

# Peculiarities of mechanical response of heavily filled polypropylene composites

## Part II *Dynamic mechanical moduli*

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Temperature dependences of dynamic moduli of polypropylene filled with flame retardant  $Mg(OH)_2$  or with  $CaCO_3$  were investigated. The filler content varied from 0 to 50 vol% and both storage ( $G'$ ) and loss ( $G''$ ) shear moduli were measured from +50 to +300 °C at frequencies 1 and 90 Hz. The influence of the filler particle shape was dominant for the origin of the physical network. Chemical adhesion aid was superfluous in composites with subcritical particle size. Two step decrease of  $G'$  and two peaks on  $G''$  temperature dependences were observed above the critical filler concentration. The explanation of this phenomenon was based on the proposal that polypropylene immobilized on the filler surface creates a new continuous phase, while primary polypropylene exists only in separated domains. Destruction of the physical network was explained using results of thermoanalysis, providing the catalytic effect of  $Mg(OH)_2$  on the thermal oxidation of polypropylene in the interlayer above 240 °C.

### 1. Introduction

The existence of the interlayer near the filler surface is a significant peculiarity which rigid fillers incorporate in the polymer matrix [1]. This interlayer is commonly considered as a thin layer of the matrix with morphology and consequent physical properties different from the matrix bulk [2]. This interlayer is created in the course of the composite preparation as a consequence of the change of thermodynamic conditions near the solid surface. Many attempts have been made to evaluate the dependence of the interlayer thickness on the filler volume fraction, shape, size and surface activity of the filler [3–6]. The evaluation of  $t_{eff}$  from the analysis of the mechanical response depends significantly on the investigated property [7, 8]. Probably this is the consequence of the diffusive character of the interlayer–matrix bulk interface. Commonly accepted interlayer thickness is from 1 to 200 nm [9, 10].

In our previous papers [11, 12], we have reported the influence of the interparticle interactions on the isothermal elastic moduli of polypropylene (PP) filled with  $CaCO_3$  or with  $Mg(OH)_2$ . A hypothesis has been proposed to describe the origin of the network of physically bonded filler particles. The bond was suggested to be caused by the interpenetration of interlayers adsorbed on the surface of neighbouring particles. Hence, the presumption of a continuous immobilized phase was considered.

The objective of this paper is to analyse the temperature dependences of  $G'$  and  $G''$  moduli of PP filled

with  $CaCO_3$  or with  $Mg(OH)_2$ . We have concentrated on explaining the relation between concentration dependence of the composite morphology and viscoelastic moduli. The probable processes causing the network destruction are also discussed.

### 2. Experimental procedure

Commercial polypropylene Mosten 58.412 (Chemopetrol, Czechoslovakia), melt index 4 g per 10 min (230 °C, 21.6 N) was used as a matrix. Maleated PP (MPP) was used as an adhesion agent. MPP containing 0.752 of wt% of chemically bonded  $-COOH$  groups was prepared by controlled degradation of iPP in the presence of initiator (dibenzoyl peroxide) and maleic anhydride in a Werner-Pfleiderer ZSK-56 twin screw extruder. PP and MPP were mixed to achieve the concentration of carboxyl groups in the matrix required for the strength of adhesion equal to the cohesion strength of PP [13].

Calcium carbonate Durcal 2 (Omya, Switzerland), magnesium hydroxide Kisuma 5B and Kisuma 7B (Kyowa, Japan) were used as fillers (Table I).  $CaCO_3$  had irregular, approximately spherical particles and  $Mg(OH)_2$  was either in the form of platelets (Kisuma 5B) or microneedles (Kisuma 7B). Further experimental details have been published elsewhere [11, 12]. The measurements were carried out on the dynamic mechanical thermal analyser with forced oscillations (PL Thermal Sciences, UK) over the temperature

TABLE I Characteristics of the fillers

Chemical nature	Grade	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Density (g cm <sup>-3</sup> )	Young's modulus* <i>E</i> (GPa)	Shear modulus* <i>G</i> (GPa)	Average aspect ratio
CaCO <sub>3</sub>	Durcal 2	3.3	2.71	72	28	Irregular, approximately spherical <i>p</i> 1
Mg(OH) <sub>2</sub>	Kisuma 5B	7	2.36	64	25	Hexagonal lamellae <i>p</i> 5
	Reachim	6.8	2.36	64	25	Hexagonal lamellae <i>p</i> 5
	Kisuma 7B	37	2.36	64	25	Needles <i>p</i> 25

\* The values for *E* and *G* moduli of Mg(OH) were estimated considering the relation between elastic moduli and hardness of materials.

interval from 50 to 300 °C at 1 and 90 Hz in pure shear.

