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Effect of Phosphorus-Nitrogen Intumescent Flame Retardant on Structure and Properties of Poly(propylene)

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Summary: Phosphorus-nitrogen intumescent product (R_{2000}) was filled into polypropylene (PP) as a flame retardant. The neat PP and flame-retarded PP blends were studied for their structural and mechanical properties after verification of the flame retardancy character of blends. In this paper, the influence of incorporation of different amount (5%, 10%, 15%, 20%, and 25%) of R_{2000} was studied. The flame retardancy is evaluated by limiting oxygen index (LOI) value, which is enhanced from 17.5 for pure PP to 22.7 for the blend comprising 15% intumescent product, phosphorus-nitrogen based (R_{2000}). The thermal degradation behaviour of the PP/R_{2000} blends was investigated using thermogravimetric analysis (TGA) under nitrogen (N_2) and oxygen (O_2) atmospheres. The influence of the R_{2000} on the PP crystallization was examined by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Further, the mechanical properties of the materials were studied by dynamic mechanical analysis (DMA). The incorporation of the flame retardant had no effect on the crystallization of the neat polymer and the mechanical properties of the materials remained unaffected.

Keywords: flame retardant; mechanical properties; poly(propylene); thermal properties; WAXS

Introduction

Polypropylene (PP) is a polymer of great importance in the industrial sector due to its low density, high water and chemical resistance, ease of process ability and being one of the most cost effective polymers available today. This combination of properties rates the material suitable for the production of a wide range of articles from house wares and industrial mouldings to fibre fabrics and transparent packing film. However, thermal resistance and flammability properties of the polymer are not enough satisfactory.[1] Like most of the synthetic polymers, PP is inflammable, and may therefore be hazardous when placed close to the open flame. It may also enhance the fire propagation due to its tendency to drip when hot. Therefore, the addition of a flame retardant is an essential requirement if we wish to achieve a PP based composite with good flame resistance. Various flame retardancy combinations can be used to delay the burning process of organic materials. These compounds include halogenous, mineral hydroxides[2,3] and organophosphorus compounds.[4,5] More recently, polymeric materials comprising inert loads like magnesium silicate or calcium carbonate,[6] and the nanocomposite based on montmorillonite (layered silicate) or carbon nanotubes[7,8] and the intumescent system[9–12] were studied in the literature. Their flame retardant effects were revealed.

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Traditionally, halogen containing compound, alone or in combination with antimony trioxide, are one of the main flame retardants of PP.[13] Some halogen containing flame retarded PP systems may produce large amounts of smoke and toxic gas on burning, and thus some of them have been banned by the European Commission (it will be forbidden by the REACH (Registration, Evaluation, Authorisation and Restriction of chemicals) reglementation. Regulation REACH will enter into force on the 1st of June 2007. (The obligation to register applies from the 1st of June 2008). As a result, most recent studies focus on the halogen-free flame retardant systems. They offer polymer flame retardancy through modifying the decomposition mode. As halogen-free products, the intumescent flame retardant Reogard2000 is expected to be used and effective in PP. The Reogard2000 is free from ‘‘milky'' water baths during extrusion and the production of ammonia odour, which can be a concern with other competitive intumescent technologies. Besides being halogen free, the intumescent flame retardant systems have the advantages of low toxicity, low corrosion and absence of melt dropping.[12,14,15]

The mechanism of fire retardance involved in intumescent systems comprising Reogard2000 can be described as follows: First, the charred layers are produced by the dehydratation of carbonizing agent in presence of acid catalyst which is simultaneously expanded by the inert gas released from the blowing agent upon heating. The non-flammable and multi-cellular charred layer thus formed almost instantly starts to provide an efficient shielding and insulation for the underlying polymeric matrix against the direct contact with the flame and oxygen and also against the heat transfer. The underlying polymeric matrix is thus effectively protected.

