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Effect of melamine polyphosphate on thermal degradation of polyamides: a combined X-ray diffraction and solid-state NMR study

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Abstract

The effect of melamine polyphosphate (MpolyP) on the thermal degradation of both polyamide 66 (PA66) and polyamide 6 (PA6) was studied using a combination of solid-state techniques. The mixtures of MpolyP with polyamides were heated for different times at 350 and 450 °C. The residues were then analyzed by X-ray diffraction and both solid-state ^{13}C NMR and ^{31}P NMR. The chemical structures formed in these oven experiments were used to study the chemical changes that take place during a standard flammability test. The mixtures of MpolyP with polyamides were also characterized by frequency-dependent rheological experiments. It was shown that MpolyP could induce significant cross-linking in PA66 and leads to dramatic depolymerization of PA6. These results were used to explain the performance of MpolyP as a flame retardant in these polyamides.

Keywords: Depolymerization; Intumescent; Char

1. Introduction

World-wide interest in halogen-free flame retardants (FRs) has been mounting recently in the light of the possible health and environmental risks associated with the use of their halogenated counterparts [1–4]. There is a great need for halogen-free FRs [5–7], especially for polyamides. Melamine-based flame retardants (MBFRs) have proved effective as non-halogenated fire-retarding agents in various types of polymers, in particular polyamides [6,7]. Despite the existence of a number of studies [8–11], the mechanism by which MBFRs act is still not fully understood. Melamine polyphosphate (MpolyP), shown in Fig. 1, is a typical MBFR which works well in polyamide 66 (PA66), but fails to improve the flammability characteristics of polyamide 6 (PA6) at reasonable loading levels. It is believed that, if the mechanism by which MpolyP acts can be elucidated, its applicability can be expanded to include other types of engineering plastics such as PA6 and polyesters.

MpolyP belongs to a class of materials known as char-forming or intumescent FRs [12]. Unlike the halogenated FRs, which act by way of chemical interference with the radical chain mechanism taking place in the gas phase [13], intumescent systems are active in the condensed phase. As a result of a series of physical/chemical processes during the combustion process, a char layer is formed, which isolates the polymeric material from the action of heat and oxygen. It also blocks the transfer of flammable materials into the gas phase, thus leading to extinguishing of the fire. The barrier properties of the char layer are most effective if it is expanded, when the process is termed ‘intumescent’ [14].

It is clear that polymer degradation and interaction with MpolyP play a decisive part in char formation [15]. The elevated temperatures ensure that the physical/chemical changes, which take place during the combustion process, occur in a matter of seconds. It has been shown by several groups that, the chemistry in the gas phase during the combustion process can be monitored in real time using, for example, advanced mass spectroscopy techniques [16] and pyrolysis-gas chromatography [17]. Owing to practical limitations, however, at least for the moment, a reliable time-resolved analysis of chemical changes in the condensed phase is extremely difficult, if not impossible. As an alternative, it was decided to simulate the combustion process by heating the polymeric mixtures in an oven for different times at different temperatures. The residues were then analyzed at room temperature using various techniques such as solid-state NMR and X-ray diffraction. It was anticipated that, using this quasi real-time approach, an

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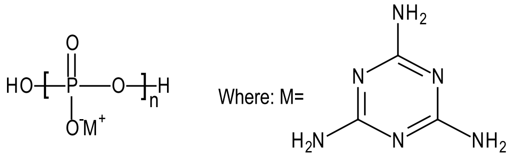

Fig. 1. Proposed chemical structure of melamine polyphosphate. For materials used in this study, $n = 10-20$, as determined by solid-state ^{31}P NMR.

insight could be gained into the chemical processes, which actually take place during the combustion process at elevated temperatures. This paper will provide evidence of the success of this strategy. Since char formation is regarded effectively as a cross-linking process, frequency-dependent rheological experiments were used to investigate the viscosity changes in the mixtures of MpolyP with PA66 and PA6. The results have been used to explain the differences in the efficiency of MpolyP as an FR in both PA66 and PA6.

2. Experimental

2.1. Sample preparation and weight loss measurements (oven experiments)

The melamine polyphosphate is prepared by polymerization of melamine phosphate (MP) (molar ratio of melamine to phosphoric acid 1:1). Details of the synthesis will be published in the near future. All the polymers are DSM products: PA6 (Akulon F223-D), PA66 (Akulon S222). The MpolyP is compounded in the polymer using a home-built mini-extruder at approximately 285 °C for both PA66 and PA6. Unless otherwise stated, all the compounds have an FR loading of 30% (w/w) and contain no glass fibers. In case glass fiber was added to PA66, the compounding conditions are as follows.

The compounds have the composition of 50 wt% PA66, 25 wt% MpolyP and 25 wt% glass fibers (PPG3660). Compounding is performed on a ZSK 30. Screw speed and throughput were 150 rpm and 10 kg/h, respectively. Set temperature for the barrel was 275 °C flat for PA66 compounds. During compounding, the MpolyP and PA66 were fed in the throat of the compounding equipment, while the glass fibers were fed with a side feeder.

For the thermal degradation experiments, the mixtures were weighed in porcelain cups and placed in an oven (under air) at the required temperatures. The weight loss was measured manually as a function of heating time.

2.2. X-ray diffraction

X-ray diffraction measurements were performed with PW1050 and PW1820 powder diffractometers in Bragg Brentano geometry using fixed slits (1 divergency slit; 0.2 mm entrance slit). Cu Kα radiation was used (40 kV, 50 mA) with a monochromator in the diffracted beam. The diffraction patterns were measured under ambient conditions on samples prepared according to the back loading principle. In some cases, intensities originating from the sample holders were detected in the diffraction data. These contributions have been removed from the graphs presented.

2.3. Solid-state NMR

Both ^{13}C and ^{31}P solid-state NMR were used to analyze the solid residues after thermal treatment of the materials, these residues being analyzed at room temperature. The NMR experiments were carried out on both Varian Inova 400 and Unity 200 spectrometers. A standard 7 mm CP-MAS probe was used. All spectra were recorded under magic angle spinning (MAS) conditions and high-power proton decoupling. The spinning rate varied between 6 and 7 kHz. The recycle time between pulses varied between 5 and 10 s.

^{31}P spectra were recorded both using single-pulse excitation (sp) and cross polarization from ^{1}H to ^{31}P (cp). The ^{31}P chemical shift is referenced relative to 85% H_3PO_4/H_2O at 0 ppm.

^{13}C NMR spectra were recorded using cross-polarization from protons to carbons. Typical cross-polarization times of between 1 and 3 ms were used. The 90° pulse on carbons and protons was 5 μs. For the ^{13}C NMR experiments, adamantane was used as the chemical shift reference.

2.4. Rheological experiments

The experiments were performed with a Rheometric Scientific RMS 800 mechanical spectrometer, with a 25 mm diameter parallel plate measurement system and a 2000 g cm range torque transducer. The materials were molten between the parallel plate and were allowed 5 min to reach equilibrium before the first measurement was executed. The samples were measured at a thickness of 1.8 mm. Three scans, at 4–7, 8–10 and 15–16 min, were performed in the above mentioned frequency range. The deformation amplitude was manually adjusted during the measurements in order, to obtain torque values within the detection capabilities of the instrument. The software used for analyzing the measured data was RSI Orchestrator. Before the experiments, the materials were dried overnight at 90 °C in a vacuum oven with a small nitrogen purge.

3. Results

3.1. Weight loss experiments

Fig. 2 shows the weight loss data of different materials as a function of heating at 350 °C, which is well above the compounding temperatures (285 °C), and 450 °C.

