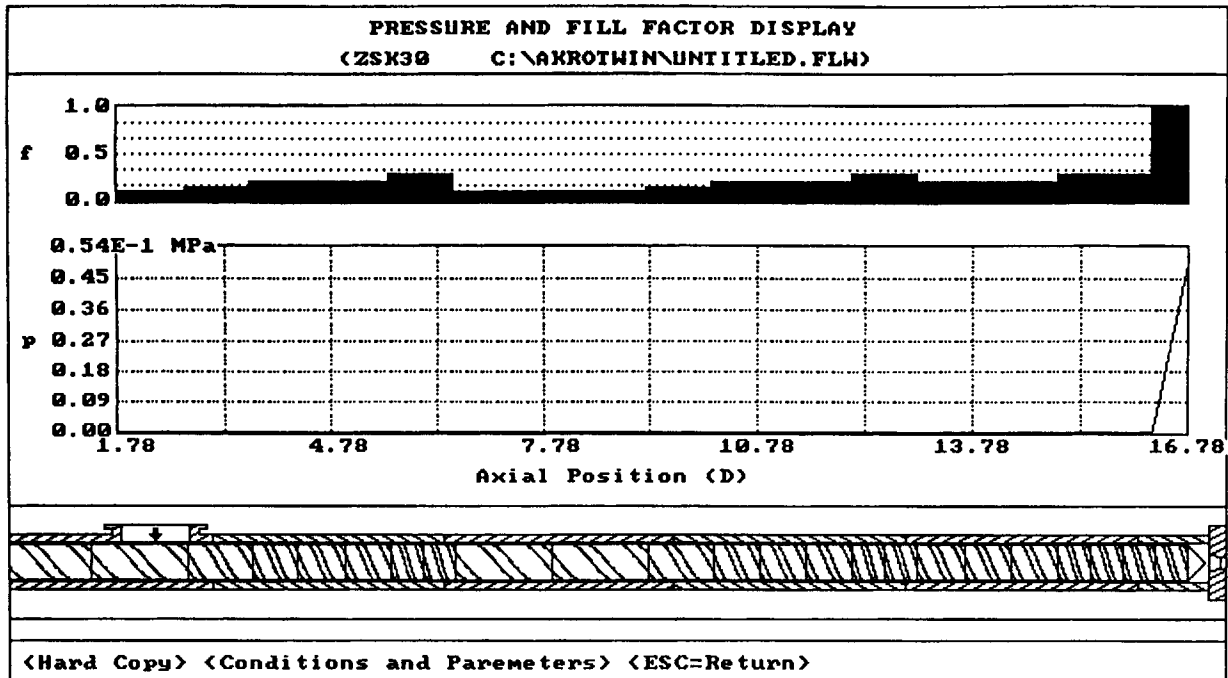| Screw Configuration	Composite Reactor Model Components
1 RHS only	SDFR + DFR + TR
2 RHS + 2LHS	SDFR + DFR + TR
3 RHS + KB	CSTR + SDFR + DFR + TR
4 RHS + 2KB	CSTR + SDFR + DFR + TR
5 RHS + 2KB + 1LHS	CSTR + SDFR + DFR + TR (3 CSTR)

SDFR, DFR, TR, CSTR see text for definitions.

