Online Monitoring of the Thermal Degradation of POM During Melt Extrusion

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ABSTRACT: Because of its high stiffness, chemical resistance, and low viscosity, Poly (oxymethylene) (POM) is of high relevance for technical applications. The thermal degradation of POM during processing affects its final properties and decreases the long-term stability. The degradation is indicated by the emission of formaldehyde (FA) gas. The aim of this study is to monitor the thermal degradation of POM online, during the melt extrusion in a co-rotating twin screw extruder (TSE). The effect of the processing conditions on the thermal stabilisation of the POM is observed by FA emission and online viscosity measurements. The effect of processing conditions on the compounding of POM with two different FA scavengers is also studied. Fourier transform infrared (FTIR) spectroscopy is used for the online measurement of FA gas and acetyl acetone colour measurement for the offline characterisation. The online viscosity is measured by passing the melt through a slit die at constant volume flow rate. An enhanced thermal degradation is found with decreasing throughput and increasing screw speed. A good correlation between the online viscosity and offline FA measurement is observed. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2394–2401, 2010

Key words: online monitoring; online FTIR; thermal degradation; poly (oxymethylene); formaldehyde gas

INTRODUCTION

Polymer degradation is a frequent problem in extrusion and compounding. Degradation usually manifests itself as discolouration, loss of volatile components or loss of mechanical properties. According to the mode of initiation, the following type of degradation can be mainly distinguished: Thermal degradation, chemical degradation, and mechanical degradation.[1]

Degradation processes are generally quite complex; often more than one type of degradation is operational, e.g., thermo-oxidative degradation, thermo-mechanical degradation, etc.[2] Thermal degradation occurs when a polymer is exposed to an elevated temperature in an inert atmosphere. The resistance against such degradation depends on the nature and the inherent thermal stabilisation of the polymer backbone. There are three main types of thermal degradation: depolymerisation, random chain scission, and unzipping of substituent groups.[3–6]

Mechanical degradation refers to molecular scission induced by the application of mechanical stress. The stress can be shear stress, elongational stress or a combination of the two. Mechanical degradation in polymer melts is essentially always combined with thermal degradation, and possibly chemical degradation, because of the elevated temperature of the melt.[7–9] When a polymer melt is exposed to intense mechanical deformation, local temperatures can rise substantially above the bulk temperature especially if the rate of deformation is non-uniform.

Chemical degradation refers to processes induced by chemicals in contact with a polymer. These chemicals can be acids, bases, solvents, reactive gases etc. In many cases, a significant conversion is only observed at elevated temperatures because of the high activation energy for these processes.[10–13]

Degradation during processing will often be a combination of thermal, mechanical, and chemical degradation.[14] The factors that are important in determining the rate of degradation: residence time and residence time distribution (RTD), stock temperature and distribution of stock temperatures, deformation rate and deformation rate distribution and presence of antioxidants and other stabilizers. The first three factors are strongly influenced by the machine geometry and by the operating conditions.

To minimise the degradation effects from processing and in the daily usage , a broad variety of different stabilisers have been developed over the years. In most cases, the efficiency of a particular stabiliser system for a compound is determined by a large number of experiments. For this reason, the

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development of new polymer compounds requires enormous time and resources. As a means to decrease, the time needed for the new compound development, online measuring techniques are used in this research. These methods were initially utilised by the pharmaceutical industry and are recently applied to the polymer chemistry research.[15]

Poly (oxymethylene) is an important engineering plastic consisting of main chains of repeating carbon-oxygen bonds in the form of oxymethylene units ($-OCH_2$). It is highly crystalline and because of its balance of properties and ease of processability it offers performance and cost advantages over many other materials. POM copolymer delivers a combination of outstanding wear resistance, long-term fatigue resistance, toughness, and creep resistance. It is widely used in injection moulding and is also processable by other conventional techniques such as extrusion, compression, roto, and blow moulding. The processing temperature of POM is 180–220°C. Because they are so versatile, POM products are used in numerous applications such as gears, springs, clips, and gaskets.[16] New additive compositions have the potential of broadening the field of application of POM, particularly when they help to stabilise the polymer against its thermal decomposition during processing.[17]