### 3. Results and discussion

#### 3.1. The effect of filler content and particle shape

##### 3.1.1. Storage *G'* modulus

The shear storage *G'* modulus increased and loss *G''* modulus was reduced, increasing the filler content (Figs 1 and 2). More thorough insight reveals that there exist three distinct temperature regions: 50 < *T* < 160 °C; 160 < *T* < 240 °C; and *T* > 240 °C.

**3.1.1.1. Temperature region 50 < *T* < 160 °C.** *G'* modulus decreased with increasing temperature for any concentration of the fillers used. The rate of the material softening was controlled by the increasing molecular mobility of amorphous PP in the bulk. The magnitude of *G'* modulus depends on the filler content, particle shape and on the filler-specific surface area. Thus, needle shaped Mg(OH)<sub>2</sub> has reinforced PP more than other fillers investigated. Except for the effect of the particle shape, *G'* modulus increases with the increasing filler-specific surface area at the same composition. This is probably caused by the greater amount of the immobilized matrix which is more rigid, as compared to PP in the bulk, due to the strongly hindered molecular mobility [14].

**3.1.1.2. Temperature region 160 < *T* < 240 °C.** Melting of the crystalline phase in PP occurred, which released further molecular mobility. Consequently, *G'* modulus steeply falls above 160 °C (DSC, determined melting point of the used PP grade, was 164 °C). The depth of this fall was reduced with increasing filler content, or with increasing the filler specific surface area. However at the same conditions this depth was determined by the filler particle shape (Fig. 3).

PP/CaCO<sub>3</sub> and PP/Mg(OH)<sub>2</sub> composites with *v<sub>f</sub>* < 0.25 were melted and behaved in the same manner as a melt of PP or as its suspension. Significant difference was observed for PP filled with more than 25 vol % of needle-shaped Mg(OH)<sub>2</sub>. The "plateau zone", very similar to the plateau zone for the real chemical network, was observed [15–17]. This indicates that only a portion of PP has the character of

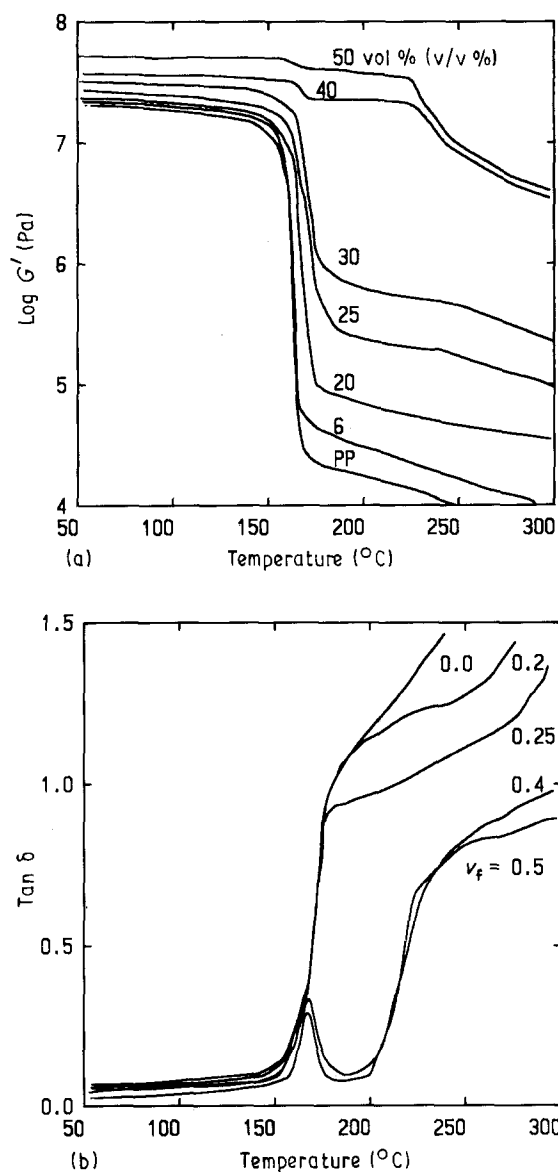


Figure 1 Temperature dependence of (a) the storage shear modulus and (b) of the loss tangent  $\tan \delta$  for PP/Mg(OH)<sub>2</sub> needle composite with various filler contents (1 Hz).