Figure 10   Computed pressure and fill factor profiles at 30 rpm, 1.41 kg/h, 170°C: (a) screw configuration 1; (b) screw configuration 2; (c) screw configuration 3; (d) screw configuration 4; (e) screw configuration 5.
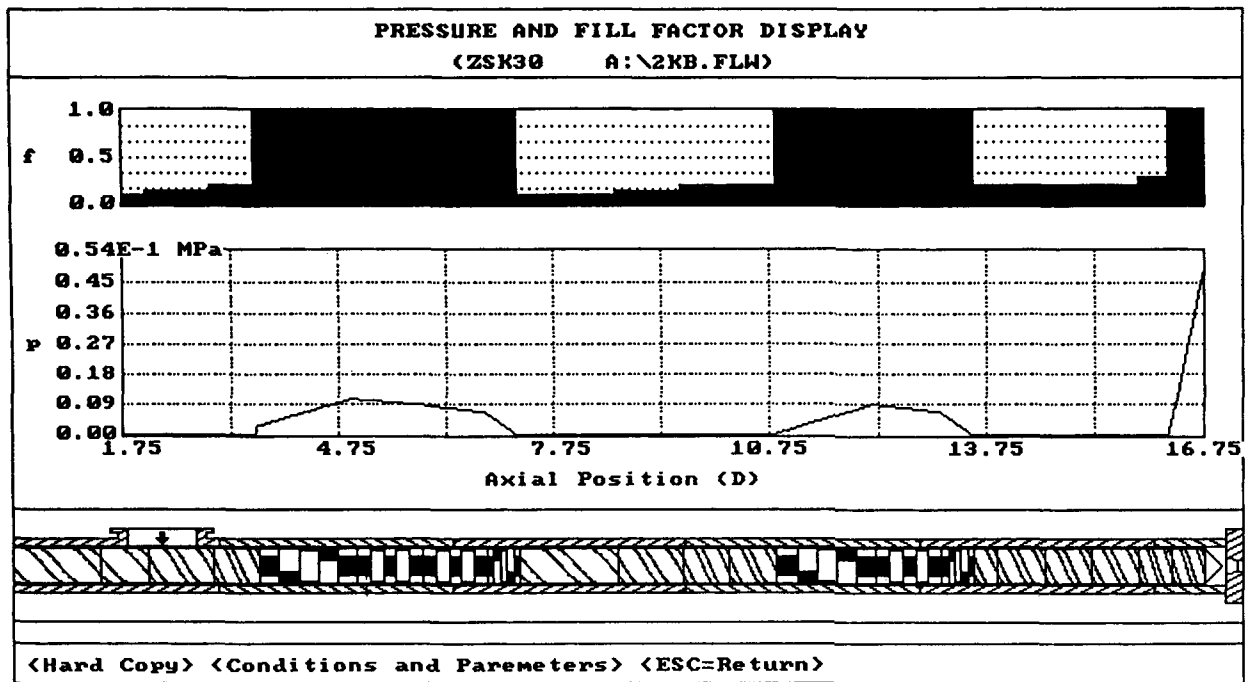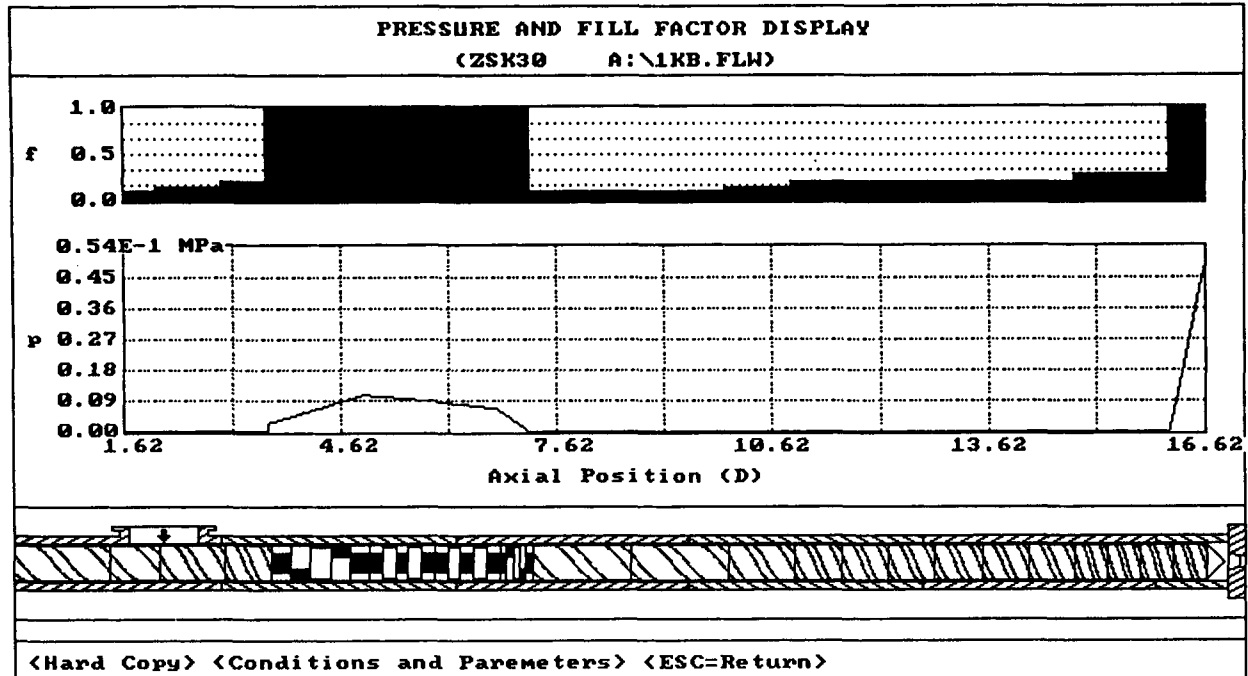
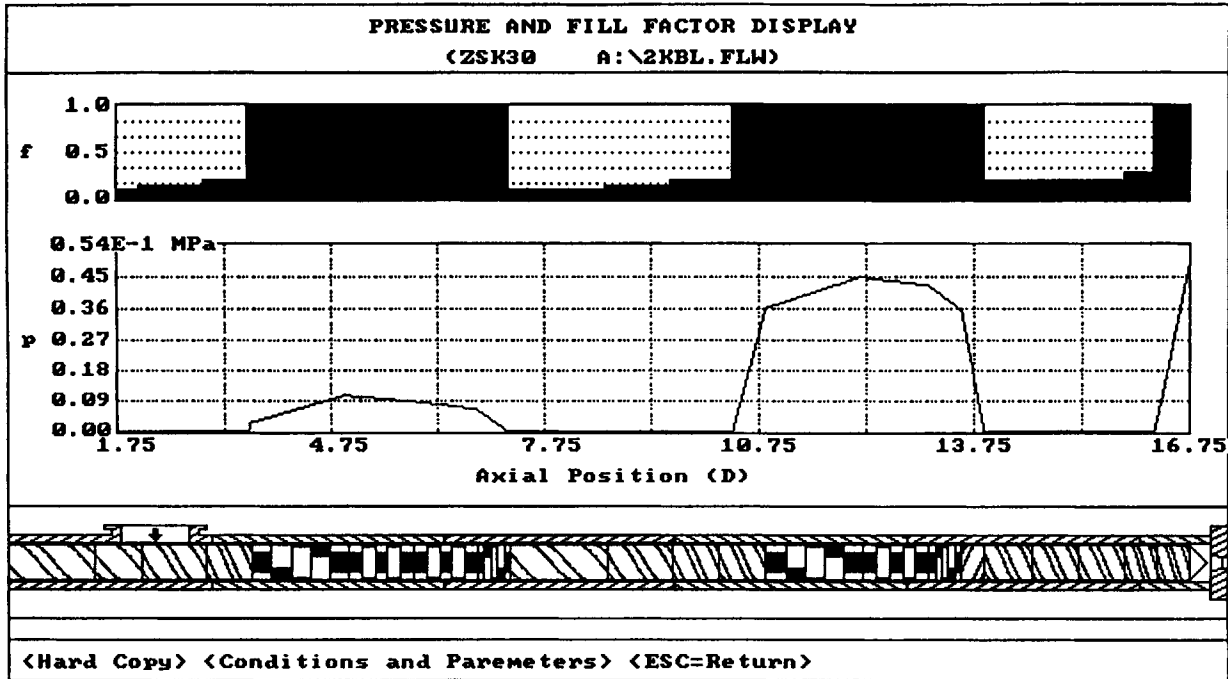**Figure 10** (*Continued from the previous page*)