It can be seen clearly that in 90 min of heating at 350 °C,

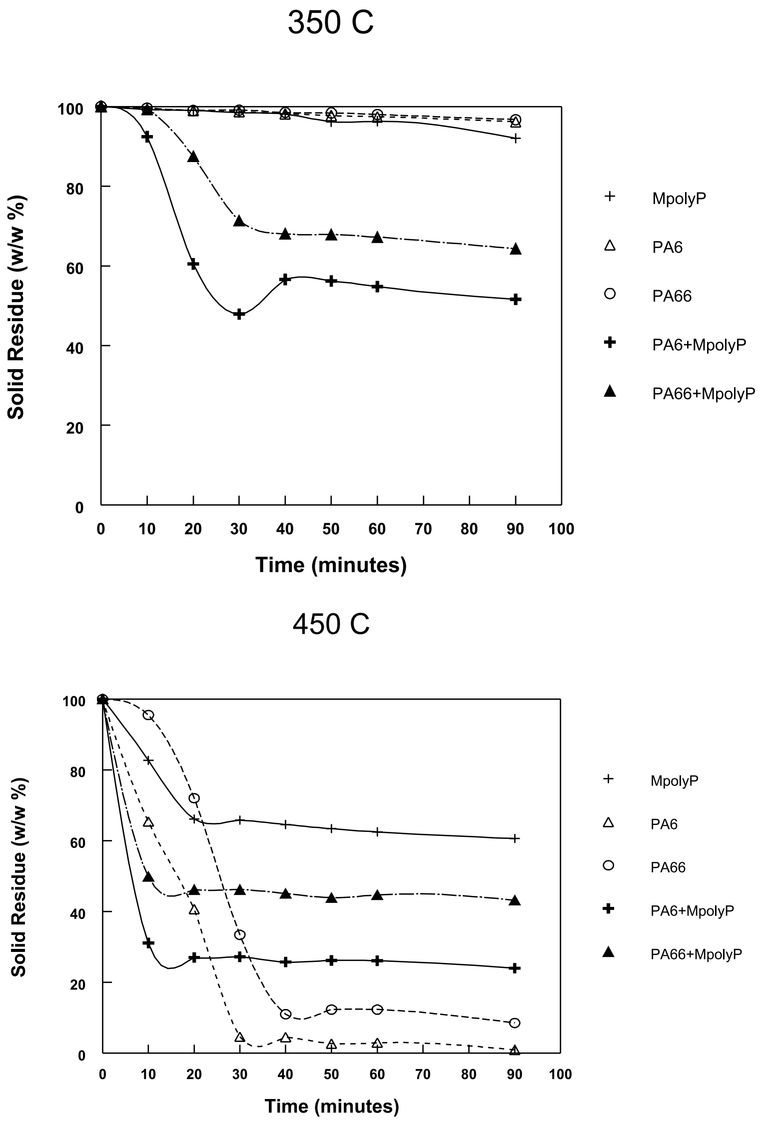

Fig. 2. Weight loss measurements carried out under air at 350 and 450 °C for PA66 and PA6 with and without MpolyP.

all the individual components, i.e. PA6, PA66, and MpolyP, showed no discernible weight loss. As a result of mixing with MpolyP, however, the stability of both polymers decreased dramatically. This shows that at 350 °C, there is already a strong interaction between polyamides and MpolyP. The chemical nature of the materials, which are released into the gas phase, has not yet been analyzed in detail, but it is believed that the materials deposited will contain melamine. Some indirect evidence for the release of melamine during heating above 350 °C is provided later in the text. It should be noted that heating a PA6 + MpolyP mixture produces less solid residue than a PA66 + MpolyP mixture. Similar observations can be made from thermal ageing experiments at 450 °C. It appears that MpolyP results in more severe weight loss with PA6 than PA66. At 450 °C, the amount of solid residues of both the virgin polyamides drops to values below 10% (w/w), with PA6 again resulting in the smaller amount of char. The degradation behavior of pure polymers is in accordance with the data presented in the literature, showing that PA66 produces intrinsically more char than PA6 at any given temperature [18].

As can be seen in Fig. 2, MpolyP loses more than 30% (w/w) of its weight after 20 min at 450 °C. The weight loss of melamine phosphate salts at such high temperatures has been attributed by Horacek and Pieh to a decomposition process during which melamine evaporates [19]. Camino et al. [20,21] have shown that as a result of heating at such high temperatures, ammonia is released, which points to the formation of melamine condensates such as melam [22,23].

3.2. X-ray diffraction measurements

Melamine and most of its derivatives such as MpolyP are highly crystalline materials [24]. X-ray diffraction has been used to investigate the changes in crystalline structure, which result from thermal ageing treatments. Fig. 3 shows

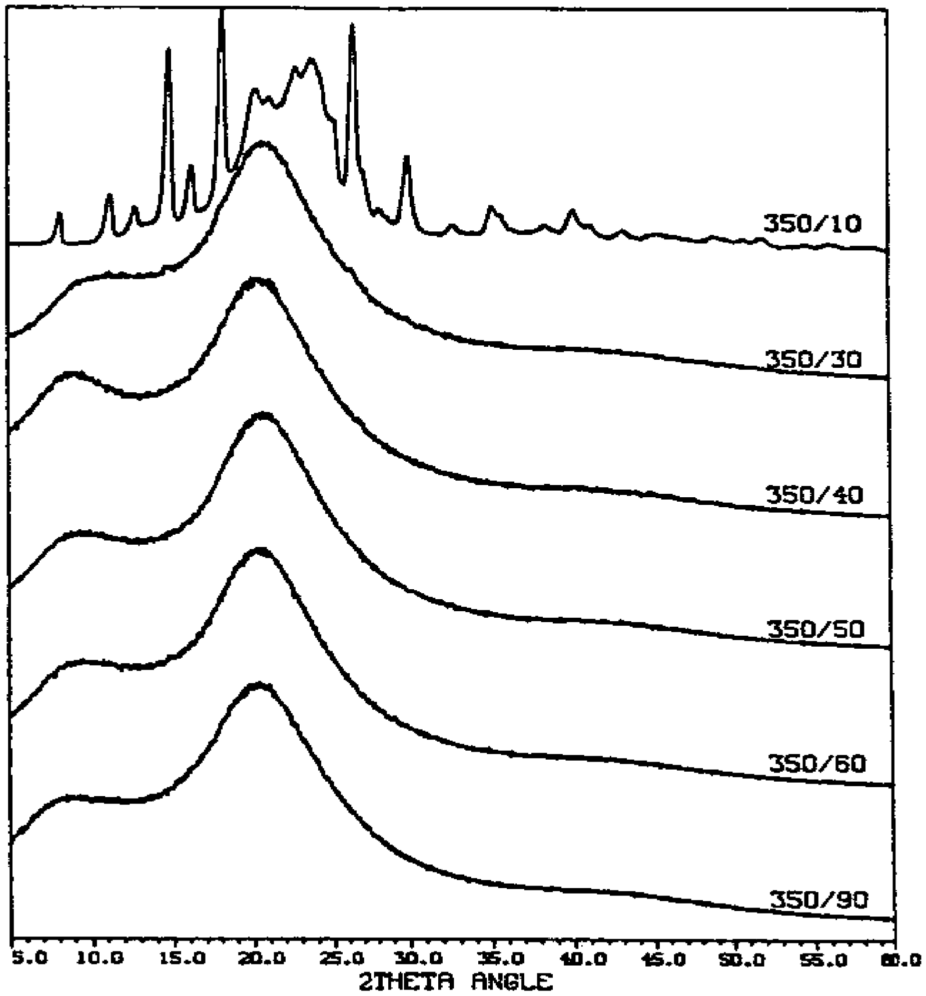

Fig. 3. X-ray diffractograms of solid residues obtained on heating PA66 + MpolyP mixtures for different times at 350 °C.

the X-ray diffractograms of PA66 + MpolyP heated for different times at 350 °C.

