Experimental Study of Maleation of Polypropylene in Various Twin-Screw Extruder Systems

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ABSTRACT: A range of continuous mixing machines were used as continuous reactors for grafting maleic anhydride onto polypropylene. The machines used were (1) a nonintermeshing modular counterrotating twin-screw extruder, (2) an intermeshing modular corotating twin-screw extruder, (3) intermeshing modular counterrotating twin-screw extruder, and (4) a Kobelco Nex-T continuous mixer. The grafting reaction of maleic anhydride onto polypropylene and degradation of polypropylene during the grafting reaction were investigated as means for comparing these different machines for reactive extrusion. The influence of processing variables such as screw speed and processing temperature on polymer characteristics also was investigated. Generally, in a comparison of the different machines, the intermeshing counterrotating twin-screw extruder had the lowest levels of grafted maleic anhydride, whereas the Kobelco Nex-T continuous mixer under the conditions used had the highest levels of grafted maleic anhydride. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1755–1764, 2003

Key words: twin-screw extruders; maleation; polypropylene degradation

INTRODUCTION

Twin-screw extrusion has become an important manufacturing process for both polymerization and modification of polymers. The early patent literature on extruder reactors largely involved single-screw extruders. The first patent application for reactive extrusion in a twin-screw extruder was filed in the 1940s by the I.G. Farbenindustrie.[1,2] The first open article on reactive extrusion was published for the continuous esterification of cellulose by Riess[3] in 1955. Modification of polymers has been one of the most common objects of reactive extrusion. Efforts to modify polyolefins with peroxides and combinations of peroxides with a second monomer have been in progress since the 1960s.[4–20] Most of the attention has been given to peroxide grafting of maleic anhydride, which has been found to produce a successful reactive compatibilizing agent in blends of polyolefins and polyamides. There have been few articles on investigations of the influence of different continuous mixing machines on levels of conversion. Kim and White[14] reported that the levels of grafted maleic anhydride in an intermeshing corotating twin-screw extruder were higher than those in an intermeshing counterrotating twin-screw extruder for all screw configurations. Cha and White[20] reported higher grafting levels in batch reactors than in a modular corotating twin screw extruder.

In this article we compare the levels of maleation achieved in a batch laboratory mixer with various continuous mixers. These experiments were undertaken in roughly equivalent conditions with four continuous mixing machines: (1) a Japan Steel Works modular intermeshing corotating twin-screw extruder, (2) a Leistritz modular intermeshing counterrotating twin-screw extruder, (3) a Leistritz modular nonintermeshing counterrotating twin-screw extruder, and (4) a Kobelco Nex-T continuous mixer. We used screw configurations for each machine with which we have had successful experiences in our laboratory.

EXPERIMENTAL

Materials

A commercial polypropylene (PP8000-GK), obtained from Quantum Chemical, was used in this study. The polymer was supplied in the form of spherical pellets with a melt flow index of 5 g/10 min (ASTM standard D 1238), density of 0.9 g/cc, and a melting temperature of 165°C.

To measure the residence time distributions, aluminum flakes (98% granules, 10–30 mesh), obtained from Aldrich, were used as a tracer.

There are various considerations in choosing the chemical species generating free radicals. The compound had to have sufficient reactivity. Specifically, the compound needed to have a half-life such that the

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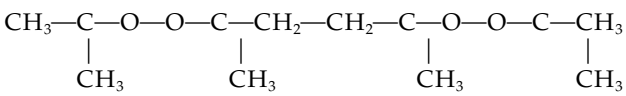
reaction would be completed within the processing machine at moderate screw speeds and the usual processing temperatures. On the basis of these criteria, 2,5-dimethyl-2,5-di-(*tert*-butylperoxy) hexane (DHBP) was chosen. This was obtained from AKZO Chemical as Trigonox® 101.



The monomer grafted was maleic anhydride, which was obtained from the Aldrich Chemical Company.

Reaction vessels

A Brabender Plasti-Corder DR-2072 laboratory mixer was used as a batch reactor for the maleation of polypropylene. Four continuous mixing machines were used in our reactive extrusion studies. They were: (1) a Japan Steel Works Tex30 modular intermeshing corotating twin-screw extruder, (2) a Kobe Steel Nex-T60 continuous mixer, (3) a Leistritz modular intermeshing counterrotating twin-screw extruder, and (4) a Leistritz modular nonintermeshing counterrotating twin-screw extruder.

We used different modular screw configurations in our investigation for the four continuous mixing machines. The screw elements of the intermeshing corotating twin-screw extruder were self-wiping metering sections and kneading disc blocks.[2] The elements of the Leistritz twin-screw extruder were thick-flighted screws, thin-flighted screws, screws with variable pitch (Kiesskalt), shearing elements, and slit stowing elements.[21,22] For the intermeshing counterrotating twin-screw extruder, we used two screw configurations. One consisted of all thick-flighted screws because we expected this configuration to be close to a positive displacement pump.[2] Shown as Screw Configuration IIA, this had the shortest residence time and probably the lowest mixing capability. The screw configurations used are shown in Figure 1.

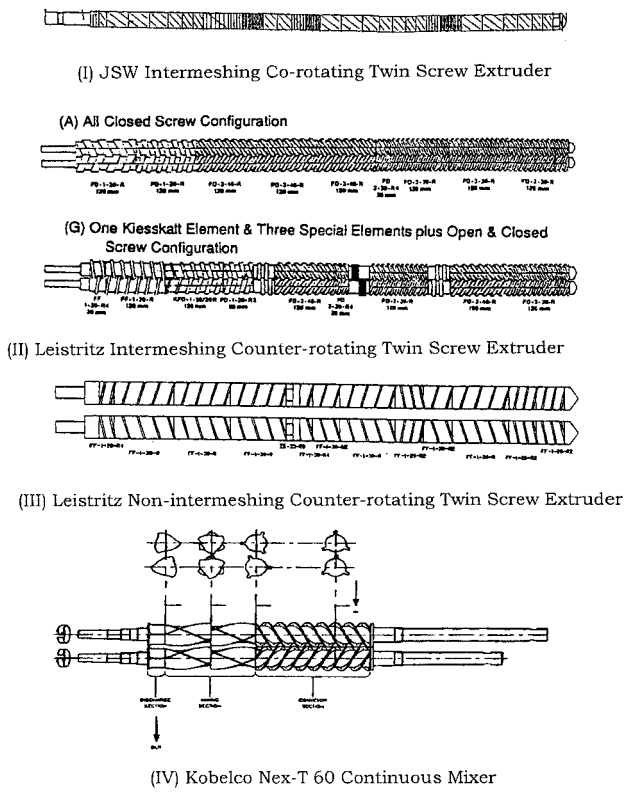


Figure 1 Screw configurations of four continuous-mixing machines.