POM, terminated with hemiformal endgroups, is subjected to degradation by several processes, i.e., stepwise thermal depolymerisation from the chain ends, oxidative attack leading to chain scission and depolymerisation, acidolytic cleavage of the acetal linkages of the polymer chain, and thermal chain scission at elevated temperatures.[18–20] Acetylation and methylation[21] of the hemiformal chain ends of POM, as means of stabilisation against thermal depolymerisation is practised. The random chain scission occurs at elevated temperature, resulting in a sudden acceleration in degradation. This acceleration is quite likely attributed to the random scission of main chains, which increases the concentration of hemiformal end groups. As the decomposition starts at unstable end groups, the degradation rate will rise rapidly. Another reason for the acceleration has been emphasized by Dudina et al.[20] Besides the random splitting of the chains, there is also ordinary thermal degradation with chain ends, and both processes interact strongly with each other. Formaldehyde (FA) is produced simultaneously by main chain cleavage.

Stabilisation against oxidative attack is a problem common to many polymers, and this mode of degradation in POM is retarded by the addition of known antioxidants.[22] The use of basic nitrogen-containing additives, capable to reacting with acidic species or with FA to prevent its oxidation is the principle behind stabilising the POM polymer.[23]

The influence of processing parameters on the degradation of polymer during extrusion is known.[24] Throughput, screw speed and processing temperature are the most important parameters for polymer extrusion. Any changes in one of these parameters strongly affect the polymer extrusion mechanism.

In this article, the thermal degradation of POM at several processing conditions are monitored by different online measuring techniques. The target of this study is to explore the possibility of using online measurement of FA gas as a faster way to analyse the degradation of POM during the compounding. In the first part of experiments, the effect of processing parameters on the thermal degradation is analysed. In the second part, POM is compounded with FA scavengers. FTIR is used for the online measurement of FA gas[19] and acetyl acetone measurement for offline characterization.

EXPERIMENTAL

Material

The polymer used in the investigation was poly(oxymethylene) copolymer (Hostaform C9021, Ticona GmbH) and the additives are named as FA scavenger 1 and FA scavenger 2.

Compounding experiments

A production size co-rotating twin screw extruder (TSE) (MEGA Compounder ZSK34Mv, Coperion Werner and Pfleiderer GmbH) with a 34 mm screw was combined with gravimetric feeding units (DDW-MDI, Brabender) for up to 4 components and one main component. The gravimetric feeding units were capable of feeding each minor component with throughputs from 0.05 kg/h to 2.5 kg/h. The compounding was done at 180°C. Different screw speeds of 300, 450, 600, 750, and 900 rpm and throughputs of 15, 20, 25, and 30 kg/h were used.

The TSE was equipped with a 3-way-melt divider. By this, one melt stream can be extruded into a film, a parallel second stream can be analysed with an online-rheometer with a slit die (Proflow, Thermo Electron Corporation) and a third melt stream can be pelletised.

The film extrusion line (Chill roll Type 136-350S, Dr. Collin GmbH) has a roll face width of 350 mm using a preceding slit die with a width of 250 mm and a lip which was adjustable between 0.3 and 2 mm. The roller conveyor, following the chill roll has a length of 3300 mm and can be adjusted to throughput velocities between 0.5 to 5 m/min. This film extrusion line offers enough space for a number of high throughput analysis methods. The POM film

extrusion was done at a velocity of 5 m/min and the thickness of the film was 0.3 mm.

Testing procedures

The online viscosity was measured by the difference in pressure, when the melt was forced through a slit die at constant volume flow rate. Measurements can be made using a range of pre-set volume flow rates. Viscosity is defined as the ratio of true shear stress to true shear rate. Following equations are used to calculate the true shear rate and shear stress.