As can be seen in the diffractogram of PA66 + MpolyP after 10 min, Bragg diffractions originating from highly crystalline MpolyP are still clearly visible. After 30 min of heating, however, the PA66 + MpolyP mixture becomes completely amorphous, with a shoulder appearing in the diffractogram corresponding with a Bragg spacing of approximately 10 Å. Interestingly, this dramatic change in the diffractograms corresponds to a weight loss of more than 30%. As shown in Section 4, MpolyP depolymerizes during heating at 350 °C to form melamine phosphate and the dimer melamine pyrophosphate (MPy). It appears that a mixture of these compounds cannot crystallize in the PA66 matrix. Similar experiments with PA6 + MpolyP mixture showed almost the same trend (not shown here). In order to gain greater insight into the chemical changes which have occurred, a series of detailed solid-state NMR studies has been carried out.

3.3. Solid-state NMR studies

Whereas X-ray diffraction is mainly used for the investigation of crystalline materials, solid-state NMR is an effective tool for characterizing both amorphous and crystalline materials and for monitoring the chemical changes which occur during combustion of polyamide mixtures. To demonstrate the power of solid-state NMR for the chemical analysis of MBFRs, the NMR results obtained on a series of basic compounds will first be presented. Fig. 4 shows the ^{13}C and ^{31}P solid-state NMR spectra of melamine (M), melamine phosphate, the dimer melamine pyrophosphate and melamine polyphosphate.

Melamine has two possible sites for complexation with phosphoric acid, i.e. nitrogen on the ring and nitrogen in the amine group. With the aid of ^{13}C NMR, the structure of MP can be examined in some detail. As can be seen in Fig. 4, MP has two resonance, at 165.7 and 157.7 ppm, which are shifted by, respectively, 2 and 10 ppm with respect to the carbon-13 resonance of pure melamine at 167.7 ppm. These two resonances have an integral intensity ratio of 1:2. These data appear to support a structure of MP in which phosphoric acid is attached to the nitrogen atom on the ring (see the inset of Fig. 4). The two carbon atoms close to phosphate groups will experience a large shift (about

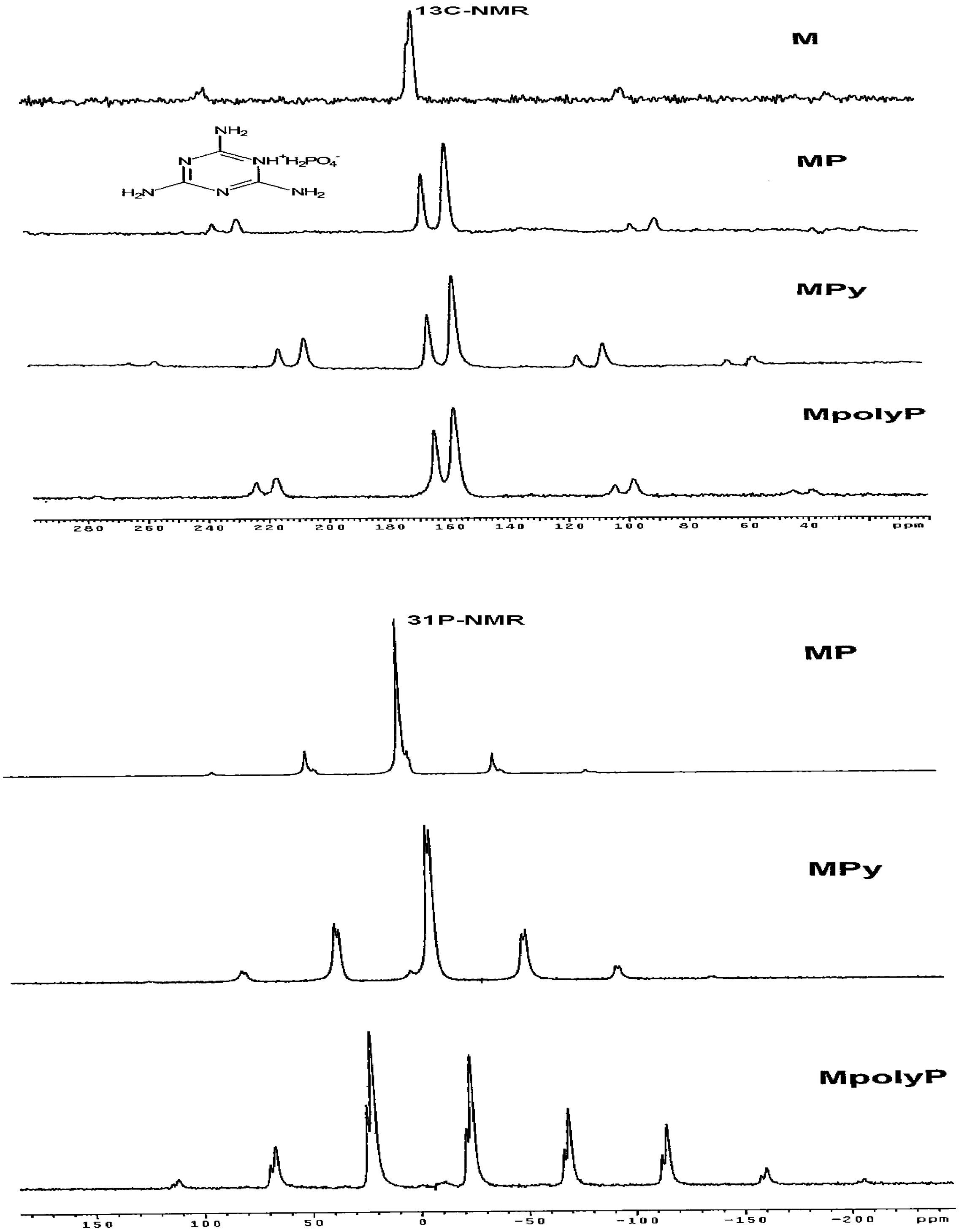

Fig. 4. ^{13}C and ^{31}P NMR spectra of melamine phosphate, melamine pyrophosphate and melamine polyphosphate. For comparison, the ^{13}C NMR spectrum of melamine (M) is also shown.

10 ppm), whereas the carbon atom which is positioned further away from the phosphate group shifts only 2 ppm relative to pure melamine. Moreover, it can be seen in Fig. 4 that, the reaction of MP to form the dimer (MPy) and higher oligomers (MpolyP) does not affect the ^{13}C NMR spectra, suggesting that for these spectra also the phosphate remains bonded to the nitrogen on the ring.

^{31}P NMR spectra of MP, MPy and MpolyP are also shown in Fig. 4. Spinning side bands positioned at equal distances relative to the isotropic main peak are visible.[1] In

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[1] The position of the isotropic peak was estimated by recording ^{31}P NMR spectra at different speeds, which causes only the spinning sidebands to shift.

the literature, it has been shown that the number of neighboring phosphate groups gives rise to a unique ^{31}P chemical shift which makes it possible to distinguish between orthophosphate, pyrophosphate and polyphosphate [25]. The isotropic ^{31}P resonance for MP is observed at 2 ppm, which is typical of orthophosphates. Careful analysis shows that, this peak is a superposition of several peaks which may be related to the crystalline structure of MP. The isotropy observed for MPy is ~ -10 ppm, which is typical of pyrophosphates. In this sample, a small amount of orthophosphate is still present, as shown by the small peak at 2 ppm. The peak at -10 ppm is clearly resolved into two peaks of equal intensity, a finding also observed by Camino et al. for MPy [26]. It is assumed that this splitting is caused by the crystalline structure in which the two phosphorus atoms of the pyrophosphate molecule are crystallographically different. This is consistent with the work of Leung and Calvo [27], who found that the two phosphorus atoms of the sodium pyrophosphate molecule are crystallographically different.