the primary polymer. Primary PP with the formal properties exists only in the more-or-less separated "domains". It seems likely that the majority of PP is immobilized in the interlayer which originates a new continuous PP phase with strongly hindered segmental mobility. This polymer phase, which originated due to the interpenetration of interlayers of the

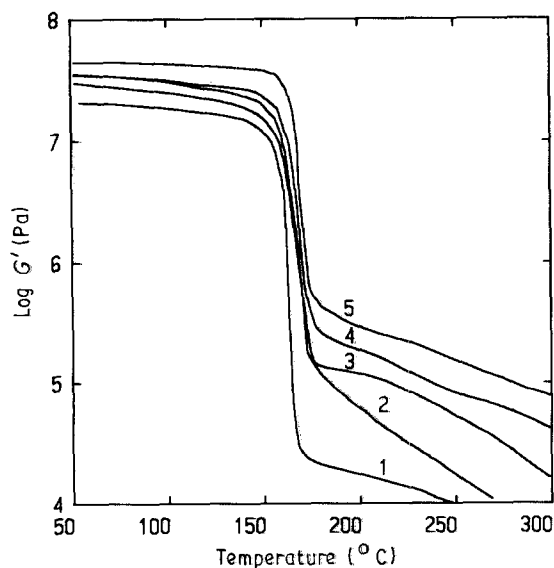


Figure 2 Temperature dependence of the storage shear modulus for the PP/CaCO<sub>3</sub> composite with various filler contents: 1, PP, 1 Hz; 2, PP/50 vol % CaCO<sub>3</sub>, 1 Hz; 3, PP, 90 Hz; 4, PP/20 vol % CaCO<sub>3</sub>, 90 Hz; 5, PP/50 vol % CaCO<sub>3</sub>, 90 Hz.

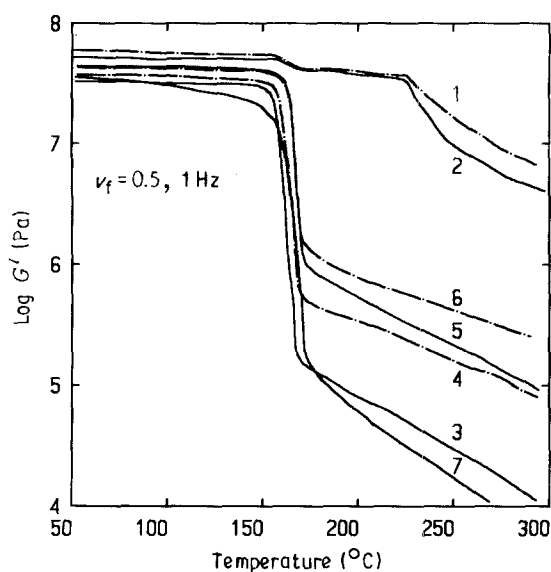


Figure 3 Effect of the enhanced interfacial adhesion (adhesion strength  $\sigma_a = 36$  MPa) on the temperature dependence of the storage shear modulus for the composites with different particle shape, specific surface area and chemical nature. 1, PP/Mg(OH)<sub>2</sub> needle; 2, M-PP/Mg(OH)<sub>2</sub> needle; 3, PP/Mg(OH)<sub>2</sub> platelet; 4, M-PP/Mg(OH)<sub>2</sub> platelet; 5, PP/CaCO<sub>3</sub> ( $d < 5 \mu\text{m}$ ); 6, M-PP/CaCO<sub>3</sub> ( $d < 5 \mu\text{m}$ ); 7, PP/CaCO<sub>3</sub> ( $d < 10 \mu\text{m}$ ).

neighbouring particles, is suggested to be the “bonding agent” for creation of the space network of physically bonded needles. The nodal points of the network are created by an overcrossing of the neighbouring needles of Mg(OH)<sub>2</sub>. Thus the melting of PP in the separated domains does not cause melting of the composite, which endures further temperature increases.