The use of additives is a common way to modify polypropylene properties. Also additions of these compounds to the polymer result in increasing or decreasing the physical and mechanical properties of the polymer.[16] Furthermore recently, Samyn et al.[17] have claimed that the efficiency of intumescent flame retardant can be reached at reasonable loading (around 25 wt. %) without compromising the other properties of the matrix polymer. Therefore, we study different blend of PP and Reogard2000 over a wide composition range (PP/Reogard2000 weight ratio: 95/5, 90/10, 85/15, 80/20 and 75/25). In this study, we focus on the measurement of the intumescent flame retardant activity of Reogard2000 and on the control of the properties of the blends. Some authors[11,18] report the poor compatibility of PP and intumescent fire retardant, consequently it is nearly impossible to prepare PP/intumescent fire retardant blends with good mechanical properties. Ma et al.[11] show a drastic decreasing of mechanical properties of PP with the addition of the intumescent fire retardant. The aim of this work is to study the effect of Reogard2000 on structural and mechanical properties of PP on PP/R_{2000} blends after verification of the fire retardant activity of Reogard2000.

Experimental Part

Materials and Sample Preparation

Isotactic polypropylene (iPP) ($Mw = 280.000 g.mol^{-1}$) containing various additives such as $CaCO_3$ and coloring agents, was purchased from Sasol Polymer Technology Centre, RSA. Reogard2000, the commercial product of Great Lakes Chemical Corporation, is based on phosphorus (of sodium, magnesium and aluminium), nitrogen, and aluminosilicates. The binary blends of the polymer with various amount of Reogard2000 (R_{2000}) were prepared using a 35 mm co-rotating ZSK 25 twin-screw extruder. The temperature of the extruder was 220 °C, the rotation speed of the screws was 150 rpm and the injection pressure: 100-120 Mpa. The R_{2000} powder was fed to the polymer melt by a side feeder situated directly behind the melting zone. The extruded material was cooled directly at the exit of the extruder in water and the material strings were subsequently pallettised. The PP/R_{2000} blends containing 0, 5, 10, 15, 20 and 25 wt.-% of R_{2000} are designated as neat PP, 95%PP/5%R_{2000}, 90%PP/10%R_{2000}, 85%PP/15%R_{2000}, 80%PP/20%R_{2000} and 75%PP/25%R_{2000} blends. The materials for the study were compression moulded at 220 °C.

Flame Retardant Analysis

Limiting Oxygen Index (LOI)

Samples shaped as rods or strips with dimensions 12.5mmx6.5mmx3mm were enclosed in an open-vent chamber in a mixed oxygen/nitrogen environment. The sample was ignited at its upper end with a hydrogen flame i.e. the sample burnt from the top downwards. The atmospheric composition that permits steady burning was determined. The limiting oxygen index (LOI) was defined as the minimum fraction of oxygen in the gas mixture that will sustain burning for 3min or 2inches, (whichever comes first). The system was calibrated using a standard sample with a defined LOI value (ASTM D-2863-77). It should be reminded that it is incorrect to assume that material with an oxygen index over 21% can not burn in practice despite the fact that the air contains only 20% oxygen in average.

Thermogravimetric Analysis (TGA)

The thermogravimetric analysis was performed on a Netzsch TG-209 instrument thermal analyzer with a heating rate of 10 °C/min in the temperature range of 20–700 °C and a dynamic gas flow of 20 ml/min. Analysis were done under 100% N_2 gaz flow or 100% 0_2 gaz flow. The amount of the sample used is 10mg. Based on the loss of weight relative to the original sample as function of temperature, the first derivative data, i.e. DTG data were obtained.

Structural and Mechanical Analysis

Attenuated Total Reflection Infrared (ATR-IR) Spectroscopy

Fourier transform infrared (FTIR) spectroscopic analysis was carried out under ambient conditions using a Perking-Elmer spectrophotometer (Avatar 360, USA) in the spectral range from 4000 to 600 cm^{-1} after collecting an average of 32 scans. The instrument provided spectral resolution of ± 4 cm^{-1}.