The spectrum of MpolyP shows two isotropic peaks at -22 and -25 ppm, which are typical of middle groups of linear polyphosphates, and a small resonance at -10 ppm, which may be either due to polyphosphate end-groups or to pyrophosphate. The origin of the two clearly resolved peaks of the middle phosphates is still unclear. It is possible that this splitting is caused by the various crystalline structures present.

In addition to characterizing various melamine phosphate salts, solid-state NMR can be used to study the thermal stability of polyamides and the effect of MpolyP on polymer degradation. In principle, thermal degradation of polyamides may involve a depolymerization process and/or various cross-linking reactions. In the case of PA6, two different depolymerization routes have been proposed which result in the release of ε-caprolactam: (a) an intermolecular back-biting process and (b) a hydrogen transfer reaction leading to scission of the C–N bond β to the amine group [28–30]. Both processes have also been identified for PA66, resulting in the formation of cyclopentanone [31–33]. A number of mechanisms have also been proposed for a cross-linking reaction [34,35], although no hard experimental evidence exists to support any of these.

Fig. 5 shows ^{13}C NMR spectra of PA66 and PA6 heated for 10 and 90 min at 350 and 450 °C. As one might expect, prolonged heating of PA66 results in extensive degradation. During 90 min at 350 °C, major chemical changes take place, resulting in the almost complete disappearance of carbonyl resonance at 182 ppm. Only a broad peak around 40 ppm remains due to some degradable aliphatic fragments. The peak at approximately 150 ppm which appears after 90 min at 450 °C points to the formation of aromatic structures. Interestingly, no discernible weight loss results from the thermal degradation at 350 °C (see Fig. 2). In contrast, on heating at 450 °C, only about 10% (w/w) of charred material is left.

PA6 appears to be more stable than PA66. On heating at 350 °C, only partial re-crystallization of PA6 occurs, changing the fractions of α, γ and the amorphous phases [36]. Extensive degradation takes place only as a result of prolonged heating at 450 °C. This is in agreement with the data presented by Hornsby et al. [37], who concluded that PA6 was slightly more thermally stable than PA66 based on TGA and DSC experiments. As has been shown previously, however, heating of PA66 produces more char than PA6. PA66 appears to be less stable than PA6, but the chemical changes in PA66, which take place at relatively lower temperatures in comparison to PA6, result in a greater quantity of solid residues. The relatively greater quantity of solid residues can be attributed to a more efficient cross-linking reaction in PA66 than in PA6. In PA6, the depolymerization reaction releasing ε-caprolactam predominates.

The effect of MpolyP on the thermal degradation of polyamides can be seen in Fig. 6, which shows the ^{13}C NMR spectra of degraded mixtures at 350 and 450 °C. When the ^{13}C NMR spectra of virgin PA66 are compared with those of PA66 + MpolyP, it is obvious that the degradation behavior has been modified. The small broad peak at 160–170 ppm originates from MpolyP. After 90 min heating at 350 °C, the carbonyl peak at 182 ppm is reduced to a lesser extent than is the case with PA66, and a new peak has appeared at about 165 ppm. On heating for only 10 min at 450 °C, extensive degradation of PA66 can be observed, indicating that MpolyP reduces the thermal stability of this polymer. Heating for 90 min at 450 °C results in the formation of a complete aromatized structure. Similar observations can be made regarding the effect of MpolyP on the degradation behavior of PA6. Unlike the ^{13}C NMR spectrum of virgin PA6, the spectra of PA6 + MpolyP heated for 90 min at 350 °C show new peaks within both the aliphatic and aromatic/carbonyl range. The relatively narrow peak at 130 ppm might be attributed to olefinic end-groups, while the underlying broader resonance is probably due to aromatic structures. In this case, heating at 450 °C also results in the formation of some type of aromatic structure, but the structure of the char material seems to be less ‘developed’ than in the case of PA66 + MpolyP. Interestingly, the chemical structure of the two polyamides formed in the presence of MpolyP after 90 min at 350 °C seems to be rather similar.

^{31}P NMR has been used to monitor the thermal degradation of MpolyP in the mixtures with polyamides which results from ageing treatments. In Fig. 7, the ^{31}P NMR spectra of the PA66 + MpolyP and PA6 + MpolyP mixtures are shown heated for 10 and 90 min at 350 and 450 °C.

In the case of both polyamides, heating at 350 °C results in depolymerization of the (melamine) polyphosphate chain into (melamine) pyrophosphate and (melamine) orthophosphate.[2] Upon further heating to 450 °C, this depolymerization

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[2] It should be emphasized that ^{31}P NMR only distinguishes between orthophosphate, pyrophosphate and polyphosphate. The presence of the melamine phosphate as a salt can only be inferred from the relatively broad ^{31}P lines compared to that of liquid phosphoric acids. But the broader ^{31}P lines may also result from the immobilization of the phosphates due to chemical and/or physical attachment of the phosphates to the polyamide degradation products.

