Kinetics of Isothermal Degradation Studies in Adhesives by Thermogravimetric Data: Effect of Hydrophilic Nanosilica Fillers on the Thermal Properties of Thermoplastic Polyurethane-Silica Nanocomposites

Jose Vega-Baudrit^{a,d,*}, Maria Sibaja-Ballester^a, Patricia Vázquez^c, Santiago Nuñez^d, Jose M. Martín-Martínez^b, Luis Benavides-Rodríguez^a

^aPolymer Laboratory - Poliuna, Universidad Nacional, 86-3000 Heredia, Costa Rica. ^bAdhesion and Adhesives Laboratory, University of Alicante, 03080 Alicante, Spain. ^cResearch and Development Centre for Applied Sciences (Cindeca), Conicet-UNLP, 47 n 257, B1900AJK La Plata, Buenos Aires, Argentina. ^dNational Nanotechnology Laboratory -Lanotec-Cenat, San José, Costa Rica

Received: February 22, 2008; Accepted: June 8, 2008; Revised: July 22, 2008

Abstract: The kinetics of thermal degradation process on thermoplastic polyurethanes (TPUs) adhesives with hydrophilic nanosilicas was studied using isothermal thermogravimetric analysis within the temperature range from 360 °C to 460 °C in nitrogen. The effect of nanosilicas with different hydrophilic degree in the thermoplastic polyurethanes was investigated. It was found that the thermoxidative degradation of polyurethane-silica nanocomposites takes place in one step. An analysis of the isothermal methods to evaluate kinetic parameters of decomposition of solids from isothermal thermogravimetric data is presented. Patents WO07146353A2 and US20070292623A1 have some relevant information about the topic develop in this study, because the principle in both cases relies on the interactions between reactive groups in the polymer (TPUs) and the silanol in the silica nano-particles.

Keywords: Kinetic analysis, isothermal degradation, adhesives, hydrophilic nanosilica, polyurethane-silica, nanocomposites, thermogravimetric analysis.

INTRODUCTION

Thermoplastic polyurethanes (TPUs) constitute a multipurpose group of phase-segmented polymers that have good mechanical and elastic properties and hardness [1]. TPUs usually exhibit a two-phase microstructure, which arises from the chemical incompatibility between the soft and the hard segments. The hard (rigid) segment segregates into a glassy or semicrystalline domain and the polyol soft segments form amorphous or rubbery matrices, in which the hard segments are dispersed. Many factors influence in the separation of the phases such as molecular weight, segmental length, crystallizability of the segment, overall composition and intra- and inter-segments interactions [1]. Fumed nanosilicas are added to increase the thermal, rheological and mechanical properties of TPUs [2-6]. Other studies have been developed by different researchers with PU (polyurethane), improving the chemical and physical properties of this polymers and changing the polyurethane to thermoset plastics [7]. Only thermoplastic polyurethanes are used in this study.

When hydrophilic fumed nanosilica is added, the degree of the phase separation increases due to the hydrogen-bond interaction between silanol groups on the nanosilica surface and the soft segments of TPUs. Therefore, the segmental incompatibility on TPUs is increased in the presence of the hydrophilic nanosilicas. Recent studies have shown that the use of this kind of materials is able to form hydrogen bonds resulting in less direct interactions between phases and

causing a higher phase separation. Furthermore, the interactions between silanol and carbonyl groups are weaker than those between NH and ester-carbonyl groups; silica addition increases the polyester chain mobility and it allows better molecular ordering with respect to TPUs without silica [8-11]. This kind of interaction has been used in the formulation of coating where the interaction between reactive groups and silica nano-particles provide enhanced scratch and resistance to deformation [12, 13-15].

In this study, nanosilica treated with silanes (Wacker-Chemie) was used to decrease its silanol group content. Thus, different TPU adhesives containing 10 wt% fumed silica, with different degree of silanization (100, 57.5 and 15 %) were prepared and later characterized by thermogravimetric analysis (TGA and DTGA). Finally, in order to study the effect of this kind of silicas in TPUs, isothermal methods were used for evaluating thermal degradation kinetic parameters from isothermal thermogravimetric data.

Recent papers show the results of evaluating these samples using thermal, rheological and mechanical analysis, and adhesion tests [14, 15].

EXPERIMENTS

Materials

Different fumed silicas (nanosilicas) manufactured by Wacker-Chemie (Burghausen, Germany) were used. A fully silanized nanosilica (HDK N20, Wacker Chemie) was progressively modified by chemical reaction with dimethyldichlorosilane (DMCS) (Scheme 1).

*Address correspondence to this author at the Polymer Laboratory - Poliuna, Universidad Nacional, 86-3000 Heredia, Costa Rica; Tel/Fax: (506) 2277 3557; E-mail: jvegab@una.ac.cr

Scheme 1.