Wide Angle X-Ray Diffraction (WAXD)

WAXD analysis was conducted with a Bruker D8 diffractometer (radiation Co Kα, $\lambda = 1.78897$ Å, reflection mode) at room temperature (20 °C). The 2θ range is from 2° to 40° with a scanning rate of 1 °C/min and a step of 0.05°.

Differential Scanning Calorimetry (DSC)

A TA Q100 DSC with nitrogen as purge gas was used to investigate the temperature of vitreous transition and crystallization behaviour of neat PP and PP/R_{2000} blends. The differential scanning calorimeter was calibrated with Indium standard. Samples of 5 ± 0.1mg were used in the tests. They were sealed in aluminium pans and heated up to 180 °C at the rate of 10 °C/min to record the melting behaviour. The samples were held at that temperature in order to erase any thermal history.

The melting temperatures (T_m) of the samples were determined from the maxima of the fusion peaks. The crystallinity (Xc) of the PP/R_{2000}blends was calculated using the equation $Xc = \Delta Hi/(xi.\Delta Hi_m)$ where ΔHi is the enthalpy of fusion directly obtained from the DSC measurement, and xi is the mass fraction of PP homopolymer in the blends. ΔHi_m, the enthalpy of fusion of 100% crystalline polymer, is 209 J/g of neat PP.[19]

Dynamic Mechanical Analysis (DMA)

The dynamic mechanical properties of PP/R_{2000} blends were investigated with TA Q800 DMA operated in the tensile mode to study the dynamic mechanical properties of the binary blends. The test specimens had the dimensions of approximately 50mmx13mmx2mm. The exact dimensions of each sample were measured prior to the DMA investigation. After clamping the sample to fudge tightness, a constant tensile force was applied to the sample. The experiment was performed in the

Table 1.
LOI value of PP/R2000 blends.

Sample	LOI value ± 0.2
95%PP/5% R_{2000}	18.2
90%PP/10% R_{2000}	18.5
85%PP/15% R_{2000}	22.7
80%PP/20% R_{2000}	22.7
75%PP/25% R_{2000}	26.7

temperature range from −100 °C to +150 °C at 1Hz with a stretching ratio of 0.1% and heating rate of 0.3 °C/min.

Results and Discussion

Flame Retardant Investigations

The investigation of limiting oxygen index (LOI) is commonly employed for the determination of the flammability performance of the plastics used in coverings and linings, and in cables as well as in wires for the construction industries. Also in this work, the flammability of PP/R_{2000} blends was studied by LOI test. The LOI values are reported in Table 1.

It was found that the neat PP used in this work has a LOI value of 17–17.5. The results further indicate that variation of R_{2000} has a significant effect on LOI value. The LOI increases from 17.5 (for neat PP) up to 26.7 (for 75%PP/25% R_{2000}). It is noteworthy that above 15% of R_{2000} in the blends, the LOI is higher than the concentration of oxygen in the air.

The thermal behaviour of the blends was studied by means of thermogravimetric analysis (TGA) both under inert and oxidizing atmosphere. TGA and derivative thermogravimetry (DTG) of neat PP and PP/R_{2000} blends under nitrogen and oxygen air are illustrated in Figures 1–4. The temperature at which 5 wt % weight loss occurs is defined as the initial decomposition temperature and report in Tables 2 and 3. The TG curves obtained under inert atmosphere are presented in Figure 1.

Under an inert atmosphere (N_2), samples were found to undergo one-step degradation process at 440 °C. The degradation of all the samples appeared to begin at different temperature depending on the composition of the PP/R_{2000} blends (see Table 2).