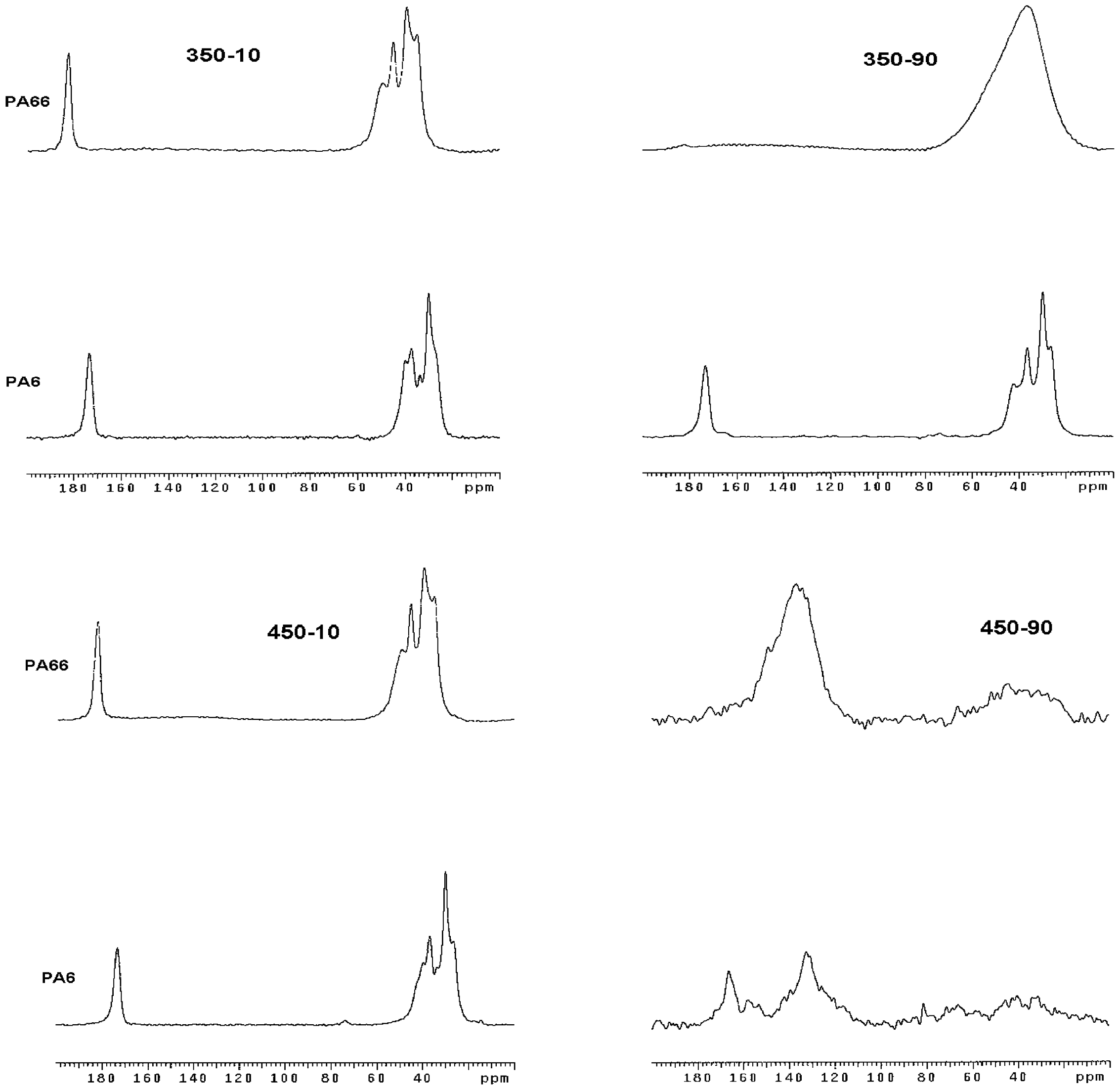

Fig. 5. ^{13}C NMR of solid residues obtained on heating pure PA66 and PA6 for 10 and 90 min at 350 and 450 °C.

process continues until melamine orthophosphate is left. The depolymerization occurs both in the presence of PA66 and PA6. For the pure MpolyP, such a depolymerization process is not observed (spectra not shown here). In addition, in the case of PA66 + MpolyP, the ^{31}P spectrum shows very sharp peaks at approximately 0 and −10 ppm after 10 min heating at 450 °C. These peaks indicate the presence of phosphoric acid and condensation products such as diphosphoric acid and higher condensates, which could not be detected in the PA6 + MpolyP mixtures. The release of acid must result from the dissociation of MP salts. In the ^{31}P spectra of PA66 + MpolyP at 450 °C, new peaks appear at −31 and −43 ppm. These new resonances cannot currently be assigned unambiguously. The resonance at −31 ppm could be due to branching points present in polyphosphates [38]. The resonance at −43 ppm may be assigned to the oxidation products of orthophosphates such as P_4O_{10}, as suggested by Bourbigot et al. [39]. An alternative explanation for these new resonances could be the formation of chemical bonds between phosphate groups and degradation products of PA66. This requires further investigation.

3.4. Analysis of char structure formed during the UL-94 flammability test

The thermal ageing experiments conducted in combination with X-ray and NMR studies have provided a credible picture of the physical/chemical processes which take place in polyamide and MpolyP mixtures as a function of time at different temperatures. It is intended to use these results in order to gain insight into the chemical changes that occur during a real flammability test, i.e. UL-94.[3] As has been

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[3] UL-94 is one of the most important tests for assessing the fire safety hazards of plastics. In this test, a flame is applied twice to the lower end of a vertically suspended test specimen for 10 s. A rating is given depending on the time the material continues to burn. For the top rating, i.e. *V*-0, the mean afterflame time of five samples after 10 applications of the flame should not exceed 5 s. For a more detailed description of this method see Ref. [40].

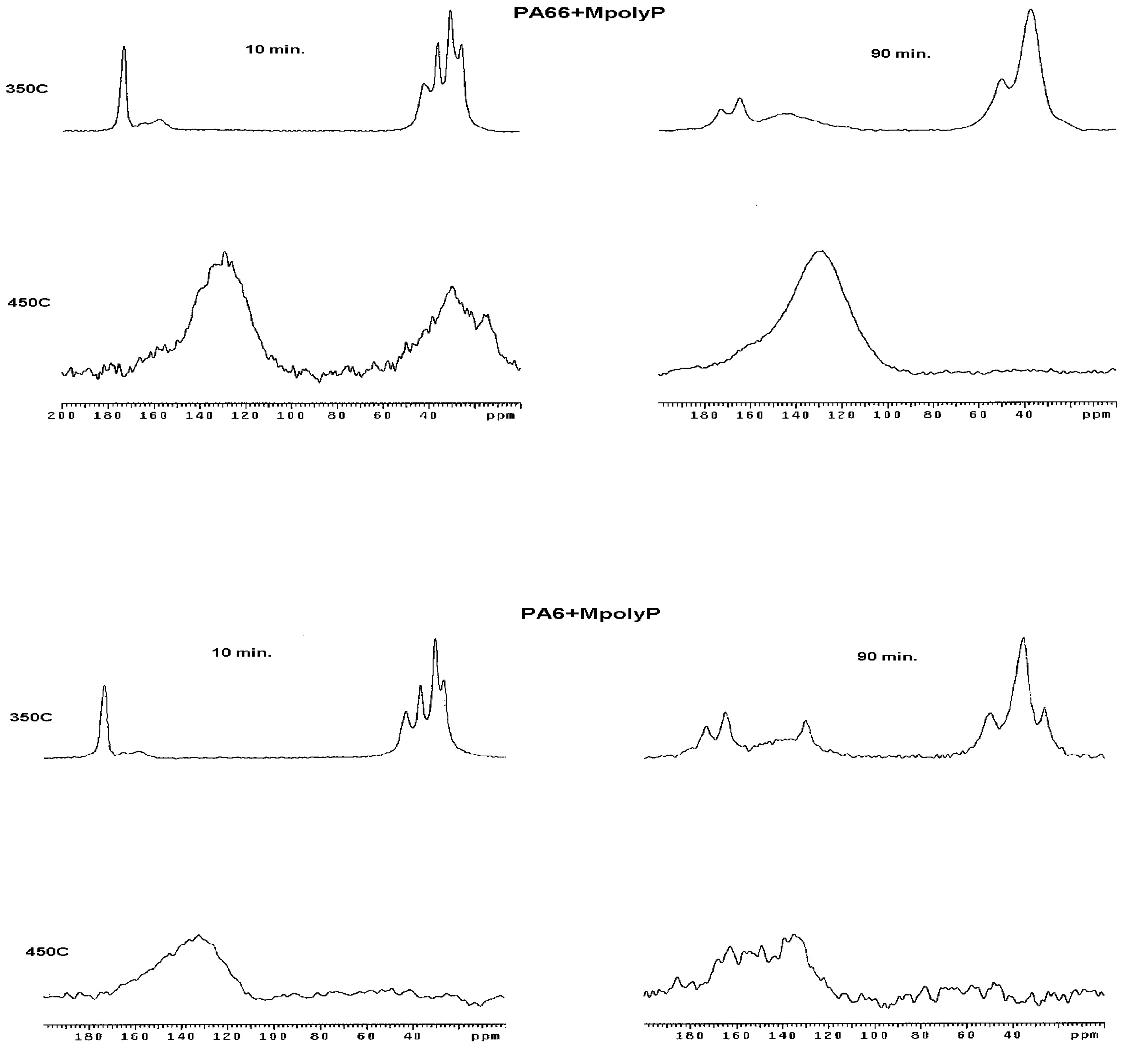

Fig. 6. ^{13}C NMR of solid residues obtained on heating PA66 + MpolyP and PA6 + MpolyP mixtures for 10 and 90 min at 350 and 450 °C.

mentioned above, the char structure which is formed, for example during the UL-94 test, protects the underlying polymeric structure from the action of heat and oxygen and inhibits the transfer of flammable materials into the gas phase. Both the physical and the chemical structure of the char are believed to be important to its action as a barrier layer. X-ray diffraction studies (not shown here) have revealed that the char material is completely amorphous, which is in accordance with the X-ray results conducted on samples thermally aged at 350 °C and above. Fig. 8 shows the ^{13}C and ^{31}P spectra of the char layer formed during the UL-94 test on a glass-filled PA66 compound containing MpolyP.