Determination of residence time distribution

The residence time distributions were determined using Delta function inputs of aluminum flakes into the second hopper after the machine had gotten to a steady-state-like temperature and flow condition. Generally a 5-or 10-g charge of aluminum flakes was introduced into the process stream at the feed throat. Extrudate samples were collected every 5–20 s after the first tracer injection at the machine exit. For example, after the first sample was collected, the second sample was collected after the same duration of time. This collection continued until the aluminum flakes disappeared from the die exit. The Kobelco NEX-T 60 continuous mixer consists of two sections, an upper mixing chamber with two counterrotating rotors and a bottom single-screw extruder. This machine discharges its products vertically downward into a single-screw extruder. Extrudate samples were collected at the gate exit before the associated screw extruder. The samples were placed in a Beringer jet cleaner (400°C, 5 h) in order to burn away the polypropylene. Subsequently, the aluminum flakes were weighed in a Mettler AE 200 balance.

The residence time distribution function, $E(t)$, was calculated using the following equation:

$$E(t) = \frac{C(t)}{\sum_{0}^{\infty} C(t) \times \Delta t} \tag{1}$$

where $C(t)$ is the tracer concentration, which is the mass of aluminum flakes divided by the amount of polypropylene in the initial sample collected at time t, and Δt is the time interval between successive samplings.

The mean residence time of the material in the continuous mixing machine was

$$\bar{t} = \frac{\sum_{0}^{\infty} t \times C(t) \times \Delta t}{\sum_{0}^{\infty} C(t) \times \Delta t} \quad (2)$$

Using this equation, we could get the values of the mean residence time of the material in the four continuous-mixing machines.

Maleation of polypropylene

In the Brabender Plasti-corder experiments, after heating to the required temperature, the rotors were started, and 54 g of polypropylene (approximately calculated 0.667 degree of fill in the molten state) was added to the preheated chamber. The sample was processed until a steady-state torque was obtained in order to make fully melted polypropylene. After melting the polypropylene, the maleic anhydride, and the peroxide were injected onto the melt.

For the maleation experiments in the twin-screw extruders and continuous mixer, maleic anhydride and peroxide was mixed with a nonreactive solvent (such as acetone, benzene, etc.). To achieve precise control of the flow rate of the feed reactants, the reactants were fed by using a liquid pump into the second feed port of the twin-screw extruder, where the polypropylene was already melted. For the continuous mixer all the reactants were fed with the polymer into the first and only hopper.

To further investigate the extent of maleation of polypropylene, we carried out experiments under almost identical processing conditions: a screw speed of 100 rpm, a feed rate of 5 kg/h, and a processing temperature of 230°C. After reaching steady-state conditions, the machine was stopped during reactive extrusion and subsequently cooled to room temperature. We then reheated the machine until we could pull out screws from the barrel. Normally the temperature at which we could remove screws was around 150–160°C, just below the melting point of polypropylene (165°C). We then measured the grafted succinic anhydride content along the screw axis.

Determination of succinic anhydride content

Two procedures were used to measure the amounts of grafted succinic anhydride in the maleated polypropylene products: a titrimetry method and an infrared method.[10,13,23]

To determine the succinic anhydride content of a grafted polypropylene sample, any maleic anhydride not grafted should be removed by dissolving the sample in hot xylene followed by precipitation of the polypropylene with acetone by vacuum filtration before measuring by both methods. Kozel et al.[23] reported that typical residual-free maleic anhydride values were less than 0.005% after cleanup with this method.

The level of grafted maleic anhydride was determined by both the tritrimetry and infrared methods. In the nonaqueous titration method any hydrolyzed grafted maleate was converted to the anhydride form by drying the precipitated resin in a vacuum oven for 24 h at 120°C. After drying, 1 g of the resin sample was dissolved in hot xylene and titrated with alcoholic potassium hydroxide (0.05*N*) to a thymol blue end point.

In the infrared method films of modified polypropylene were pressed between polytetrafluoroethylene sheets at 180–200°C and 5.0–6.5 MPa for 1 min. The spectra were recorded with a Perkin–Elmer FTIR 16 using 32 scans at a resolution of 4 wave numbers (4 cm^{-1}). The intensity of the carbonyl absorption peak at 1785 cm^{-1} divided by that of the CH_3 absorption peak at 1165 cm^{-1}, defined as the carbonyl index, was used as a measure of the amount of grafted maleic anhydride.[10,13,23]

Characterization of molecular weight reduction

We also studied the degradation of polypropylene during the maleation reaction along the screw axis. We obtained four samples removed from cooled-down screws in the same way as the above experiment and evaluated the extent of degradation (viscosity reduction) of polypropylene by measuring the complex viscosity, $\eta^*(\omega)$, along the screw axis. The complex viscosity [$\eta^*(\omega)$] was measured by using the parallel plate geometry at 180°C and 0.1 rad/s. The zero frequency complex viscosity, $\eta^*(0)$, was the same as the zero shear viscosity, whose relationship to the 3.4 power of weight-average molecular weight of polypropylene is well known.[24,25]

RESULTS

Maleation in batch reactor

Preliminary experiments were carried out in order to find the concentrations of maleic anhydride and peroxide suitable for the grafting experiments. First, we did experiments on the influence of reaction time to find suitable reaction times for the grafting reaction. Figure 2 shows the effect of reaction time on the level of grafting with different reactant concentrations under constant processing conditions such as a chamber temperature of 230°C and a rotor speed of 100 rpm. We found that the percent grafting increased initially for 2 min and then remained constant.