The addition of R_{2000} induced the initiation of degradation process at lower temperature (313 °C for 75%PP/25%R_{2000} against 386 °C for neat PP); and the amount of Reogard2000 was found to have an effect in the thermal degradation behaviour. Figure 1 shows that R_{2000} is degraded just before neat PP inducing a shift in the temperature degradation of neat PP ($\Delta T = 73 \pm 4$ °C). The temperature is shifted toward the higher temperature because a protective char layer at the beginning of the

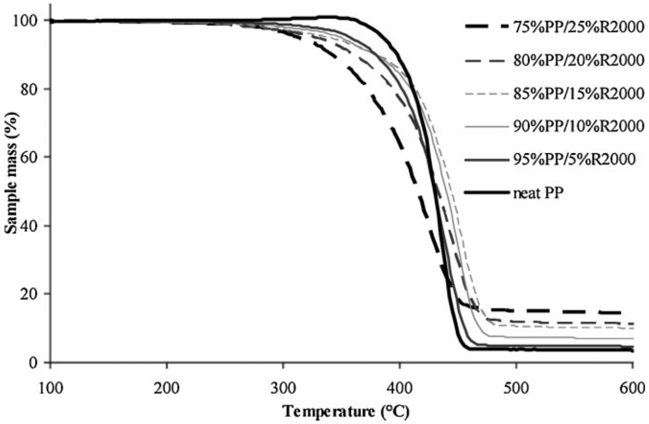

Figure 1.
Thermogravimetric curves obtained on neat PP and PP/R2000 blends under inert atmosphere.

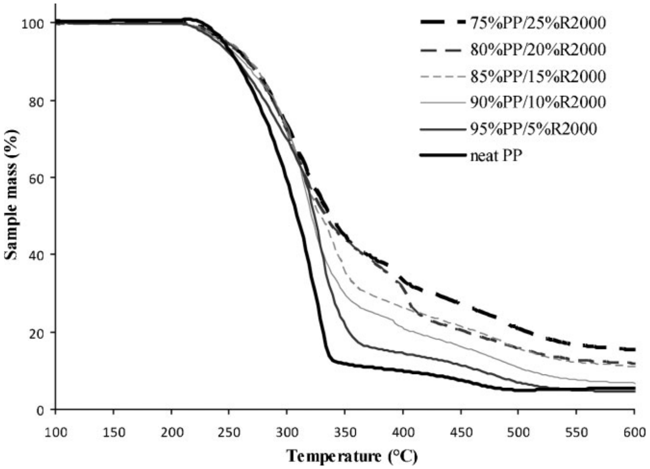

Figure 2.
Thermogravimetric curves obtained on neat PP and PP/R_{2000} blends under oxidizing atmosphere.

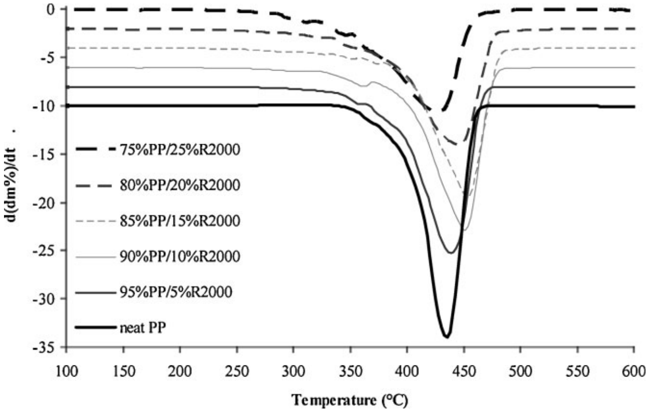

Figure 3.
Derivative thermogravimetric curves obtained on blends PP/R_{2000} and neat PP under N_2 atmosphere.