3.1.1.3. *Temperature region  $T > 240^\circ\text{C}$ .* A peculiarity of the composites with physically bonded particle networks is the steep fall of  $G'$  for temperatures above

240°C, while for the other composites investigated, only a relatively slow  $G'$  modulus decrease continues above the melting temperature. This steep decrease is thought to be caused by the physical network destruction.

### 3.1.2. Loss modulus

The reduction of  $\tan\delta$  with increasing  $v_f$  is due to the reduction of the amount of polymer phase, and the reduction of the mobility of the rest of the PP, caused by intensive immobilization on the filler surface (Figs 1 and 2).  $\tan\delta$  reduction is more intensive for the PP/Mg(OH)<sub>2</sub> composite since Mg(OH)<sub>2</sub> has ten times greater specific surface area in comparison with CaCO<sub>3</sub>. The differences in the surface activity of these fillers were not taken into account. PP filled with more than 30 vol % of Mg(OH)<sub>2</sub> needles was not completely melted, and thus a well-pronounced loss peak was observed at 165°C. This can be considered as evidence for the idea about the presence of primary PP in the dispersed domains, while immobilized PP creates a new continuous phase. It seems likely that a phase inversion occurred and the polymer exists as a “blend” of immobilized and bulk PP. The space arrangement of this “interpenetrated PP network” was given by the space packing of the filler particles. CaCO<sub>3</sub>-filled PP was completely melted, thus there is no  $\tan\delta$  peak at 165°C and losses have increased with increasing temperature in a monotonic way. The second loss peak has occurred at about 240°C for systems with a particle network. We assume that this peak was caused by the release of molecular mobility of the immobilized PP, or by the destruction of the network.

### 3.1.3. Network destruction

Processes causing network destruction probably have the nature of the chemical change of the PP–Mg(OH)<sub>2</sub> interface. Additionally, the thermal kinetic energy of segments is greater than the energy of adsorption  $E_A$  above 240°C. For the temperature 250°C, the product  $RT$ , which can be considered as a measure of the thermal kinetic energy of segments, is equal to 4.3 kJ mol<sup>-1</sup>. This value is equal to the energy commonly considered for the London’s disperse forces [18]. The disperse forces can act at physisorption on the filler surface and also as a weak interaction between molecular segments of interpenetrated interlayers, that is, as a physical bond in the slightly entangled system.

Figs 4 and 5 provide the catalytic effect of the Mg(OH)<sub>2</sub> surface on the thermal oxidation of PP immobilized in the interlayer. The filler surface is probably devoid of the low molar weight surfactant which has decomposed above 200°C. Weight losses at 240°C increased with increasing filler content, in spite of the thermal stability of the filler at this temperature (Fig. 4). On the other hand, thermal degradation of PP in the bulk had its maximum at about 410°C. The exothermal peak was observed on the DTA curves at 240°C, which corresponds with the proposed explanation.

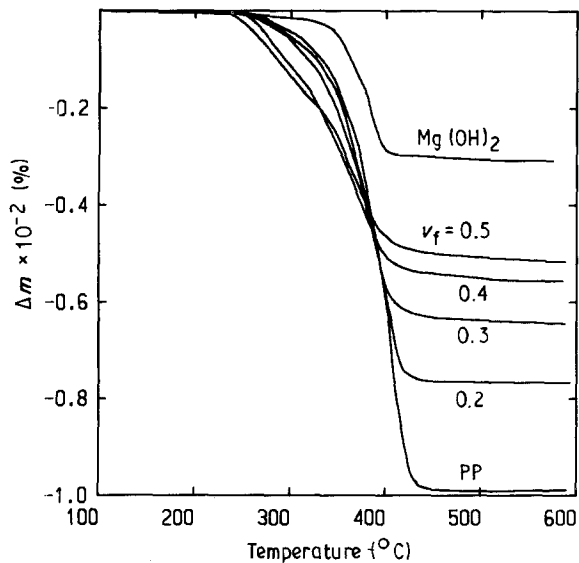


Figure 4 Thermogravimetric curves for the PP/Mg(OH)<sub>2</sub> needle composite with various filler contents.