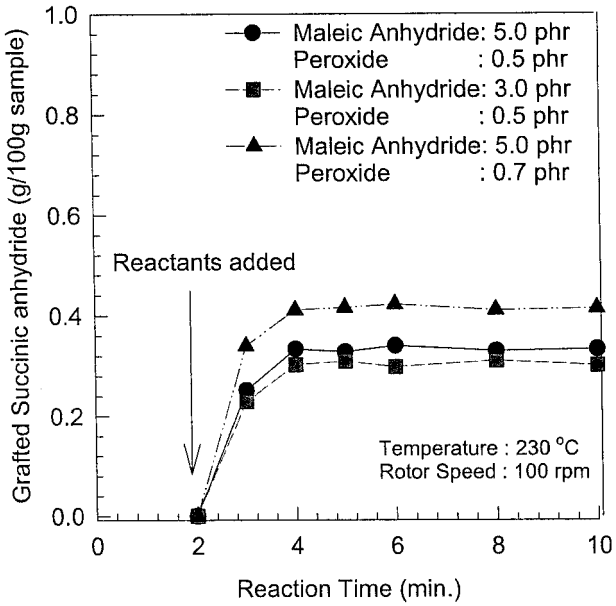


Figure 2 Grafted succinic anhydride as a function of reaction time with different concentrations of reactants for the internal mixer.

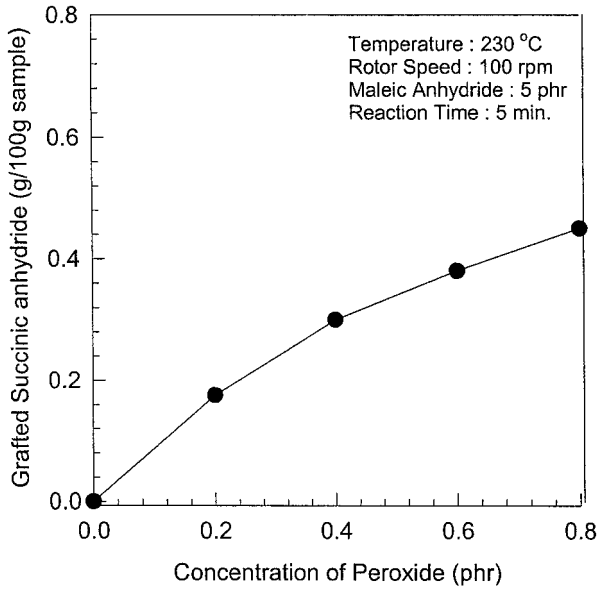


Figure 4 Grafted succinic anhydride as a function of concentration of peroxide for the internal mixer.

Figure 3 shows the level of conversion after a 5-min reaction time as a function of maleic anhydride concentration with a constant concentration of peroxide (0.5 phr) at a processing temperature of 230°C and rotor speed of 100 rpm. Up to a certain concentration of the initial maleic anhydride, the amount of grafted maleic anhydride increased when the initial maleic anhydride concentration increased. Beyond this concentration, there was a decrease in the grafted maleic anhydride. The optimum concentration of the maleic anhydride was between 4.0 phr and 6.0 phr. Therefore, we used 5.0 phr of maleic anhydride to see the effects of processing conditions and to compare different continuous mixing machines in their application to reactive extrusion.

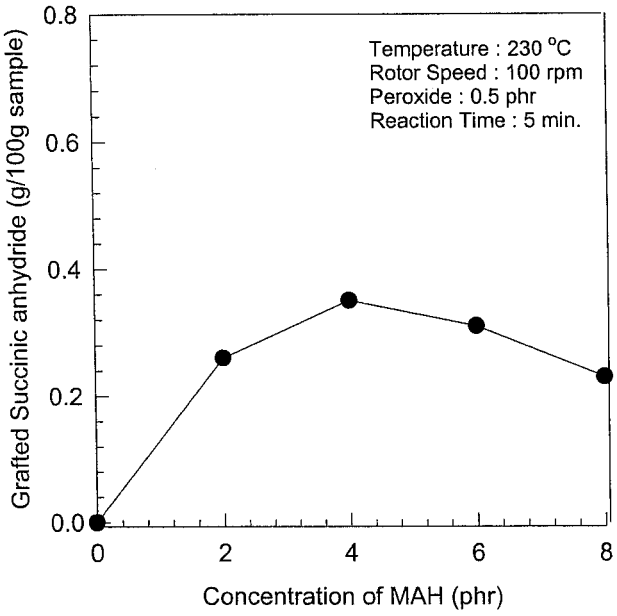


Figure 3 Grafted succinic anhydride as a function of concentration of maleic anhydride for the internal mixer.

Figure 4 shows the effect of peroxide concentration on the level of conversion at a maleic anhydride concentration of 5.0 phr, processing temperature of 230°C, and internal mixer rotor speed of 100 rpm. As shown in Figure 4, more maleic anhydride was grafted onto polypropylene as the initiator concentration was increased. However, because peroxides always degraded polypropylene at the same time as maleic anhydride grafted onto the backbone, the concentration of initiator was critical for obtaining maximum possible succinic anhydride grafting level, with reasonable rheological and mechanical properties of the final products. This led to the selection of 0.5 phr of initiator concentration for our twin-screw continuous reactors.

Residence time distribution

In the maleation experiments we added maleic anhydride and peroxide into the second hopper in order to achieve easy and accurate feeding because the addition of a liquid feed together with pellets can interfere with the transport of the pellets. Therefore, we measured the residence time distribution from the second hopper to the die in order to compare our results with maleation data. We present in Figure 5 differential residence time distributions from the second hopper to the die for the four continuous mixing machines that were presented at the same screw speed and at the same throughput. It can be seen that the residence

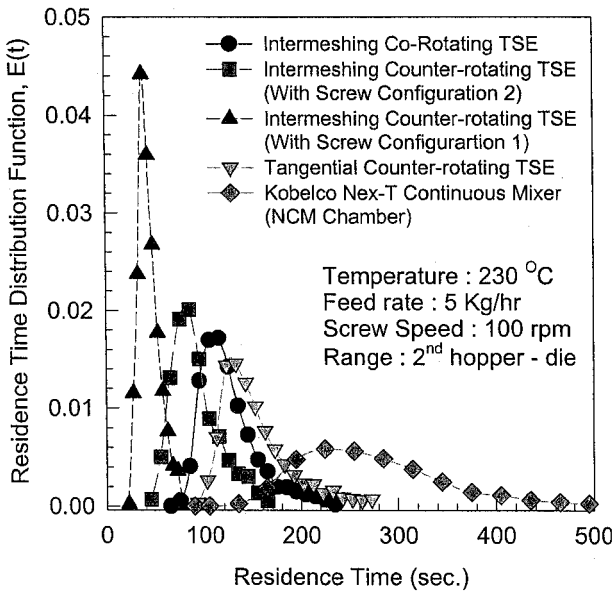


Figure 5 Comparison of residence time distributions at same throughput and screw speed for the different continuous-mixing machines.

time was shortest and the distribution the narrowest for the Leistritz intermeshing counter-rotating machine with screw configuration 1. Leistritz screw configuration 2 had a longer mean residence time and a broader distribution. The JSW modular corotating machine had a broader residence time distribution. The Leistritz nonintermeshing counterrotating twin-screw extruder was broader still. The Kobelco Nex-T continuous mixer had the highest residence time at the same screw speed and at the same feed rate as the other machines. The broadest distribution of residence time by The Kobelco Nex-T continuous mixer seemed to have under the operation conditions.