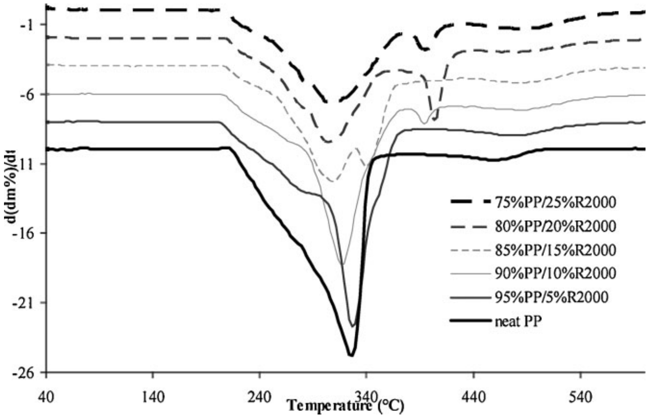

Figure 4.
Derivative thermogravimetric curves obtained on blends PP/R_{2000} and neat PP under O_2 atmosphere.

Table 2.
Thermal degradation of PP and PP/R_{2000} blends under inert atmosphere.

Sample	$T_{5\%}$ (°C) ±4 °C	T_{max} (°C) ±4 °C	Char residue at 600 °C ± 2%
Neat PP	386	436	3%
95%PP/5% R_{2000}	357	441	5%
90%PP/10% R_{2000}	350	449	7%
85%PP/15% R_{2000}	347	445	10%
80%PP/20% R_{2000}	328	448	11%
75%PP/25% R_{2000}	313	430	14%

Table 3.
Thermal degradation of PP and PP/R2000 blends under oxidizing atmosphere.

Sample	$T_{5\%}$ (°C) ±4 °C	T_{max} (°C) ±4 °C	Char residue at 600 °C± 2%
Neat PP	245	326	5%
95%PP/5% R_{2000}	240	329	5%
90%PP/10% R_{2000}	244	319	7%
85%PP/15% R_{2000}	249	310	11%
80%PP/20% R_{2000}	249	308	12%
75%PP/25% R_{2000}	249	309	15%

degradation is created. The residue at 600 °C is accounted for by the R_{2000} content of the blend.

Figure 2 shows thermogravimetric curves for the investigated samples under an oxidizing atmosphere (i.e. in presence of air or oxygen).

On heating in the presence of oxygen, neat PP undergoes a radical peroxidation chain process starting at relatively low temperature ($T = 225\,°C$).[20] It is well known that neat PP volatilization begins at a lower temperature in air than under nitrogen environment ($T_{5\%} = 244\,°C$ in O_2 and 386 °C in nitrogen). Under this condition, the start of degradation for all samples appeared to begin at about the same temperature, i. e. around 220 °C (Table 3).

So under nitrogen environment, the addition of R_{2000} induces a perturbation of stability, but this perturbation does not appear under oxygen environment. The rate of the degradation process can be obtained directly from the first derivative of the mass loss versus temperature curve (see Figures 3 and 4).

Figure 3 shows that the rate of degradation decreases with the addition of R_{2000} under inert atmosphere. Under oxidising atmosphere, on Figure 4, we observe the same effect; furthermore the degradation appears in two steps for high level of R_{2000} (higher than 15%). To resume, the more the amount of R_{2000} in the blend, the lower will be the rate of degradation. This evolution also demonstrates a decrease in the rate of production of the volatile products and so a decrease in the heat production. For the production of heat, it is necessary to have a combustible material (i.e. PP), a comburant (O_2) and the energy (i.e. heat). By increasing the production of heat, the degradation, afterwards oxidations, then the flame were counter. The introduction of more and more R_{2000} causes the formation of less flame. For the blends studied in this work, R_{2000} has been shown to play an efficient protective role against the oxygen initiated of polymer volatilization.

Study of Structural and Mechanical Properties

Figure 5 shows the infrared spectra of neat R_{2000}, neat PP and PP/R_{2000} blends.