Figure 10 (*Continued from the previous page*)

filled and stressed flow regimes exist. To accomplish this we used the isothermal Akro co Twin Screw program[18] based on the modular corotating twin screw extruder simulation.[2,19]

This flow simulation of screw and kneading disc block elements is based on solutions of the non-Newtonian lubrication equations that balance pressure gradient $\partial p/\partial x_j$ against shear stress $\eta \partial v_j/\partial x_2$, that is,

$$0 = -\frac{\partial p}{\partial x_1} + \frac{\partial}{\partial x_2}\left(\eta \frac{\partial v_1}{\partial x_2}\right) \qquad (12a)$$

$$0 = -\frac{\partial p}{\partial x_3} + \frac{\partial}{\partial x_2}\left(\eta \frac{\partial v_3}{\partial x_2}\right) \qquad (12b)$$

Table V   Comparison of Predictions of Reactor Models with Experiment

Screw Configuration	Composite Reactor Model	Plug Flow Model	Experiment
1	15.9	11.2	19.0
2	16.3	12.8	21.7
3	18.3	15.1	26.7
4	20.8	18.3	30.6
5	21.3	19.7	31.8

Throughput = 1.41 kg/h; screw speed = 30 rpm; temperature = 170°C.

for the self wiping screw and kneading disc block elements to give screw characteristic $Q - N - \Delta p$ curves where Q is throughput, N is screw speed, and Δp the pressure rise in an element. The calculation is initiated at the end of the screws, where pressure is determined from the known flow rate and the die characteristics. It is presumed that Q is the same in all elements and pressure p is continuous.

The states of fill and starvation under the conditions of a 30 rpm screw speed and 1.41 kg/h throughput were computed using the Akro co Twin Screw and are shown in Figure 10(a-e). We must distinguish between filled and starved drag flow (SDFR) reactors, and indeed note that each screw element is a different reactor.

We have made computations for all five composite reactor models and compared the results with experiments. The computations are summarized in Table V. We also compare our results with those plug flow reactors in our machines using experimental residence times. The more complex modular screw models predict higher conversions then the plug flow. The predictions of conversion are reasonable compared to the experimental conversion data for all screw models of screw configurations 1 and 2 but are notably low when kneading blocks are included.

There are several problems in the above analysis. First, the kinetics obtained from the batch mixer may not be accurate due to temperature gradients

in the mixing chamber. Second, the analysis is only a first iteration, as heat of reaction effects and viscous dissipation heating influence reaction rates and rheological properties which in turn influence degree of screw fill, residence time, and conversion. Third, detailed intermixing of the reactive ingredients is not included in the analysis we have presented. This is an effect that could be of great importance.

CONCLUSIONS

An experimental study was presented of transesterification of EVA copolymer in a twin screw extruder using a range of screw configurations, screw speeds, and feed rate. Conversion was increased by reducing screw speed, reducing feed rate, and by modifying screw design by introducing left-handed screw elements and kneading disc elements. The results may be explained qualitatively using fluid mechanics models of modular corotating twin screw extrusion. Hypothetical reactor models representing the twin screw reactive extrusion process were used to predict conversion in the different screw configurations.

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