Comparisons were done of mean residence times at screw speeds for the four continuous mixing machines shown in Figure 6. The Kobelco Nex-T continuous mixer had the longest mean residence times. The nonintermeshing counterrotating twin-screw extruder was second, and the JSW corotating machine followed it. The intermeshing counterrotating machine had the smallest mean residence times among these machines. It can be also observed that an increase in the screw speed decreased the mean residence time.

Maleation in twin-screw reactors

The uniformity of the feed reactants and feeding rate control is critical for homogeneous products. It is very important to precisely control the flow rate of feed reactants. This was achieved by adding the peroxide and maleic anhydride mixture with a solvent (acetone in this experiment) into the second feed port via a liquid pump that was calibrated to measure the flow rates of the feed reactants.

To make a comparison of reactive extrusion in different continuous-mixing machines, maleation experiments were performed in each of the four machines over a range of screw speeds and processing temperatures. These machines include a modular intermeshing corotating twin-screw extruder, modular intermeshing counterrotating twin-screw extruder, modular nonintermeshing counter-rotating twin-screw extruder and Kobelco continuous mixer, as shown in Figure 1.

At constant processing conditions, the grafted succinic anhydride exhibited small change after increases in screw speed. The grafted maleic anhydride level was lowest for the Leistritz intermeshing counter-rotating twin-screw extruder (~0.12 for screw configuration 1 and 0.18 for screw configuration 2). The JSW intermeshing corotating machine had the next higher values (~0.20), followed by the value, of the Leistritz nonintermeshing counterrotating twin-screw extruder (~0.27). The Kobelco Nex-T continuous mixer had the highest level of grafted maleic anhydride at the same processing conditions compared to the other machines (~0.3).

The effect of barrel temperature on the maleation reaction at the same screw speed for the different continuous mixing machines was considered. Figure 7 shows an increase in grafted maleic anhydride up to a barrel temperature of 250°C and from there a decrease in grafted maleic anhydride with further increases in

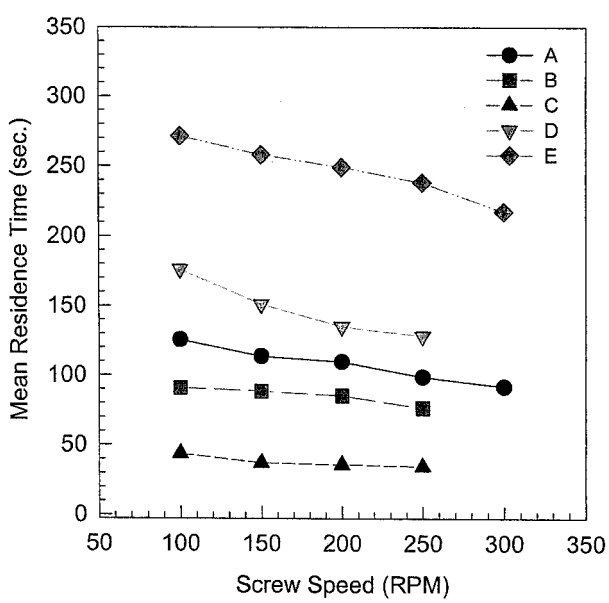


Figure 6 Comparison of mean residence times at different screw speeds for the different continuous mixing machines (temperature: 230°C; feed rate: 5 Kg/h, range: second hopper—die): (A) intermeshing corotating TSE); (B) intermeshing counterrotating TSE with screw configuration 2; (C) intermeshing counterrotating TSE with screw configuration 1; (D) tangential counterrotating TSE; (E) NCM chamber of Kobelco Nex-T continuous mixer.

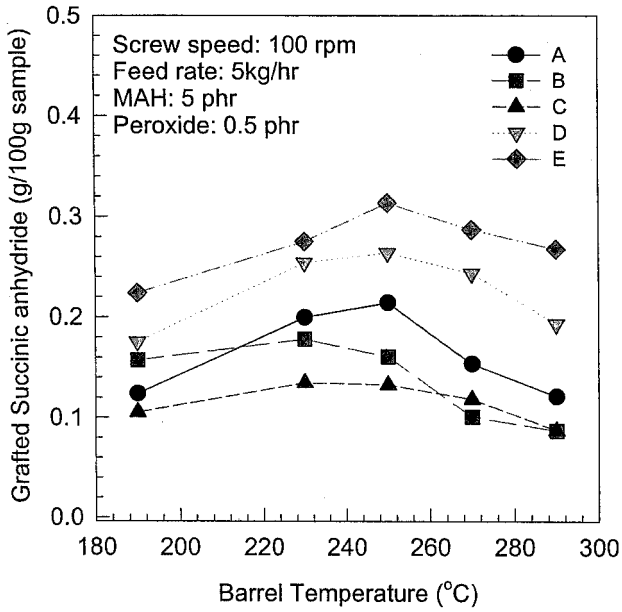


Figure 7 Grafted succinic anhydride content as a function of barrel temperature for the different continuous-mixing machines (screw speed: 100 rpm, feed rate: 5 kg/h, MAH: 5 phr, peroxide: 0.5 phr): (A) intermeshing corotating TSE; (B) intermeshing counterrotating TSE with screw configuration 2; (C) intermeshing counterrotating TSE with screw configuration 1; (D) tangential counterrotating TSE; (E) NCM chamber of Kobelco Nex-T continuous mixer.

the barrel temperature. As shown in Figure 7, the ordering of continuous mixing machines seemed to change with barrel temperature. However, the order of the continuous mixing machines for high levels of conversion at temperatures of 230°C and 250°C was; Kobelco continuous mixer > tangential counterrotating twin-screw extruder > intermeshing corotating machine > intermeshing counterrotating machine with screw configuration 2 > intermeshing counterrotating machine with screw configuration 1. The values were low for the corotating twin-screw extruder at 190°C and for the intermeshing counterrotating twin-screw extruder at 270°C.