Apparent shear rate was calculated using the eq. (1),[25]

$$\dot{\gamma}_{app} = \frac{6 \cdot V}{B \cdot H^2} \tag{1}$$

B is the width of the die in millimeters, H is the thickness of the die in millimeters, V is the volume flow rate in cubic millimeters per second.

The eq. (1) is valid only for Newtonian liquids. As plastics melts do not generally exhibit Newtonian behaviour, a correction procedure known as Weissenberg-Rabinowitsch correction method is applied to determine the true shear rate at the slit die and is given by eq. (2),[25]

$$\dot{\gamma} = \frac{\dot{\gamma}_{app}}{3} \left(2 + \frac{d \log \dot{\gamma}_{app}}{d \log \tau} \right) \tag{2}$$

τ is the true shear stress and was calculated using the equation,[25]

$$\tau = \frac{HB}{2(H+B)} \times \frac{dp}{dl} \tag{3}$$

dp/dl is the longitudinal pressure gradient in pascals per millimeter measured using pressure transducers placed along the length of the die.

To calculate the zero shear viscosity the Carreau model was used.[25] The viscosity measurements were done at 190°C.

The online analysis of FA gas during compounding was done by FTIR spectroscopy (Multigas 2030, MKS). A dome was built in the degassing section of the extruder, and it was directly connected to online FTIR using a heated tube. The tube as well as the gas cell of the FTIR was heated to 150°C to avoid condensation and oligomerisation of FA at lower temperatures. A pure nitrogen gas was used to carry the FA gas from the degassing section to the online FTIR. The flow rate was 0.2 LPM. Before starting the experiment pure nitrogen gas was passed through the online FTIR to clean the gas cell and also to calibrate the machine by taking the concentration of all
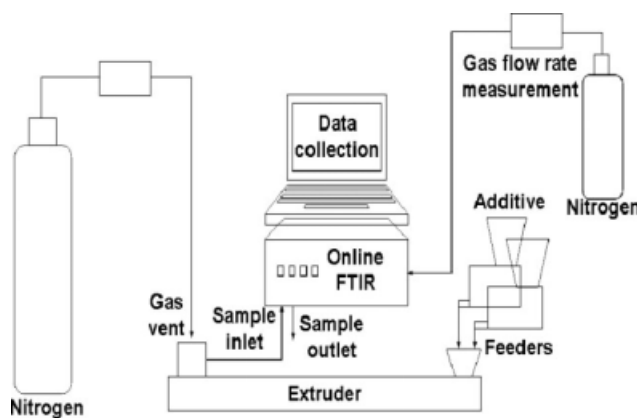
Figure 1 Schematic representation of measurement of formaldehyde gas by online method.

gases at that point as zero. Each spectrum was recorded in FTIR every 15 s, with a resolution of 0.5 cm^{-1}. A schematic representation of the measurement is depicted in Figure 1. The offline measurement of residual FA in the film was done by the acetyl acetone method.[26] In this method, the sample was placed in a bottle along with water and was heated for 3 h at 60°C. The sample was kept in such a way that it does not make contact with the water. After cooling, the sample to room temperature acetyl acetone was added to the water. It was then kept at 95°C for 15 min to reach equilibrium. The concentration of FA gas was then measured photometrically.

To determine the residence time, a pellet of a red colour masterbatch was added to the feeding unit while compounding and the time required for the red colour to reach the exit of the die is measured using a stop watch and is taken as the residence time. The measurement was taken three times and the average was calculated. The torque is monitored by an electrical current metering device of the extruder automatically, which measures the current consumption of the drive means for the screws.