Most interestingly, the ^{13}C NMR spectrum of the char resembles in great detail the spectra of PA66 + MpolyP heated for 90 min at 350 °C. It appears that the char layer consists not of a carbonaceous aromatic structure resulting from highly degraded PA66 at all, as is commonly suggested in the literature [41,42], but of ‘moderate’ degradation products of PA66 similar to compounds which are formed on heating at temperatures close to 350 °C.

The agreement between the ^{31}P NMR spectra of the char and the thermally treated samples at 350 °C is less obvious, but the spectrum of the char layer still clearly shows the presence of phosphate, pyrophosphate and polyphosphate. HPLC experiments on hydrolyzed char samples have excluded the existence of a high level of melamine; the concentration of triazine rings was below 3%. This suggests that the source of these phosphates is not melamine phosphates such as MP, MPy and MpolyP, but phosphates, which are incorporated in the char by either chemical or physical interactions. It must further be noted that the ‘new peaks’ at −31 and −43 ppm (which are usually formed at 450 °C and are attributed to branched polyphosphates and an unknown phosphorus-containing compound) are absent from the ^{31}P NMR spectrum of the char. This suggests that the formation of these new products at elevated temperatures (≥450 °C) plays no part in the intumescence process during the UL-94 test and hence in the extinguishing of the flame.

It should be stressed that the good qualitative agreement observed between the oven experiments and UL-94 does not

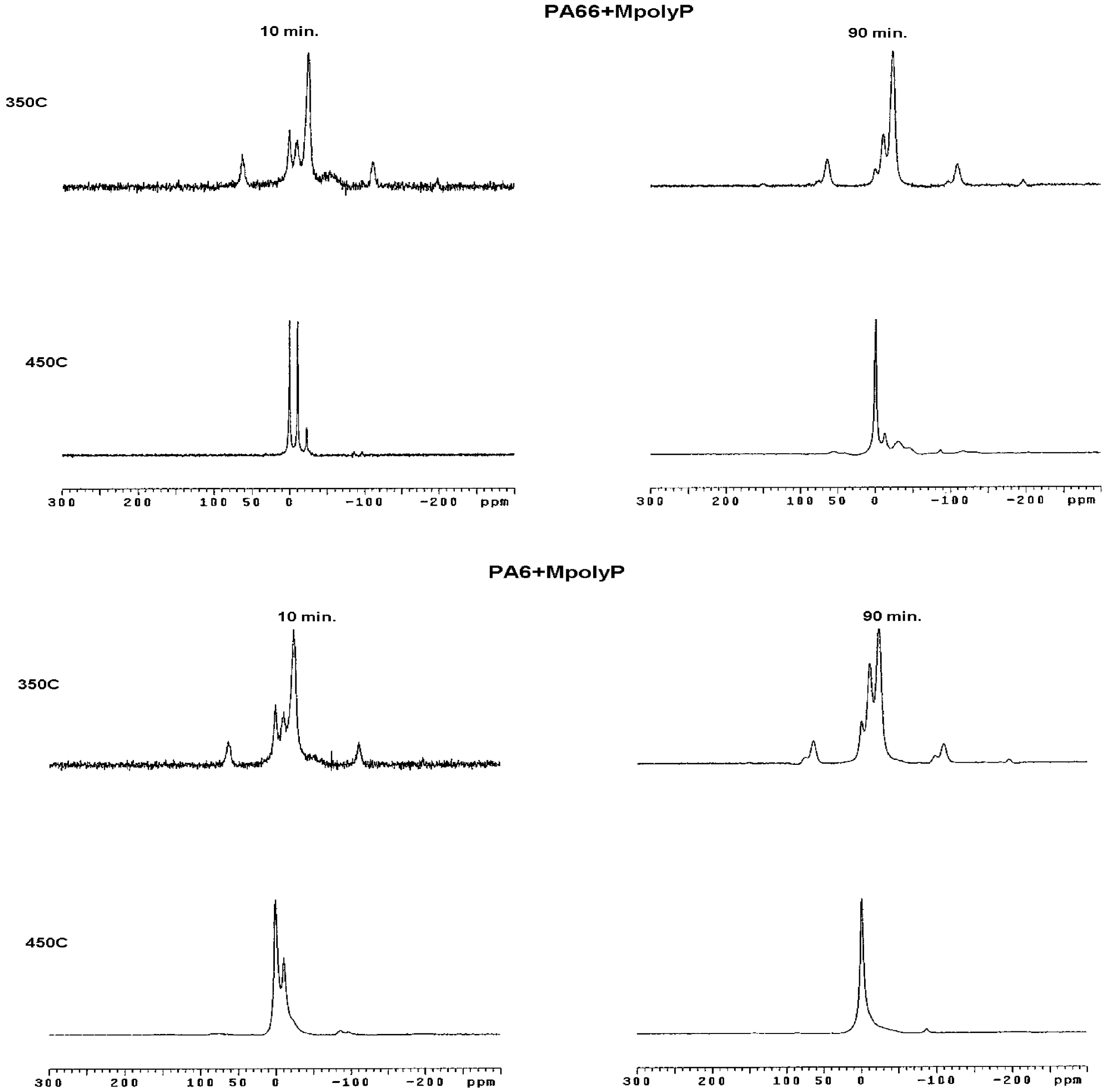

Fig. 7. ^{31}P NMR of solid residues obtained on heating PA66 + MpolyP and PA6 + MpolyP mixtures for 10 and 90 min at 350 and 450 °C.

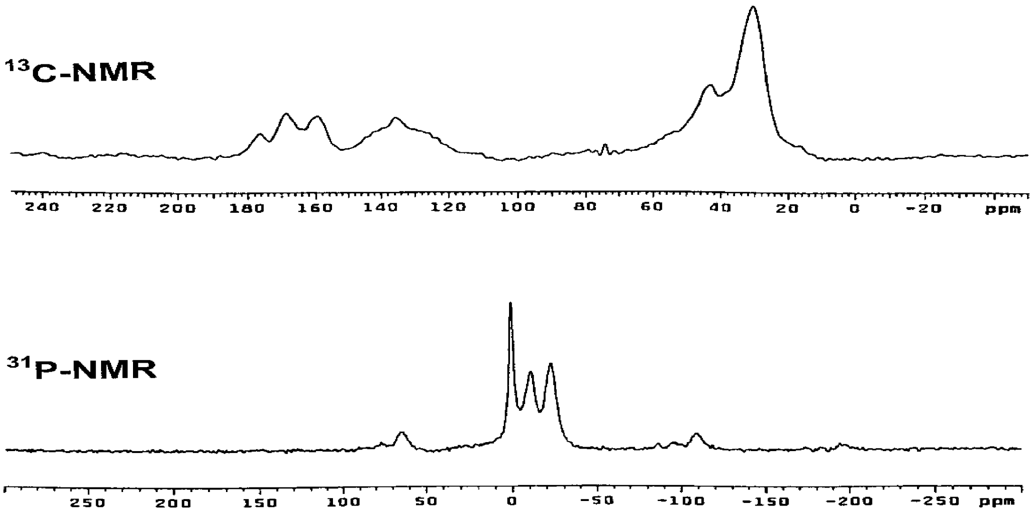

Fig. 8. ^{13}C and ^{31}P NMR spectra of char material produced during the UL-94 test on PA66 + MpolyP + Glass (50/25/25) compounds.