Whether reactants were fed into the first hopper or the second hopper make no significant difference. We expected Polypropylene should have been fully melted after the first kneading disc block was passed. However, when reactants with considerable nonreactive solvent (acetone) were fed into the second feed port, the evaporation of the solvent with the reactants resulted in partial resolidification of the polypropylene.

To further investigate the maleation of polypropylene during the maleation reaction, we also carried out a screw-pulling experiment with processing conditions including a screw speed of 100 rpm, a feed rate of 5 kg/h, and a processing temperature of 230°C held constant. After reaching steady-state conditions, the machine was stopped during reactive extrusion and subsequently cooled to room temperature. We then reheated the machine until we could pull out screws from the barrel. Normally the temperature at which we could remove screws was around 150–160°C, just below the melting point of polypropylene (165°C). This enabled us to measure the grafted succinic anhydride content along the screw axis. Figure 8 shows the levels of grafted maleic anhydride obtained along the screw axis in the intermeshing corotating twin-screw extruder for samples removed from cooled-down screws. This experiment was performed under starved flow conditions, with a screw speed of 100 rpm and a feed rate 5 kg/h. Fully filled zones exist before and through the kneading disc blocks and in front of the die in this machine. The screw configuration that we used in the intermeshing corotating twin-screw extruder had three kneading disc blocks at positions where the L/D was about 8.5, 13, and 25. The maleation reaction was found to occur mostly in the positions of the kneading disc block that were fully filled. After the materials passed through this block, the succinic anhydride grafting level did not significantly increase with position along the screw.

The grafted maleic anhydride level along the screw axis in the intermeshing counterrotating machine with screw configuration 2 is shown in Figure 9. For screw configuration 1, a fully filled region occured before the die exit due to die pressure. The maleation reaction

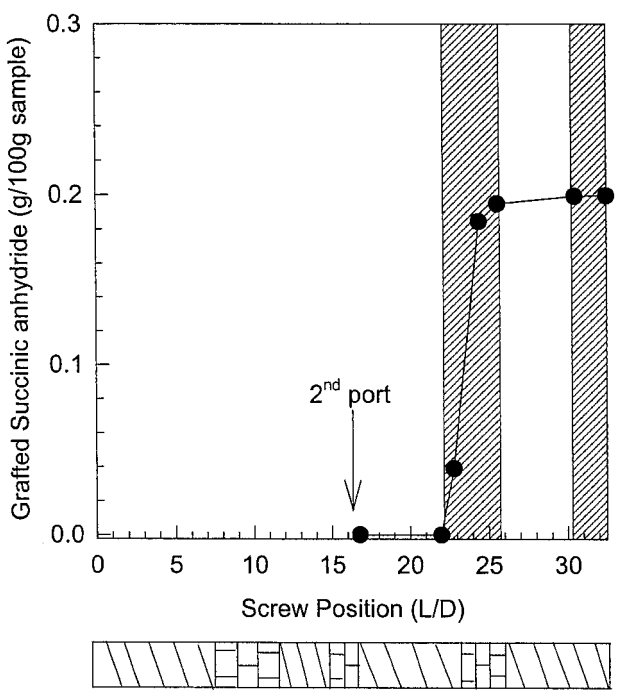


Figure 8 Grafted succinic anhydride content along screw axis for the intermeshing corotating twin-screw extruder (temperature: 230°C, screw speed: 100 rpm, feed rate: 5 kg/h, MAH: 5 phr, peroxide: 0.5 phr; reactants added into the second port; shaded portion: Fully filled region).

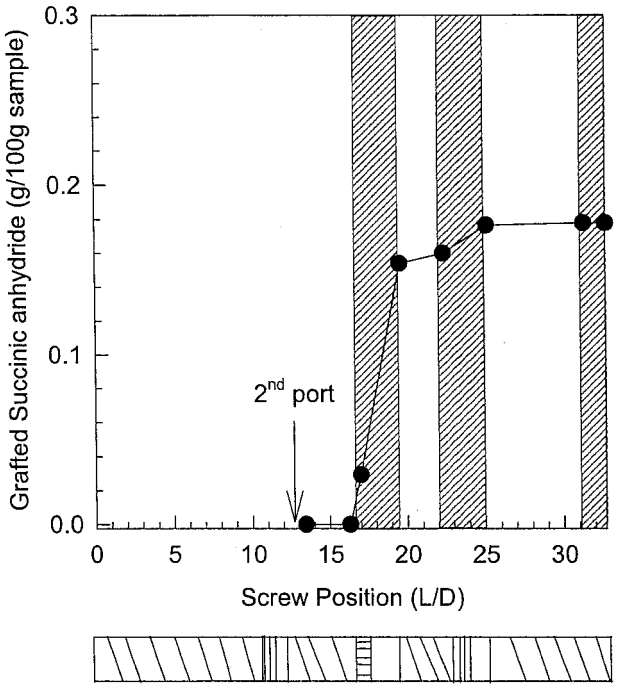


Figure 9 Grafted succinic anhydride content along screw axis for the intermeshing counterrotating twin-screw extruder with screw configuration 2 (temperature: 230°C, screw speed: 100 rpm, feed rate: 5 kg/h, MAH: 5 phr, peroxide: 0.5 phr; reactants added into the second port; shaded portion: Fully filled region).

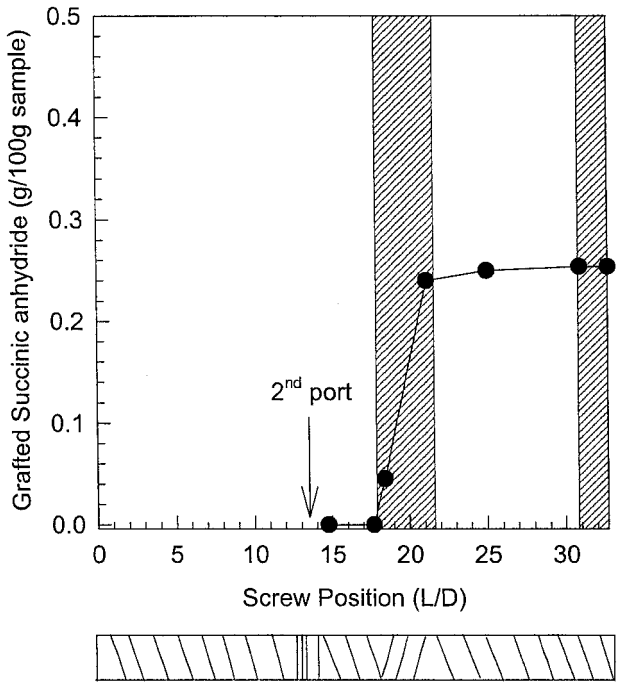


Figure 10 Grafted succinic anhydride content along screw Axis for the nonintermeshing counterrotating twin-screw extruder (temperature: 230°C, screw speed: 100 rpm, feed rate: 5 kg/h, MAH: 5 phr, peroxide: 0.5 phr, reactants added into the second port, shaded portion: Fully filled region).