RESULTS AND DISCUSSION

Compounding without formaldehyde scavengers

The influence of screw speed on the torque during the compounding of POM at different throughput level is shown in Figure 2. As expected and typical, the torque decreases with screw speed and increases with throughput. At a lower throughput, the decrease in torque value is less pronounced than at higher throughput with increasing screw speed. The above observation is explained on the basis of fill factor of the channel of the screw. Fill factor is defined as the percent fill of the extruder by the ingredients. With increasing throughput at constant screw speed, the fill factor is increased and,
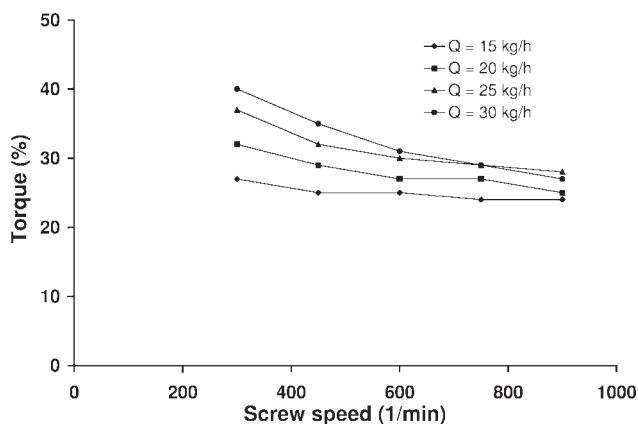
Figure 2 Torque as a function of screw speed for different throughputs for the compounding of POM.

therefore, the power consumption or the torque of the extruder is increased.[27] The decrease of torque with increasing screw speed is mainly due to two factors. First, the fill factor and second is the shear and elongational deformation. With increasing screw speed more space is created in the TSE per unit time for a constant throughput level. The increased space decreases the fill factor and, therefore, the torque level. Also, increasing screw speed at constant throughput causes additional heating of the melt due to shear and elongational deformation and this factor also favours decreasing torque value.[28] The additional heating of the melt enhances the thermal degradation of the polymer, therefore, decreases the molecular weight and thereby the viscosity of the polymer. These factors also influences the decreases torque value with increasing screw speed.

The residual FA measurements of POM extrudate as a function of screw speed for two different throughputs are shown in Figure 3. The residual FA concentration in the film increases with screw speed. The increase of gas concentration with screw speed has two regions. There is an initial region up to a screw speed of 450 rpm, where the increase in gas concentration is marginal. After that, a large increase in the concentration of gas with the increase of screw speed is substantial. There is an exponential behaviour in the emission of FA gas. Also, the FA gas content is lower at 30 kg/h throughput compared to 20 kg/h throughput level. The enhanced degradation with decreasing throughput can be explained considering two factors: First, at constant screw speed decreasing throughput causes increasing residence time: at 600 rpm and a throughput of 20 kg/h the residence time was 42 s. For the throughput of 30 kg/h, the residence time was decreased to 31 s. This shows that a reduction of 26% in residence time is achieved when the throughput is increased from 20 to 30 kg/h. Long residence time allows the degradation reaction to perform lon-

ger and therefore higher levels of FA is observed. Second, at lower throughput the melt is exposed to shear and elongational deformations for longer times.[28] This leads to additional heating by conversion of mechanical energy, which can cause additional thermal degradation. Simultaneously chain rupture occurs. The increased degradation with screw speed is again explained as above. Increasing screw speed at constant throughput causes additional heating of the melt because of shear and elongational deformation. The heat input due to conversion of mechanical energy is responsible for the screw speed dependent degradation for throughputs of 20 and 30 kg/h. This phenomenon will be discussed in detail in Figure 10. On the other hand, increasing screw speed tends to reduce residence time. The increase in mechanical impact with increasing screw speed most likely over compensates the effect of reduction of residence time. Indeed, the reduction of residence time with screw speed is not much pronounced.

The mechanical energy impact due to shear and elongational deformation which can lead to both, temperature increase and/or chain rupture, is described by the specific mechanical energy (SME). For a deeper understanding on how throughput and screw speed influence the process induced degradation of POM, the values of SME were evaluated using eq. (4).[29]

$$SME = (2\pi N\tau)/Q \tag{4}$$

N is the screw speed (1/s), τ is the torque (Nm), and Q is the throughput (g/s). The unit of SME is J/g.