The intensities of the peaks at 2840–2953 cm^{-1} are assigned to the CH_2 or CH_3 asymmetric and symmetric vibrations, and 1374 and 1455 cm^{-1} are assigned to the CH_2 or CH_3 deformation vibration of aliphatic groups. These absorption bands, characteristic to CH_3 and CH_2 groups, displayed no

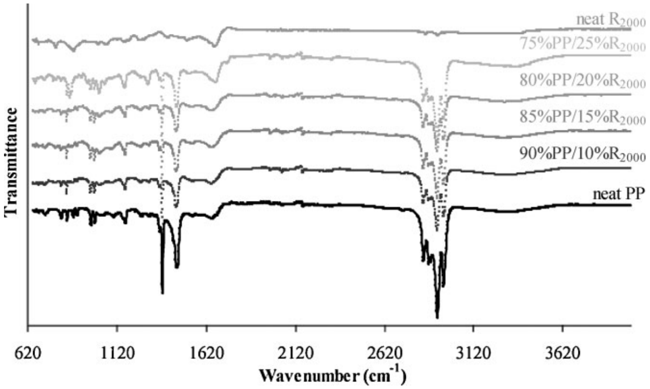

Figure 5.
Infrared spectra of PP/R_{2000} blends. Curves have been shifted for clarity.

modification in intensity and appearance. Accordingly, R_{2000} displays any effect on chemical structure of PP.

It is well known that isotactic polypropylene (iPP) can exist in several crystal polymorphisms depending on crystallization conditions as well as on isotacticity. So far four crystalline forms have been described.[21,22] The monoclinic α-modification with cross-hatched lamellae structure is predominantly formed during slow cooling from the melt. Higher content of trigonal (sometimes referred to as hexagonal) β-modification can be obtained during fast cooling (quenching) of the melt, directional crystallization through a thermal gradient, under shearing conditions or using specific nucleating agents.[23] Among the crystal modifications of iPP, the γ- or triclinic form is the least common one, which is observed in low molecular weight samples and its formation is promoted by hydrostatic pressures.[21,24] In this work, WAXD analysis was performed to investigate the effect of R_{2000} on the crystalline structure of PP. Figure 6 shows the X-ray diffractograms in which the intensity is plotted as a function of scattering angle 2θ.

One can see that six most intense WAXD reflections (see also Table 4) occur at 2θ angles of 16.4°, 18.4°, 19.8°, 20.8°, 21.5° and 23.6°corresponding respectively to the γ(111) and α(110), γ(008) and α(040), α(130), γ(117), γ(202) and α(111), and

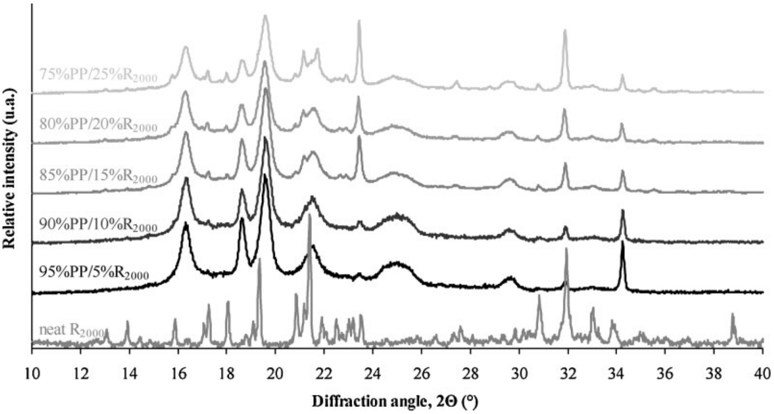

Figure 6.
XRD spectra of PP/R2000 blends and neat R2000. Curves have been shifted for clarity.

Table 4.
Correspondence between most intense WAXD reflections at 2Θ angles and lattices planes.

Diffraction angle, 2Θ (°)	γ triclinic structure	α monoclinic structure
16,4	γ (111)	α (110)
18,4	γ (008)	α (040)
19,8		α (130)
20,8	γ (117)	
21,5	γ (202)	α (111)
23,6	γ (026)	α (041)

Table 5.
Non isothermal crystallisation parameters for neat PP and PP/R2000 blends.