occured in this fully filled region. Screw configuration 2 had two mixing sections after feeding the reactant. Normally, there are starved zones in screw elements before the mixing section, where the fully filled zone starts to build up. Most of the reaction takes place in the first fully filled zone. There is a smaller increase in conversion in the second fully filled zone, and then it levels off.

For the tangential counterrotating machine, the fully filled sections occurred in backward pumping screw elements. Figure 10 shows that the grafting reaction mostly occured in the mixing zones that were fully filled regions, as in the other machines.

From Figure 11 it can be seen that the reaction took place primarily in the fully filled zone on the two counterrotating rotors in the Kobelco Nex-T continuous mixer.

Degradation of polypropylene

The degradation of polypropylene during the maleation reaction was investigated with experiments in four different continuous-mixing machines under the same processing conditions. We evaluated the extent of degradation (viscosity reduction) by measuring the complex viscosity, η^* (ω), at 0.1 rad/s.

Figure 12 shows the extent of viscosity reduction along the screw axis in the intermeshing corotating

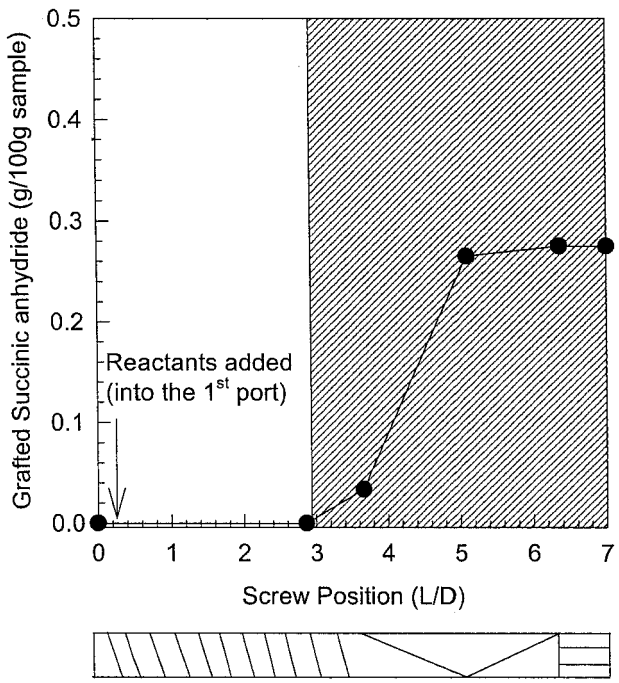


Figure 11 Grafted succinic anhydride content along screw Axis for the NCM chamber of the Kobelco Nex-T continuous mixer (temperature: 230°C, screw speed: 100 rpm, feed rate: 5 kg/h, MAH: 5 phr, peroxide: 0.5 phr; shaded portion: Fully filled region).

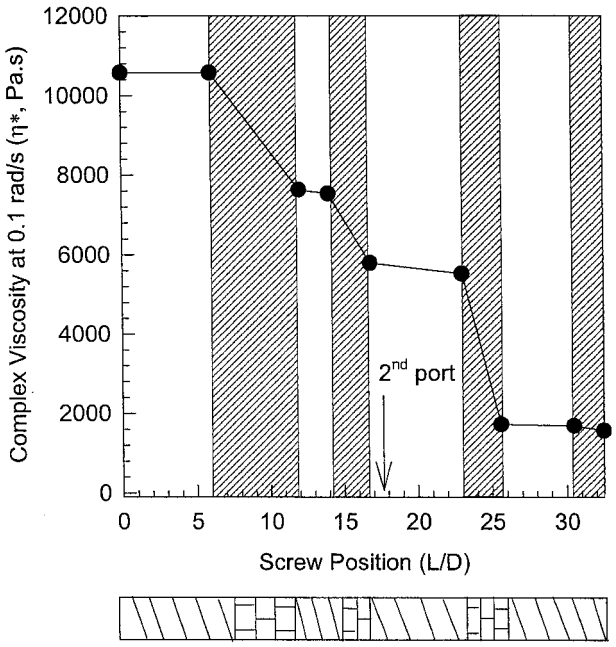


Figure 12 Complex viscosity along screw axis for the intermeshing corotating twin-screw extruder (temperature: 230°C, screw speed: 100 rpm, feed rate: 5 kg/h, MAH: 5 phr, peroxide: 0.5 phr; reactants added into the second port, shaded portion: fully filled region).

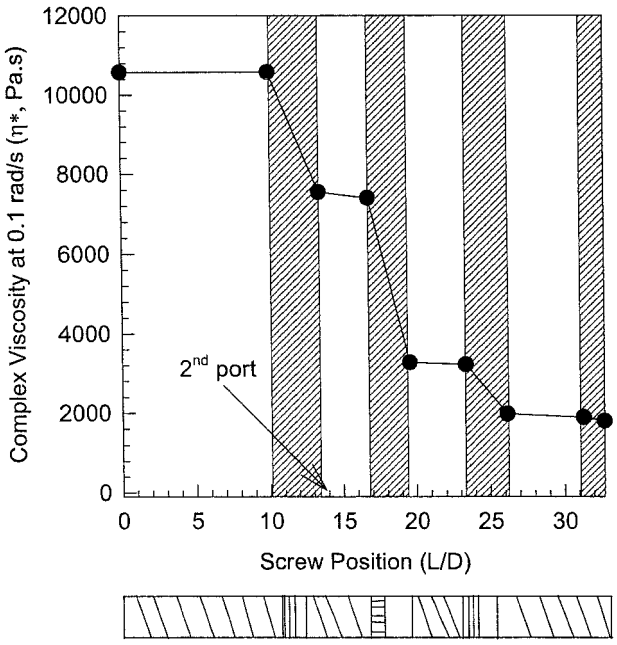


Figure 13 Complex viscosity along screw Axis for the intermeshing counterrotating twin-screw Extruder with screw configuration 2 (temperature: 230°C, screw speed: 100 rpm, feed rate: 5 kg/h, MAH: 5 phr, peroxide: 0.5 phr; reactants added into the second port, shaded portion: fully filled region).

twin-screw extruder during maleation experiments for samples removed from cooled-down screws. From this Figure 12, it can be seen that most degradation occured in the kneading disc block, and there seems to have been very little degradation in the screw regions.