In Figure 4, the residual FA is plotted against SME. Obviously, the degradation of POM is stronger for higher SME. It is seen that the FA concentration increases strongly after an SME value of $1.3E+05$ J/g. This finding also agrees well with Figure 3 where for the higher screw speed the FA concentration increases sharply. The strong increase in degradation
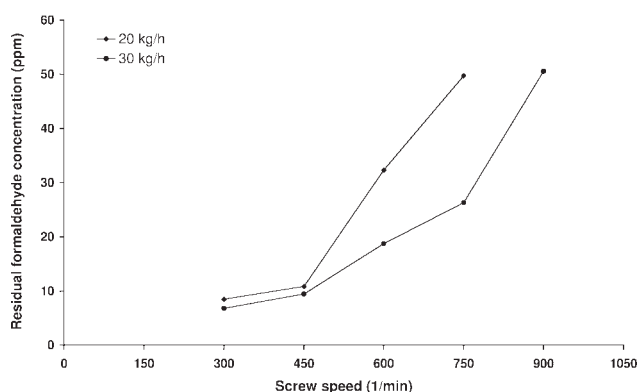

Figure 3 Residual formaldehyde measurements as a function of screw speed for two different throughputs.
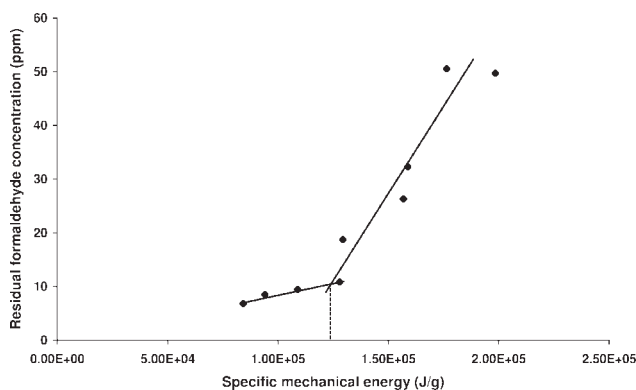
Figure 4 Residual formaldehyde measurement as a function of specific mechanical energy.

at higher SME is due to the additional heating of the melt due to shear and elongational deformation.

The chemistry of degradation of POM is explained in detailed as follows: First remarkable evolution of FA observed at the initial stage of degradation for the POM proves the fact that POM tends to split off FA starting at unstable chain-ends. This behaviour has been described in early publications[19,30,31] as a stepwise process until the thermally unstable hemi-formal end groups (—OCH$_2$OH) is unzipped into the stable hydroxyethyl ether (—CH$_2$CH$_2$OH) end groups. The chain-ends decomposition mechanism discussed above is explained in Figure 5.

Then, the random chain scission occurs at high screw speed and SME as shown in Figures 3 and 4, resulting in a sudden acceleration in degradation with the formation of FA gas. This acceleration is quite likely attributed to the random scission of main chains, which increases the concentration of hemi formal end groups. As the decomposition starts at unstable end groups, the degradation rate will rise rapidly. Another reason for the acceleration is that[20] besides the random splitting of the chains, there is also ordinary thermal degradation with chain ends, and both these processes interact strongly with each other. The mechanism of formation of FA gas by main-chain cleavage is shown in Figure 6.[20]

Figure 7 shows the shear viscosity of POM as a function of shear rate for a throughput of 30 kg/h and for different screw speeds. From the measured values, the graph is fitted with the Carreau model to get the zero shear viscosity in each case. The Carreau model fits the polymer melt data quite well in the low shear rate region. The zero shear viscosity
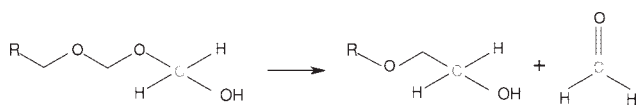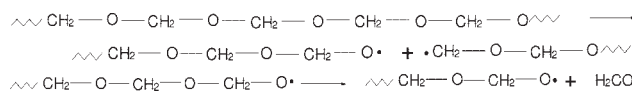

Figure 6 Formation of formaldehyde gas by main chain cleavage.

decreases with screw speed at constant throughput levels.