The degree of silanization was decreased between 15.0 and 57.5 %. Primary nominal particle size in all nanosilicas was 7nm. Table 1 shows the nomenclature of nanosilicas and some of their characteristics provided by Wacker-Chemie. According to Wacker-Chemie, the nominal specific surface area of all nanosilicas was 200m²/g.

Table 1. Some Characteristics of Fumed Nanosilicas According to Wacker-Chemie

Sample	SiOH (%)	mmol SiOH/g _{nanosilica}
HDK N20	100	0.60
HDK H20	57.5	0.34
HDK H20RD	15.0	0.09

TPUs were prepared using the prepolymer method [14, 15]. The prepolymer was obtained by reacting the polyadipate of 1,4-butanediol ($M_w = 2440$ Daltons) with 4,4-diphenyl methane di-isocyanate - MDI. An isocyanate/macroglycol equivalent ratio of 1.05 was used. 1,4-butanediol was used as chain extender. High purity solid MDI was supplied by Aldrich (Cat. 25.643-9) as well as a mixture of 98 wt% of the 4,4'-isomer and 2 wt% of the 2,4'-isomer. The NCO content of the prepolymer was determined by titration with dibutylamine (UNE-EN 1242 standard). Polyadipate of 1,4-butanediol (Hoopol F-530) was supplied by Hooker S.A. (Barcelona, Spain) and was heated for 4 hours at 70°C under reduced pressure (5 Torr) in order to remove residual water. The 1,4-butanediol supplied by Aldrich (Cat. B8, 480-7) was dried using 4 Å molecular sieves.

The reaction temperature was kept below 65°C under a stirring speed of 80 rpm, hence avoiding cross-linking reactions during polyurethane synthesis. Polyurethane synthesis was carried out in a dry nitrogen atmosphere in order to avoid water in the reactor. The prepolymers containing unreacted isocyanate ends were completely reacted with the necessary stoichiometric amount of 1,4-butanediol. The reaction time was 2 hours. TPUs were annealed in an oven at 80°C for 12 hours (curation time).

TPU adhesive solutions were prepared by mixing 20 wt% solid polyurethane and 2 wt% nanosilica with 2-butanone in a Dispermix DL-A laboratory mixer equipped with a Cowles mechanical stirrer (diameter = 50 mm) and a water jacket to maintain the temperature at 25°C during process. Adhesive preparation was carried out in two consecutive stages: *i*) the nanosilica was mixed for 15 min at 2500 rpm with a 1/3 volume of butanone required by the adhesive. *ii*) the TPUs and 2/3 volumes of butanone were added to the previous solution, stirring the mixture for 2 hours at 2000 rpm. TPU adhesive solutions were kept in a hermetic container until use. A TPU adhesive solution without silica was also

prepared as a control solution. Most of the properties of the polyurethanes were measured using solid films, which were prepared by placing approximately 100 cm³ of adhesive solution in a mould and allowing slow evaporation of the solvent at room temperature for 2 days. The thickness of the obtained polyurethane films ranged in between 0.7mm and 0.9mm.

The nomenclature of the polyurethane-nanosilica mixtures was PU0 (TPUs without silica), PU15, PU57.5 and PU100 for the TPU's containing nanosilicas with 15%, 57.5% and 100% of weight silanol groups, respectively.

Experimental Techniques

Isothermal thermogravimetric studies were carried out on a Mettler TGS DTA thermobalance (model 851e/1600/LF) in nitrogen flow at a rate of 100 mL/min. Isothermal conditions were maintained stable during 30 minutes and then samples (4-5mg) were heated until 800°C. The heating rate was 10°C/min in nitrogen.

Kinetic parameters were studied using the degradation standard equation, the Arrhenius method, the Klaric method and the MacCallum method [16-27].

RESULTS AND DISCUSSION

Thermal Analysis

The thermogravimetric analysis (TGA) results of samples in nitrogen are shown in Fig. (1).

Fig. (1). TGA curves of TPU's samples with and without nanosilica at 10°C/min, in nitrogen.

In all polyurethane samples, thermal degradation starts at 380°C (onset temperature- T_i) and proceeds in one step. At 500°C, decomposition can be considered as complete. The temperatures of the maximum rates of weight loss ($[dw/dT]_{max}$) were obtained using DTGA (Fig. 2).

DTGA curves show similar thermal stability for TPUs with nanosilica, higher than that in PU0. According with the segmental nature of thermoplastic polyurethanes, samples show two events for degradation. According to some studies of polyurethane, urethane bonds present lower stability than structures with soft segments (polyols) [16-18]. Therefore, in PU0 a first peak related to the urethane linkages degradation is observed at 380°C. The second peak at 416°C is related

Fig. (2). DTGA curves of TPU samples with and without nanosilica at 10°C/min, in nitrogen.

with the polyol chain scission. In TPU-silica composites, both degradations are overshadowed. The analysis shows that nanoadditives increased the thermal stability of TPUs.

In all samples, no significant peaks over the maximum rates of weight-loss temperature were observed. TGA and DTGA data are summarized in Table 2.