In the intermeshing counterrotating twin-screw extruder with screw configuration 1, there was no significant change in viscosity until the material was near the die section, which was the only fully filled zone because of die pressure. Figure 13 shows the extent of viscosity reduction in the intermeshing counterrotating twin-screw extruder with screw configuration 2 along the screw axis in the same processing conditions. From Figure 13 it can be seen that the viscosity of the material decreased rapidly during and after passing the fully filled region in the mixing sections, whereas the viscosity decreased very slowly in the screw elements.

In the nonintermeshing counterrotating twin-screw extruder, the complex viscosity of the material primarily decreased while passing through the fully filled zones, a result of the mixing and backward-pumping screw elements.

Figure 14 shows the extent of viscosity reduction in the Kobelco Nex-T continuous mixer along the screw axis at a feed rate of 5 kg/h, a screw speed of 100 rpm, and a barrel temperature of 230°C. As in the other machines, little degradation occurred in the fully filled zone, which was induced by a long backward pumping blade. Most of degradation occurred before this zone.

Figure 15 shows plots of the complex viscosity as a function of frequency for the four kinds of continuous-mixing machines. As can be seen in Figure 15, the

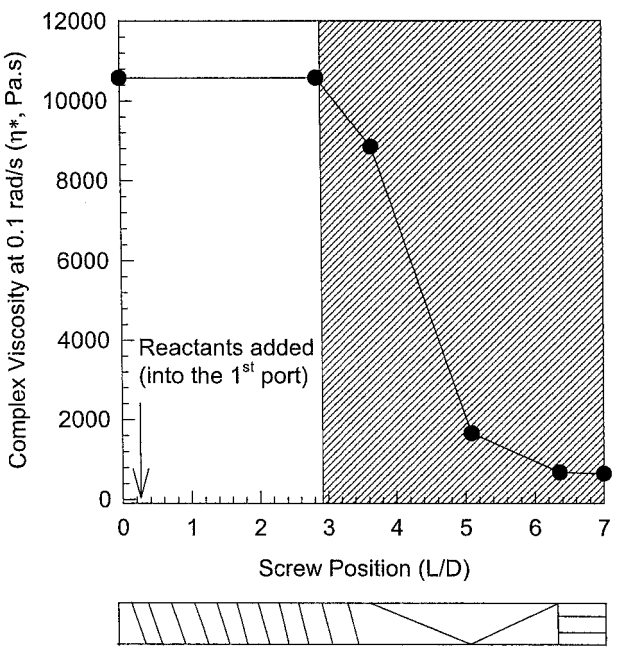


Figure 14 Complex viscosity along screw Axis for the NCM chamber of the Kobelco Nex-T continuous mixer (temperature: 230°C, screw speed: 100 rpm, feed rate: 5 kg/h, MAH: 5 phr, peroxide: 0.5 phr; shaded portion: fully filled region).

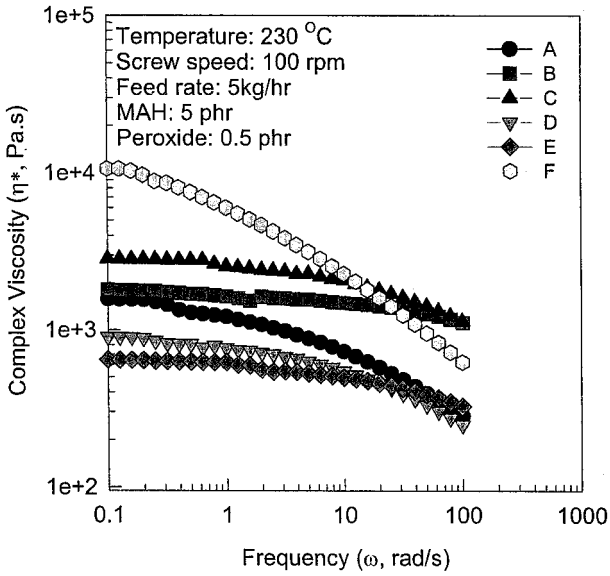


Figure 15 Complex viscosity as a function of shear Rate for the different continuous mixing machines (temperature: 230°C, screw speed: 100 rpm, feed rate: 5 kg/h, MAH: 5 phr, peroxide: 0.5 phr): (A) Intermeshing corotating TSE, (B) intermeshing counter-rotating TSE with screw configuration 2, (C) intermeshing counterrotating TSE with screw configuration 1, (D) tangential counterrotating TSE, (E) NCM chamber of Kobelco Nex-T continuous mixer, (F) initial polypropylene.

Kobelco continuous mixer produced the most degradation of polypropylene at the specified processing conditions. For the nonintermeshing counter rotating twin-screw extruder, the extent of degradation was greater than that in the intermeshing corotating and intermeshing counterrotating machines. The intermeshing corotating twin-screw extruder had higher levels of degradation than did the intermeshing counterrotating twin-screw extruder with screw configuration 2. The intermeshing counterrotating twin-screw extruder with screw configuration 1 exhibited the least degradation of polypropylene.

During the maleation experiments we measured the complex viscosity, $\eta^*(\omega)$, of each degraded sample in order to know the extent of degradation. The complex viscosity measured through the Cox-Merz correlation[24] is quantitatively identical to the shear viscosity shear rate relationship. The zero shear viscosity of polypropylene is related to weight-average molecular weight and the shear rate dependence to the molecular weight distribution.[25] Therefore, we could obtain the relative extents of degradation of the degraded samples by measuring complex viscosities. The correlation of Fritz and Stöhrer[26] was used to relate $\eta(O)$ to M_W. The weight-average molecular weight of the initial polypropylene was 598,000 g/mol. The weight-average molecular weight of the polymer leaving the NCM chamber of the Kobelco continuous mixer was 262,000 g/mol. The weight-average molecular weights of the other machines were 290,000 g/mol for the nonintermeshing counterrotating machine, 341,000 g/mol for the intermeshing corotating machine, 355,000 g/mol for the intermeshing counterrotating machine with screw configuration 2, and 406,000 g/mol for the intermeshing counterrotating machine with screw configuration 1.