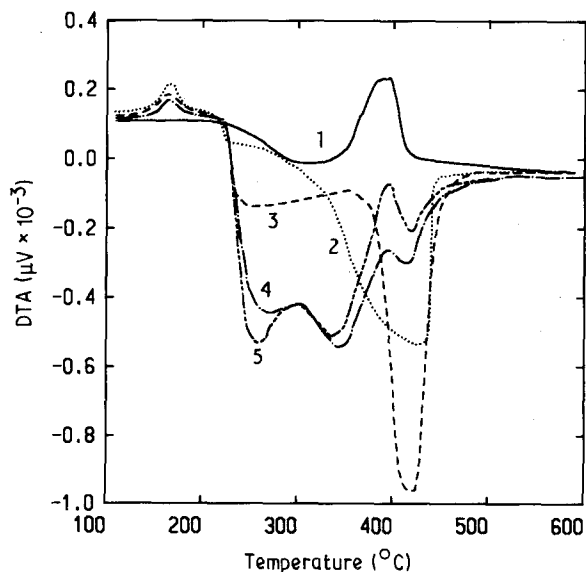


Figure 5 DTA curves for the PP/Mg(OH)<sub>2</sub> needle composite with various filler contents. 1, Mg(OH)<sub>2</sub>; 2, PP; 3,  $v_f = 0.2$ ; 4,  $v_f = 0.4$ ; 5,  $v_f = 0.5$ .

Maximum decomposition rate of the pure Mg(OH)<sub>2</sub> is at about 380 °C and from the DTA plots the flame retardant efficiency of this filler can be seen. Its decomposition endotherm suppresses the oxidation exotherm of PP due to the release of water [19] when the composite contains more than 30 vol% of Mg(OH)<sub>2</sub>. A sample containing 20 vol% of Mg(OH)<sub>2</sub> still exhibits a sharp exothermic peak of PP oxidation with a maximum at about 410 °C (Fig. 5). With an increase in Mg(OH)<sub>2</sub> content, the prominence of this peak decreases and for  $v_f > 0.3$  it disappears. Thermal analysis of the investigated composites will be discussed in Part III of this work.

### 3.2. Penetrometry

Penetrometry curves for PP, PP/CaCO<sub>3</sub> and PP/Mg(OH)<sub>2</sub> composites containing 50 vol% of the fillers (Fig. 6) exhibited temperature dependence very

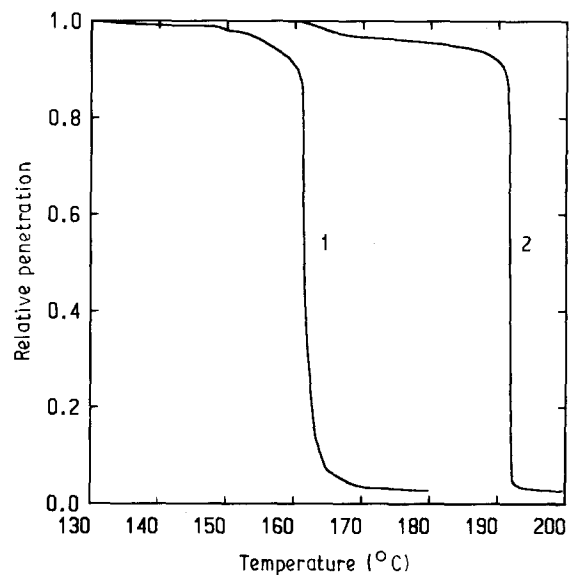


Figure 6 Temperature dependence of penetrometric data for the investigated composites with the same filler volume fraction, differing by the particle shape and specific surface area (load 1 N mm<sup>-1</sup>). 1, PP, PP/50 vol% CaCO<sub>3</sub>; 2, PP/50 vol% Mg(OH)<sub>2</sub> needles.

close to that for the  $G'$  modulus (Figs 1 and 2). Above 160 °C, the softening caused by the melting of PP occurred in domains with PP bulk properties. However, as there is a relatively small amount of primary PP, this does not lead to the probe interpenetration through pp/mg(OH)<sub>2</sub>. The network, which is partly deformable due to the flexibility of the physical bond, changes its topology slightly. The compressed network endures the external loading, in spite of the further increasing of the temperature, up to 200 °C. For 160 <  $T$  < 200 °C, the softening is relatively slow, and can be considered, by an analogy, as a "plateau zone". The steep softening, connected with the mechanical destruction of the physically bonded network of the Mg(OH)<sub>2</sub> particles, was observed at 200 °C.