Sample	*Tm* (°C)	Δ*Hi* (J/g(PP content))	Xc (%)
Neat PP	165	83	40
95%PP/5% R_{2000}	164	83	40
90%PP/10% R_{2000}	163	86	41
85%PP/15% R_{2000}	163	82	40
80%PP/20% R_{2000}	164	86	41
75%PP/25% R_{2000}	164	87	41

γ(026) and α(041) lattices planes of the γ-triclinic crystalline structure and α-monoclinic crystalline structure of PP.

One can also observe a peak at $2\theta = 32°$ appears for the blend which is absent for the neat PP and corresponds to the R_{2000}. So, the crystalline nature of the PP is not modified by the introduction of R_{2000}.

The influence of the presence of the R_{2000} on the crystallisation and melting behaviour of the PP polymer was also evaluated by means of DSC analysis. In Figure 7, different curves are presented concerning the melting of pure R_{2000}, neat PP, and PP/ R_{2000} blends.

From this figure, it was deduced that the R_{2000} does not possess any thermal transition within the temperature range. Furthermore, the PP and PP/R_{2000} blends show a melting endothermic peak around 164 °C. The melting temperature, Tm, heat of melting, ΔHi, and the calculated degree of crystallinity, Xc, are reported in the Table 5.

Obviously, no significant changes in the full width of the melting peaks or the melting temperatures are detected among the samples. For all blends, values obtained after normalisation at the rate of PP are constant; one can observe a constant crystallinity (about 40%) which indicates that the addition of R_{2000} has no obvious effect on the crystallinity of PP. The XRD and DSC analyses confirmed that the R_{2000} has no significant influence on the crystalline morphology of the PP. And also Both, DSC and WAXD results suggest a constant degree of crystallinity in the samples. These results explain the repartition of R_{2000} in the blend. It seems that R_{2000} is located in the amorphous part and not in the crystalline part which was influenced by a foreign

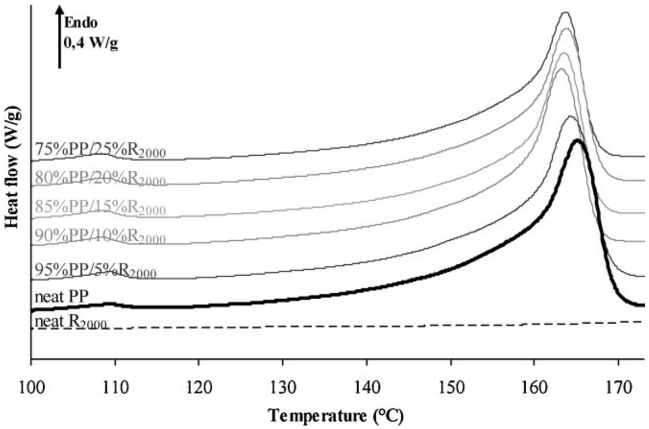

Figure 7.
DSC second heating of neat PP, neat R2000 and PP/R2000. Curves have been shifted for clarity.

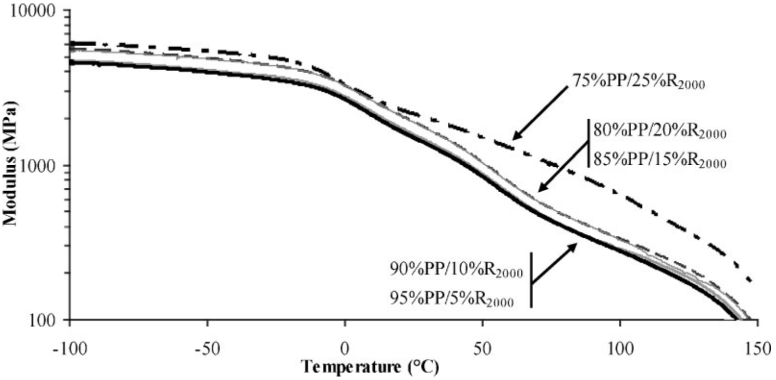

Figure 8.
Storage modulus versus temperature, as a function of R_{2000} content.

particle in it. In addition, R_{2000} have not the effect of nuclei centre.