DISCUSSION

Residence time distribution

We compared the residence time distribution and grafting of maleic anhydride onto polypropylene in different continuous-mixing machines— a JSW intermeshing corotating twin-screw extruder, Leistritz intermeshing and nonintermeshing counterrotating twin-screw extruders, and a Kobelco Nex-T continuous mixer—as functions of screw speed and processing temperature. We saw that the Leistritz intermeshing counterrotating twin-screw extruder had the shortest mean residence time and narrowest distribution of residence times and the lowest grafting level of maleic anhydride onto polypropylene. The residence time was short because the intermeshing counterrotating twin-screw extruder was closely intermeshing and therefore consisted of a series of C-shaped chambers in which material was transported toward the die.[2] The intermeshing corotating machine was found to have longer mean residence times and greater levels of the maleation reaction than did the intermeshing counterrotating machine. The Leistritz nonintermeshing counterrotating machine had the higher residence

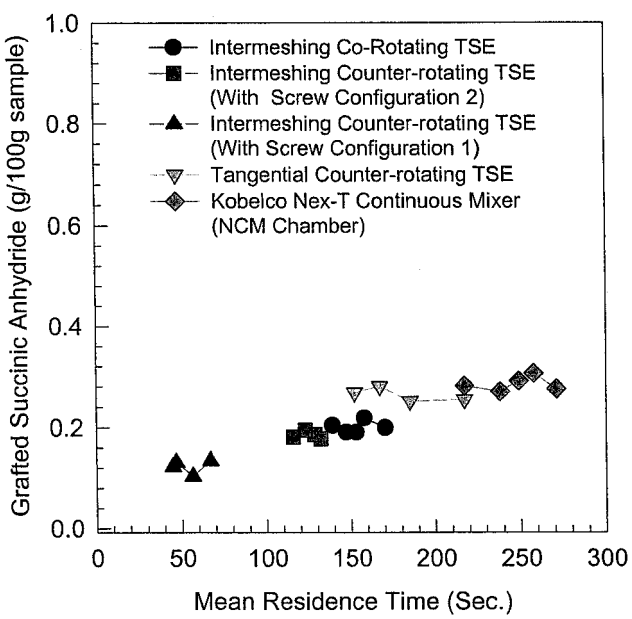


Figure 16 Grafted succinic anhydride content as a function of residence time for the different continuous-mixing machines (temperature: 230°C, screw speed: 100 rpm, feed rate: 5 kg/h, MAH: 5 phr, peroxide: 0.5 phr).

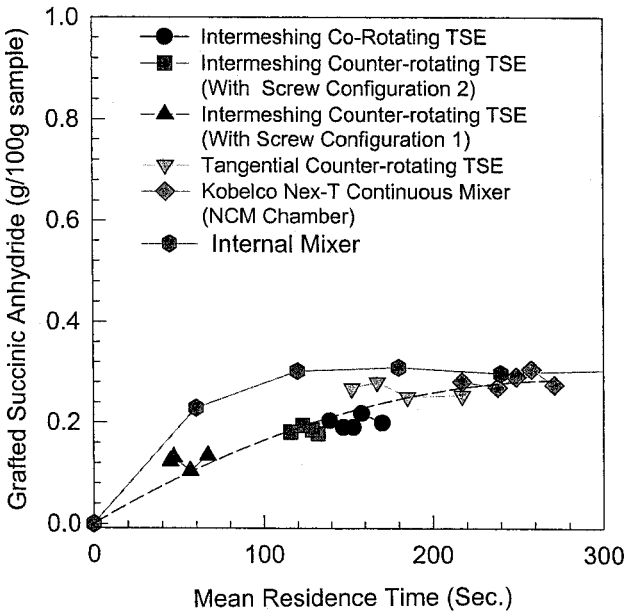


Figure 17 Comparison of grafted Succinic Anhydride Content as a function of batch reactor Time and continuous mixer residence time (temperature: 230°C, screw speed: 100 rpm, feed rate: 5 kg/h, MAH: 5 phr, peroxide: 0.5 phr).

time and a broader residence time distribution and produced a higher grafting level than did the intermeshing corotating and counterrotating twin-screw extruders. The Kobelco Nex-T continuous mixer had the longest mean residence time and broadest residence time distribution and the largest grafting level among these continuous-mixing machines. The fully filled zone is very important for the flow profile in, and the mixing efficiency of, the extruder.

The throughput in the Kobelco Nex-T continuous mixer was very low compared to the machine's capacity, and low throughput leads to a artificially high residence time. According to Valsamis and Canedo[27] and Galle and White[28] the residence time distribution of this type of machine becomes narrower than that of an intermeshing corotating twin-screw extruder at higher feed rates.

Level of maleation as a function of residence time

Figure 16 shows the plot of the amount of grafted maleic anhydride as a function of mean residence time for the various twin-screw extruders and the continuous mixer, for which there is a good correspondence.

Figure 17 shows the results of a comparison of the continuous reactors with the extent of maleation versus time found for the batch reactor, as shown in Figures 2–4. It can be seen that the extent of maleation was higher in the batch reactor. This was also observed by Cha and White[20]. The apparent reason for this behavior is that in the batch reactor the antioxidants are destroyed by oxygen, whereas in a continuous reactor the melt is better protected from oxygen, and the antioxidants destroy many of the free-radical fragments from the peroxides.[20]

CONCLUSIONS

Maleation of polypropylene was investigated in different continuous mixing machines. These experiments were undertaken for four different continuous mixers, described above. We also investigated and compared internal mixer behavior, between the continuous mixing machines and the batch mixer. We considered the effects of the variables screw speed, processing temperature, and position of the screw axis on the degree of maleation of polypropylene. During the study of this reactive extrusion process, several factors that affect the reaction were investigated, including residence time, temperature, and mixing efficiency. The order of continuous mixing machines for level of conversion from highest to lowest was: Kobelco continuous mixer > tangential counterrotating twin-screw extruder > intermeshing corotating machine > intermeshing counterrotating machine. This order is in good agreement with the order of the residence time distributions. The extent of maleation was correlated with the mean residence time.

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