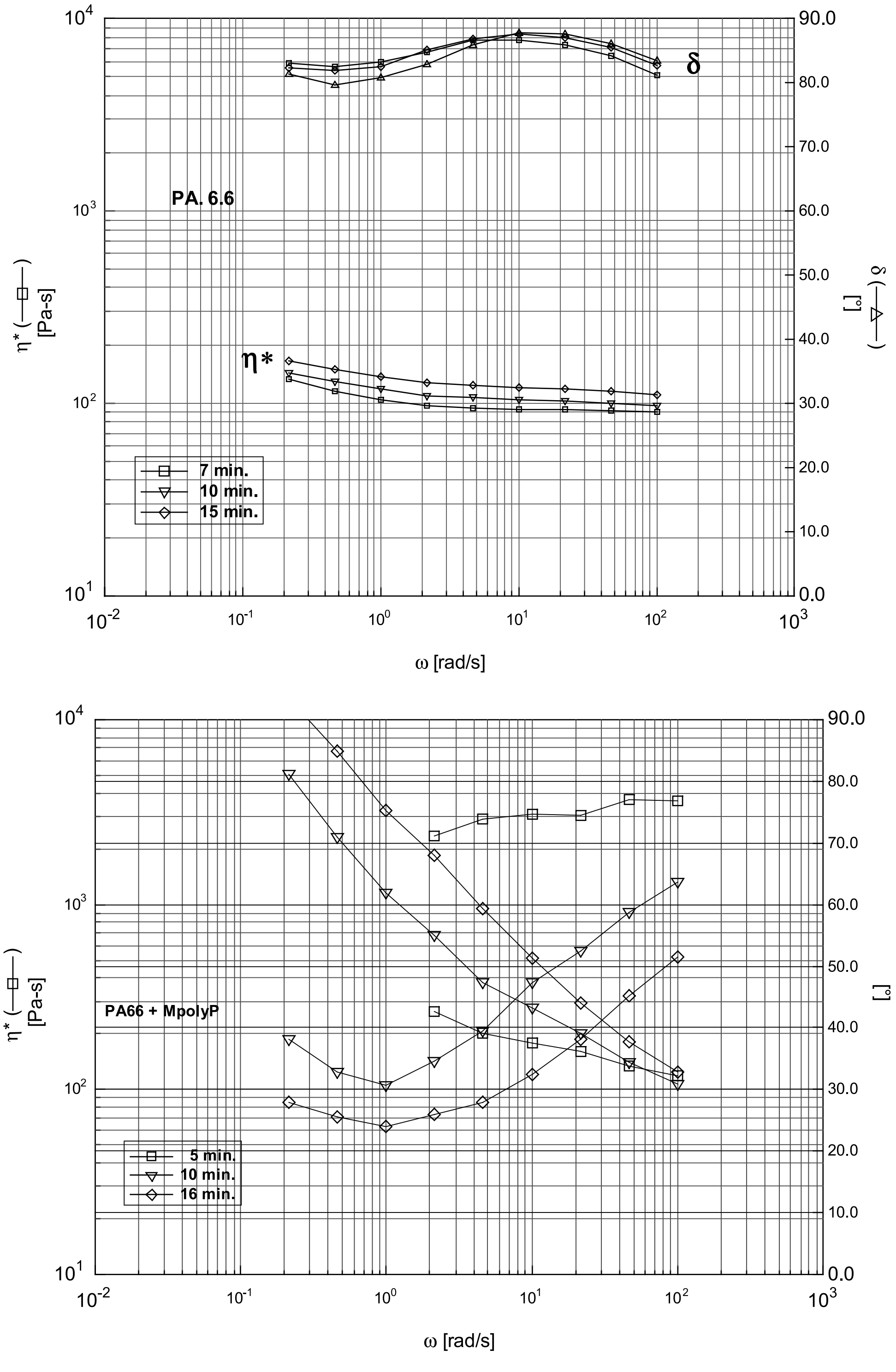

Fig. 9. Measurements of complex viscosity (η^*) and loss angle (δ) as a function of frequency at a temperature below 350 °C. The experiments were carried out on PA66 and PA6 with and without MpolyP after different heating times.

necessarily imply that the temperature of the char formed during this UL-94 test is around 350 °C. These results simply mean that the conditions in the oven experiments can, as far as the time and temperature are concerned, be selected in such a way as to match the chemical changes during the UL-94 test. This is an important observation which indicates that, at least for PA66, the oven experiments can in principle simulate the conditions of the UL-94 test.