A closer analysis of the results from viscosity reveals that the influence on zero shear viscosity starts above a screw speed of 450 rpm. This correlates with the FA gas measurement as shown in Figure 3. When the screw speed exceeds 450 rpm Figure 3 shows a large increase in the FA gas concentration. Both factors, i.e., offline measured FA gas and online-monitored decrease in viscosity, are a corresponding indication of the degradation of the polymer.

The zero shear viscosity of POM, which is related to the molecular mass, is plotted against SME in Figure 8. The viscosity is constant for low SME input. From a value above $1.30E + 05$ J/g, the viscosity decreases significantly as a result of the degradation.[27]

Figures 3, 4, and 8 show the manifestation of POM degradation. In Figures 3 and 4, the degradation is manifested in the form of residual FA and in Figure 8, it is manifested in the form of viscosity reduction. This opens up two new possibilities. One is to correlate the residual FA concentration with the viscosity results and the second, most importantly, is that being viscosity measurement an online method and FA measurement an offline method a correlation between online-offline methods can be done. This is what exactly done in Figure 9 in which the offline FA measurement is plotted against online viscosity measurement for different SME values. The points show a good fit between the online and the offline measurement.

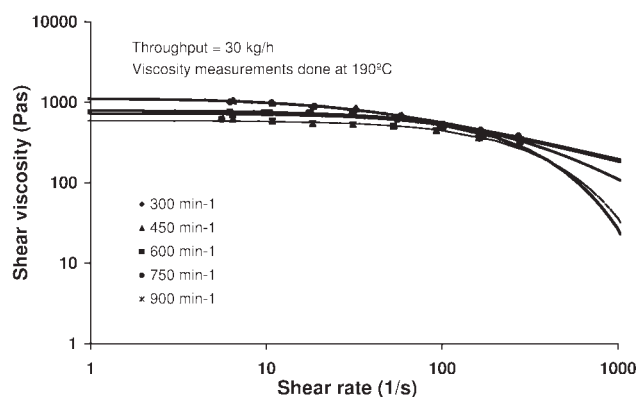In Figure 10, the online emitted and residual offline measurement of FA concentration at zero

Figure 5 Chain-end decomposition mechanism for POM.

Figure 7 Viscosity of POM as a function of shear rate at 30 kg/h for different screw speeds.
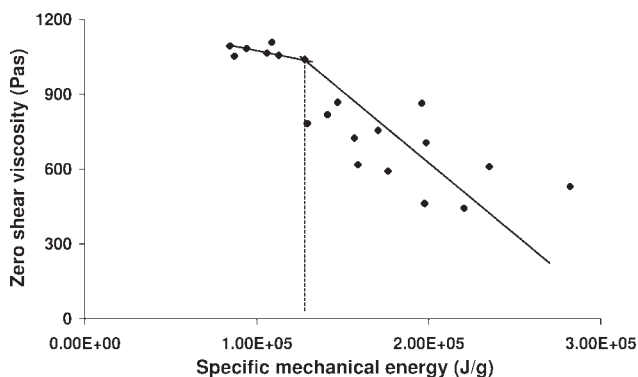
Figure 8 Viscosity of POM as a function of specific mechanical energy.

concentration of FA scavenger as a function of screw speed at 180°C is shown. The increase in the melt temperature as a function of screw speed and its influence on the emission of FA gas is also depicted. In both measurements, the FA gas content as well as the melt temperature increases with screw speed. The aim of this graph is to show the temperature dependence of POM degradation and the correlation between two measurement methods used. The online method of measuring FA gas allows following the reaction pattern of POM in the extruder, whereas the offline measurement shows the amount of FA gas remained in the final product after the processes.