### 3.3. Effect of interfacial adhesion and specific surface area

#### 3.3.1. Storage modulus

With increasing PP–filler adhesion, effective interlayer "thickness" increases and the molecular mobility in this interlayer is even more reduced. The more intensive immobilization of the matrix accounted for the increasing of the composite rigidity. The enhancement of the interfacial adhesion did not influence the behaviour of the system with the existing network significantly (Fig. 3). A two-step decrease of  $G'$  modulus with increasing temperature was observed again. The only difference, in comparison with the system without adhesion, was the slower second-step decrease at 240 °C. We assume the acid–base interaction between MPP and CaCO<sub>3</sub> or Mg(OH)<sub>2</sub> surfaces. The chemical bond between MPP and Mg(OH)<sub>2</sub> accounts for the increasing of the energy of adsorption and, probably, for the more compact arrangement of MPP molecules on the filler surface comparing with the physisorbed PP chains. The energy of this interaction is at least ten times greater than the energy of London's disperse

forces. The chemisorbed molecules' mobility is hindered much more than the physisorbed ones'. The release of their mobility requires a greater thermal kinetic energy comparing with the composite with "zero" adhesion.

The increase of  $\text{CaCO}_3$  specific surface area provided a greater increase of  $G'$  modulus than increasing the adhesion up to the cohesion of the matrix, at the same material composition and experimental conditions. This is probably caused by the subcritical particle size for  $\text{CaCO}_3$  with the greater specific surface area. Particles smaller than about  $4\ \mu\text{m}$  have a dewetting stress greater than the stress for pseudo-crazing or forming of shear bands. Thus, chemically induced adhesion aid was superfluous [20].  $\text{CaCO}_3$  grade Durcal 2 has particles mostly within the interval  $4\text{--}10\ \mu\text{m}$ , while the second  $\text{CaCO}_3$  grade used has particles within the interval  $1\text{--}3\ \mu\text{m}$ . However, neither the enhanced interfacial adhesion nor greater specific surface area led to the "mechanically effective" particle network origin in PP/ $\text{CaCO}_3$  composites. Only the one-step reduction of  $G'$  modulus was observed. Thus the particle shape probably plays a principal role in the network creation. On the other hand, the specific surface area controls the amount of immobilized PP and hence the amount of the "physical binder" in the composite. Thus the physical network was observed for the needle-shaped filler with the greatest specific surface area.

#### 4. Conclusions

Some experimental evidence for the principal role of particle shape for the origin of the filler particle network was obtained. The effect of the enhancement of interfacial adhesion was superfluous, increasing the specific surface area of the filler. The  $\text{CaCO}_3$  specific surface area of three times greater led to significantly more increment of the  $G'$  modulus than three times greater adhesion strength.

There were two significant peculiarities of the viscoelastic response of the  $\text{Mg}(\text{OH})_2$  needle-filled PP: the two-step reduction of the  $G'$  modulus with increasing temperature and the existence of two distinct loss peaks on the  $\tan\delta(T)$  dependence. The first steep fall of  $G'$  modulus was observed at the PP melting point where also the first  $\tan\delta$  peak occurred. Then the "plateau zone" was observed, very similar to that for real chemical networks, on the  $G'(T)$  curves. The second steep decrease of  $G'$  modulus occurred at about  $240^\circ\text{C}$ , which was in correspondence with the destruction of the particle network. This was considered to be evidence for the proposed idea about the origin of the network of physically bonded filler particles. PP immobilized on the filler surface was proposed to be the "bonding agent". This immobilized PP created a new continuous phase due to the interpenetration of interlayers adsorbed on the neighbouring particles. The majority of the primary matrix exists in the more-or-less dispersed domains. As the immobilized PP had

hindered segmental mobility due to interaction with the filler surface, temperature dependence of its  $G'$  modulus differed significantly when compared with PP in the domains. The presence of the primary PP only in the dispersed domains caused the physical network to endure external loading at higher temperatures than composite with the continuous primary matrix, which melted at  $165^\circ\text{C}$ .

Independently measured thermopneumatic data provided results very close to the dynamic mechanical measurements. We have suggested that a joint acting of the thermo-oxidation of the immobilized PP catalysed by  $\text{Mg}(\text{OH})_2$  surface, and sufficiently high thermal kinetic energy of segments, are responsible for this destruction. This suggestion was supported by evidence obtained by an analysis of thermogravimetric and thermoanalytic data.

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