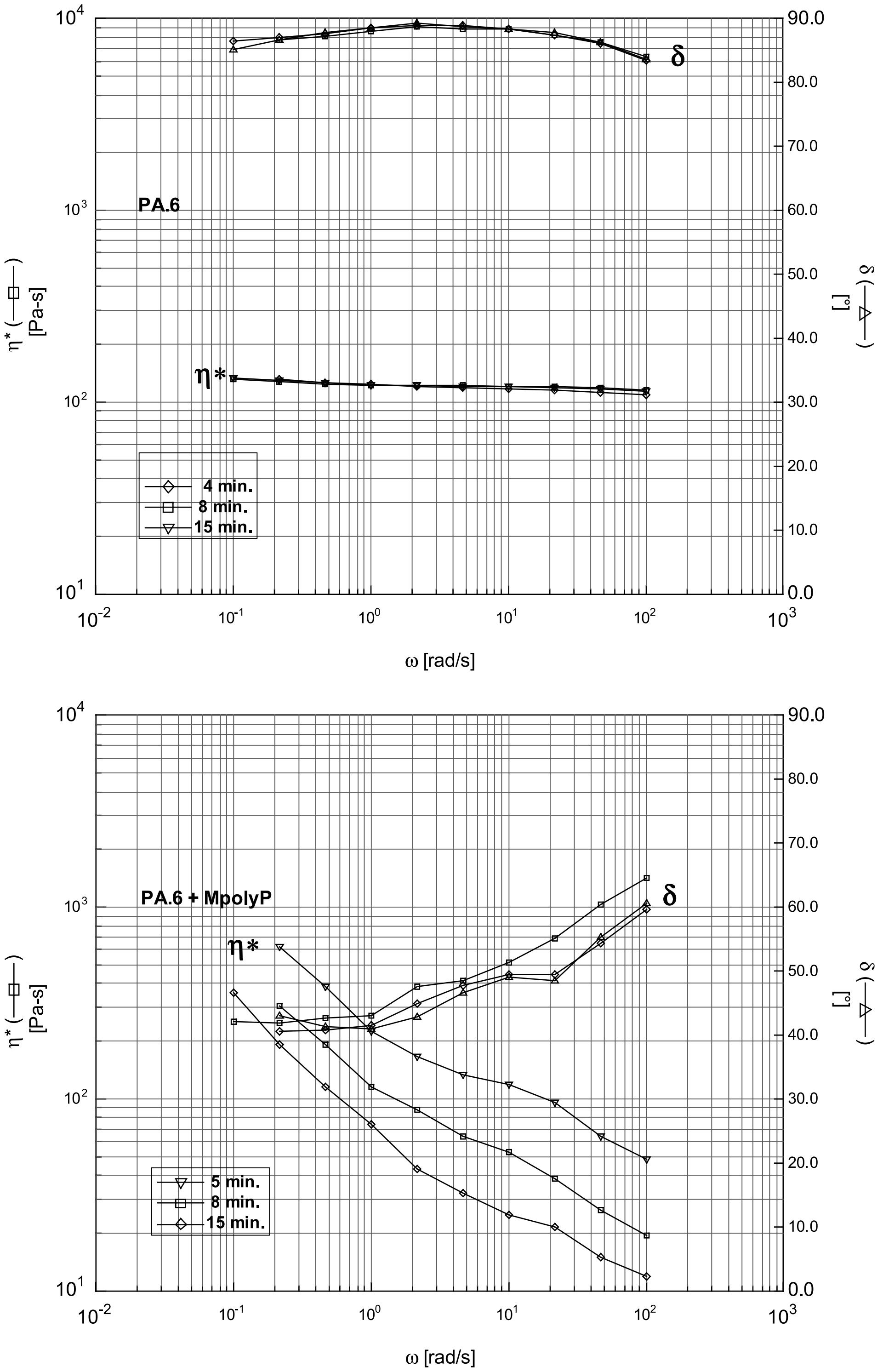

Fig. 9 (*continued*)

3.5. Rheological measurements

Char formation may effectively be regarded as a cross-linking process in which the formation of networks with a consequent increase in viscosity can be perfectly monitored by means of frequency-dependent rheological experiments. Fig. 9 shows the measurements of complex viscosity (η^*) and loss angle (δ) as a function of frequency, which were carried out on PA66 and PA6 both with and without MpolyP. The measurements were made in situ after different heating times at a temperature below 350 °C. Rheological experiments at higher temperatures were rendered possible by extreme foaming of the sample.

As can be seen in Fig. 9, virgin PA6 is very stable after 15 min of heating. Some increase in viscosity can be observed for PA66 as a function of heating time, and this is attributed to both post-condensation and cross-linking reactions. Similar conclusions can be drawn from the phase angle data analysis, which is not discussed here further. The change in melt viscosity due to post-condensation is characteristic of polyamides. The addition of MpolyP has a dramatic effect on the viscosity profile of both PA66 and PA6. In the case of PA6, a significant drop of η^* at high frequencies occurs within 15 min of heating, which points to polymer degradation. The behavior of η^* and δ at low frequencies indicates that some cross-linking also occurs during thermal treatment. It appears that the polymer degradation and the cross-linking reaction occur simultaneously during heating. Overall, however, it can be stated that the addition of MpolyP to PA6 results in an abrupt decrease in viscosity during thermal treatment of only 15 min of heating.

Almost the opposite behavior can be observed for PA66 + MpolyP. In this instance, as a result of the addition of MpolyP, cross-linking is by far the predominant reaction within the same time interval. The fact that the phase angle does not reach a plateau value and increases again at very low frequencies is indicative of network structures of a temporary character [43].

It is believed that the action of MpolyP as an FR is somehow reflected in the rheological measurements shown above. The addition of MpolyP to PA66 results in rapid cross-linking and increased viscosity. At elevated temperatures, i.e. during the combustion process, this effect will intensify, leading finally to the formation of char. By contrast, the addition of MpolyP to PA6 leads to an abrupt drop in viscosity owing to depolymerization. Again this effect should be more pronounced at higher temperatures.

4. Discussion

This report presents a series of results, which highlight some distinct differences between the thermal degradation of PA66 and that of PA6, both in the presence and in the absence of MpolyP. In this section, these results will be used to explain the differences in effectiveness of MpolyP as an FR in PA66 and in PA6. The role of the two chemical ingredients of MpolyP, i.e. melamine and phosphoric acid, during the combustion process will also be discussed.

As mentioned in the introduction, MpolyP acts by forming a barrier layer of char during the combustion process. This barrier layer is produced in the case of PA66 + MpolyP, but the combination PA6 + MpolyP produces no effective coherent layer of char at similar loading. Clearly, the capability for forming char is in the first instance related to the intrinsic thermal degradation behavior of polyamides. PA66, much more than PA6, is prone to cross-linking, a process which is believed to be essential for char formation. As observed in the rheological experiments, and as confirmed by, for example, solid-state NMR studies, the thermal stability of both polymers is influenced dramatically by the presence of MpolyP. However, in the case of PA66 + MpolyP, a significant cross-linking process, i.e. an increase in viscosity, is already observable at moderate temperatures, the addition of MpolyP to PA6 results in severe depolymerization, i.e. a decrease in viscosity. The depolymerization of PA6 under the influence of MpolyP compromises the flammability behavior for two reasons: (1) the ε-caprolactam which is released, functions as a fuel to sustain the flame, and (2) depolymerization depletes the supply of polymeric precursor which is necessary for char formation.

Phosphoric acid is believed to be the active center (catalyst) in MpolyP. This catalyst should be introduced into the polymer during the compounding step without affecting the backbone structure of the polymer. Since engineering plastics are often produced by polycondensation and are hence vulnerable to hydrolytic attack, the phosphoric acid should be neutralized before mixing with polymer. Complexing the phosphoric acid with melamine, leaving a salt, attempts to do this. If phosphoric acid is indeed the (only) active center, it must be released at a defined time/temperature during the combustion process if there is to be effective char formation. As a salt, the phosphoric acid remains at all times in equilibrium with melamine. On raising the temperature, this equilibrium will shift, and it can be distorted in the presence of competitive basic or acidic reagents. On heating to temperatures above 350 °C, it has been shown that MpolyP depolymerizes in the mixtures with both polyamides, but only in the case of PA66, it was possible to detect the presence of phosphoric acids. The various phosphoric acids are able to catalyze the formation of a char and at the same time act as a cross-linking agent between the degradation products of PA66. The melamine, which is released owing to salt dissociation will sublime or volatilize, depending on the physical state in the polymer matrix. The dilution of the flame with melamine may also contribute to extinguishing of the flame. It is, however, difficult to determine the exact contribution made by this mode of action, as compared with char formation. It is further observed from elemental analysis (not shown here), that all the phosphorus compounds remain in the char and do not enter the gas phase. Poisoning of the flame by phosphorus is therefore improbable. Polyamide + MpolyP samples, which had been subjected to thermal treatment in the rheometer were analyzed. Solid-state NMR detected no discernible chemical changes and certainly no ‘free’ phosphoric acids. There are two possible reasons for this: either the quantity of phosphoric acid released below 350 °C is below the detection threshold of solid-state NMR, or the MpolyP, as a salt, is also able to induce catalytic effects.

This is an important question, and calls for further investigation.

5. Conclusion

A study of the thermal degradation of MpolyP as a function of time at different temperatures has revealed that this FR depolymerizes above 350 °C in compounds with both PA66 and PA6. It has been established that phosphoric acid forms when PA66 + MpolyP mixtures are heated. The frequency-dependent rheological experiments demonstrated that MpolyP induces significant cross-linking in PA66 and leads to a dramatic depolymerization of PA6. These results are used to explain the performance of MpolyP as a char-forming (intumescent) FR in both PA66 and PA6. A comparison of the chemical structure of the char formed during a standard flammability test, UL-94, with the structures formed on heating the PA66 + MpolyP mixtures in an oven revealed some very interesting results. The chemical structure of UL-94 char appeared to agree rather well with the chemical structures formed in the oven after 90 min of heating at 350 °C. Against the general belief, the char structure is not fully aromatized but consists of mildly degraded polyamide species.

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