Compounding with formaldehyde scavengers

In this section, the compounding of POM with different FA scavengers is discussed. Compounding is done by gradient feeding technology. In gradient feeding mode, the individual throughput of the components are changed continuously in such a way that the total throughput is constant all the time. This gives the opportunity to scan the effect of a specified range of concentration of additive in the
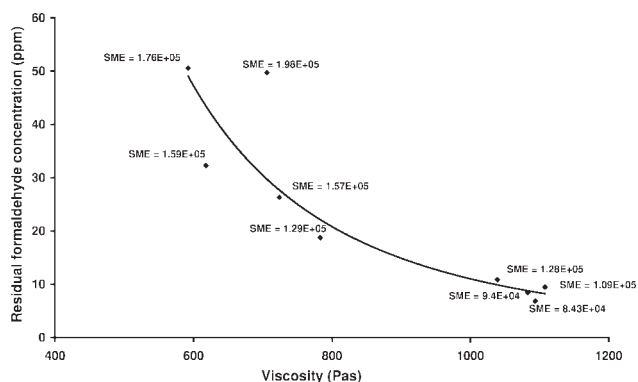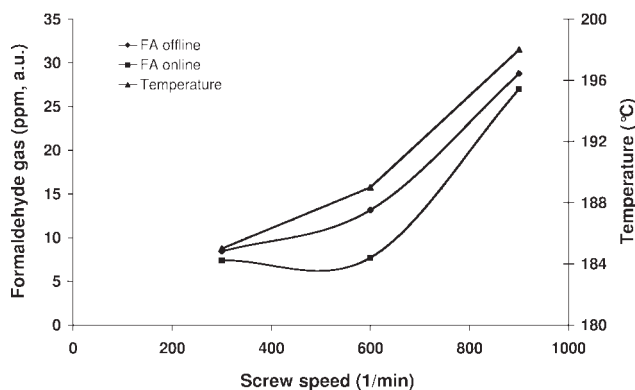

Figure 10 Online and offline formaldehyde gas measurement against different screw speed at zero FA scavenger concentration.

polymer. The offline gas content is measured in ppm whereas the online method is a relative measure of FA concentration and has no units.

Figure 11 shows the residual formaldehyde gas concentration with the increase in concentration of FA scavengers 1 and 2. The throughput was 25 kg/h and screw speed was 600 min^{-1}.

The FA concentration decreases linearly with the increase in the concentration of FA scavenger 2, whereas with FA scavenger 1, the gas concentration remains constant throughout the entire range of additive used. As scavenger 2 proves to be much more efficient than scavenger 1, further experiments were concentrated on scavenger 2.

In Figure 12, the residual FA concentration is plotted against the content of FA scavenger 2 for three different screw speeds. As expected, the concentration of FA gas decreases with the increase in concentration of the FA scavenger and increases with screw speed. The measurements found to be reproducible with the results obtained in Figure 11. For a certain screw speed or a certain specific energy input, the concentration of FA could be reduced by increasing the content of the scavenger, but from a certain
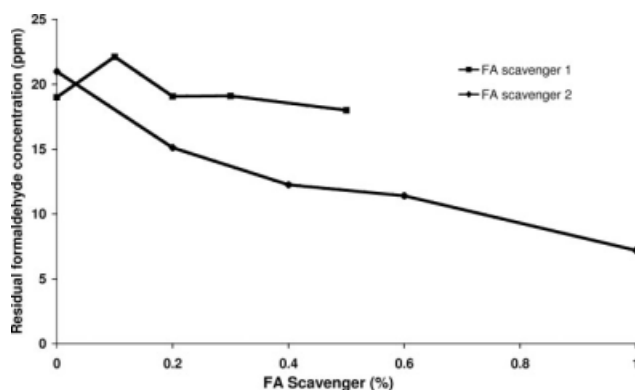

Figure 9 Residual formaldehyde concentration as a function of online viscosity for different specific mechanical energy values.

Figure 11 Residual formaldehyde gas concentration with FA scavengers.

amount of scavenger, more than 1%, there seems to be a limit when additional scavenger has no or just a little additional effect. An explanation for the levelling off effect of FA with the increase in FA scavenger is given below:

a. The residence time for the reaction between the scavenger and the gas in the extruder is 30 s, which is very short for removing the last traces of FA molecules. The mobility of FA scavenger 2 in the POM matrix to reach at all the FA molecules is also important.
b. Some of the FA gas can be dissolved in the POM matrix and therefore not be scavenged by the FA scavenger.