By means of DSC measurement, no significant thermal transition was observed in the temperature ranges studied (from −50 °C to 180 °C) which suggests a restricted mobility of PP. However, this is not a surprising result. Indeed, the detection of the glass transition phenomena by means of DSC requires that there exists a large enough value of ΔCp (Cp_{liquid}-Cp_{glass}) at the glass transition. Since DSC could not offer quantitative results on the glass transition behaviour of the samples, DMA measurements were performed. The dynamic mechanical spectra in Figure 8 show the α-transition of the PP ($T\alpha_{PP}$) at the low temperature region.

The results are similar for all the PP/R_{2000} blends. It can be noticed that the decreasing modulus at −20 °C is not modified independent of the R_{2000} content. In contrary, the decreasing modulus at ~ +20 °C is modified with R_{2000} content. The Figure 9 highlights the evolution of modulus for the PP/R_{2000} blends.

We observe for low temperatures (−50 °C and 0 °C), no evolution of the modulus with the rate of R_{2000}. Nevertheless, for higher temperature (50 °C and 100 °C) we observe a variation of the modulus. A great modification is observed for 25%PP/75%R_{2000} blend. This evolution is in accordance with the WAXS results (for memory, the crystalline nature of the PP is not modified by the introduction of R_{2000});

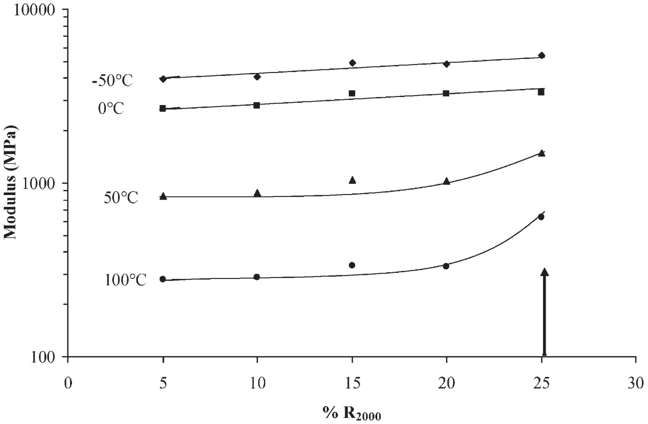

Figure 9.
Storage modulus versus R2000 content, as a function of temperature (−50 °C, 0 °C, 50 °C and 100 °C).

the R_{2000} is localised in the amorphous part of the PP.

Conclusion

The thermal behaviour of PP was improved by introducing a phosphorus-nitrogen intumescent flame retardant (R_{2000}), which was studied by LOI and TGA. The limiting oxygen index (LOI) was found to increase with increasing R_{2000} content, which was even higher than for atmospheric oxygen for the blends containing 15% of R_{2000}. According to the analysis of the results of experiments, it was evident that neat PP had low resistance to combustion. In the blends studied, R_{2000} is found to play an efficient protective role against oxygen initiated polymer volatilization. In this work, we have studied the effect of R_{2000} on the thermal and the mechanical properties of polypropylene where the R_{2000} used as intumescent product. By means of FT-IR, WAXD, DSC measurements, it has been shown that the R_{2000} has no effect on the chemical and crystalline structure of PP. This lack of influence on the crystalline phase of PP shows that the R_{2000} is located in the amorphous phase of the PP. In addition, for a high percentage of R_{2000}, mechanical properties of the amorphous phase of PP are modified. Consequently the optimal concentration to avoid any modification of PP properties is closed to 15% of Reogard2000 (R_{2000}).

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