The online measurement of FA gas with FTIR during the compounding of POM with FA scavenger 2 at different screw speeds is shown in Figure 13. The online measurements are done from the extruder. The FA gas concentration increases with increasing FA scavenger 2 during the online measurement at all screw speed levels. The reason for the increase in concentration of FA gas in the online measurement during the compounding of POM with FA scavenger 2 is explained as follows. The reaction of FA scavenger with FA already proceeds at temperatures of 40–80°C. The reaction is reversible with the equilibrium being on the side of FA scavenger 2 and FA at high temperatures. In this case, it would observe the formation of FA at 180°C, while at lower temperatures, the FA scavenger 2 effectively scavenges the free FA. The observation of an increased amount of FA at the degassing opening of the extruder with increasing amounts of FA scavenger 2 is the result of a thermal decomposition of FA scavenger 2-FA reaction products, which had been formed earlier in the process.[28] A very high pressure inside the extruder keeps the reaction in the forward direction even though the temperature is 180°C but at the
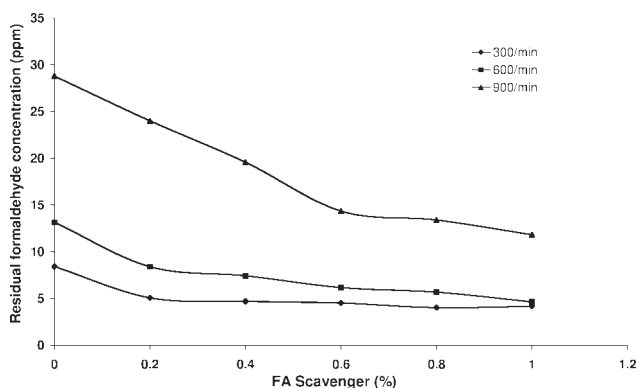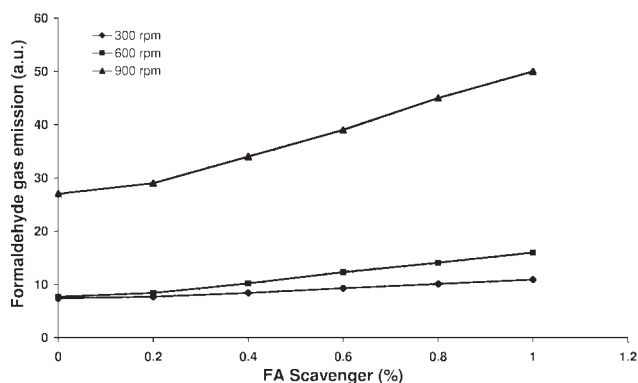

Figure 13 Online formaldehyde gas measurement with FA scavengers 2 at different screw speeds.

degassing zone, the pressure is released and the decomposition occurs.

CONCLUSIONS

During the compounding of POM, the thermal degradation is successfully monitored by means of online – viscosity and FTIR – methods. In the first part of the research it is seen that, processing parameters like screw speed and throughput strongly influences the thermal degradation. Offline FA measurement and online viscosity signal show a significant degradation of POM with the change in processing parameters. The degradation of POM is explained on the basis of chain-end and random chain scission mechanism. A correlation is found between offline and online measurements when plotted with SME values. The gradient feeding technology combined with the online measurement of viscosity and gaseous degradation products at the degassing segment could be proven as an efficient method to investigate and optimise the stabilisation of compound recipes. The online FTIR has been shown as an appropriate method to analyse the emission of FA gas during the compounding of POM. The reaction mechanism between the FA scavenger and the polymer in the channel of the screw is followed with online FTIR.

Figure 12 Residual formaldehyde concentration against FA scavenger 2 at different screw speeds.

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