Table 2. Thermal Properties of Polyurethane-Silica Composites in Nitrogen at 10°C/min Measured by TGA.

Sample	Temperature (°C)	
	Maximum rates of weight loss ((dw/dT) _{max})	Onset (T _i)
PU0	416	380
PU15	418	384
PU57,5	419	386
PU100	422	390

The thermal stability of TPU-silica nanocomposites is related with the degree of phase separation in the polyurethanes. Recent studies [10, 11, 14, 15] have demonstrated that the addition of fillers that able to form hydrogen-bonds-such as silica- results in less direct interactions between phases, thus causing a higher degree of phase separation in the polyurethane. On the other hand, the interactions between the silanol groups and the carbonyl groups in the polyurethane are weaker than those between the N-H and ester-carbonyl groups, and consequently silica addition increases the polyester chain mobility in polyurethane by allowing the creation of more ordered phases with respect to the polyurethane without silica.

Kinetic analysis

Under isothermal conditions, the fractional reaction-time (α - t) curves are expressed as is indicated by equation 1.

$$g(\alpha) = kt \quad (1)$$

where k is the rate constant and the function $g(\alpha)$ depends on the mechanism controlling the reaction [19]. The decomposition ratio (α) was determined using equation 2.

$$\alpha = \frac{w_i - w(t)}{w_i - w_f} \quad (2)$$

where w_i is the initial mass, $w(t)$ is the mass in time t and w_f is the final mass. Figs. (3) to (6) show the plots for the isothermal decomposition of TPU-silica nanocomposites. The decomposition ratio increased when the temperature of the isothermal thermogravimetric analysis increased. At 440°C and 460°C, the decomposition ratio decreased, indicating that complete thermal decomposition of the polyurethanes was reached.

Fig. (3). Plot of isothermal decomposition for PU0.

Fig. (4). Plot of isothermal decomposition for PU15.

Fig. (5). Plot of isothermal decomposition for PU57.5

Fig. (6). Plot of isothermal decomposition for PU100.

Kinetic parameters from TGA data may yield additional insight into the mechanism of thermal degradation. It is generally accepted that materials obey equation 3 [27].

$$\frac{d\alpha}{dt} = k(T)(1 - \alpha)^n \quad (3)$$

where n is the order of the reaction. The temperature dependence in equation 3 is defined via the reaction rate term k which is assumed to be in the Arrhenius form (equation 4),

$$k = Ae^{\frac{-E_a}{RT}} \quad (4)$$

where A is the pre-exponential factor, E_a is the activation energy and R is the gas constant. Equation 3 needs to be

fitted against experimental data from the isothermal thermogravimetric analysis in order to obtain n and k . Repeating the process at several temperatures leads to $k(T)$, which can be used in equation 4 to obtain A and E_a for degradation. Plotting $\ln[k(T)]$ against the reciprocal temperature Fig (7) yields a straight line with a slope proportional to the activation energy. The intersection of them yields the pre-exponential factor.

Fig. (7). Linear dependence in the Arrhenius method used for TPU-silica nanocomposites.

In order to compare the kinetic parameters, the results of the Arrhenius method are summarized in Table 3. TPU-nanosilica nanocomposites show a smaller activation energy and pre-exponential factor in comparison with PU0. In TPU-nanosilica samples, both parameters raise with the increase of the silanol group contents on the silica surface used in the nanocomposites. This correlated increment implies that any increase in the activation energy is accompanied by an increase in the pre-exponential factor to keep the rate constant nearly unchanged. This tendency is known as the kinetic compensation effect (KCE) [20, 21].

Table 3. Kinetic Parameters for TPU-Silica Nanocomposites (Arrhenius Method)

Sample	E_a (kJ/mol)	$\ln A$
PU0	89.8	26.5
PU15	66.4	18.9

In order to obtain k and n , the kinetic standard equation (equation 5) was used. Assuming a kinetic model function $f(\alpha) = (1 - \alpha)^n$, equation 5 can be transformed into equation 6 [22, 23].

$$\ln \left(\frac{d\alpha}{dt} \right) = \ln[k(T)] + \ln[f(\alpha)] \quad (5)$$

$$\ln \left(\frac{d\alpha}{dt} \right) = \ln[k(T)] + n \ln(1 - \alpha) \quad (6)$$

Plotting $\ln (da/dt)$ against $\ln(1 - \alpha)$ yields a straight line with slope proportional to the reaction order and the intersection of the yield rate constant. Fig (8) and Fig (9)

show the comparison of the rate constant and reaction order obtained from the kinetic standard equation respectively.

Fig. (8). Comparison of the rate constant obtained from the kinetic standard equation.

When the temperature of the isothermal analysis was incremented during the experiment, an increase in the rate constant was observed Fig. (8). At 420°C, important changes appear in the rate constant. As mentioned above, incorporation of nanosilica in TPUs increases the temperature of the maximum rate for weight loss ($[dw/dT]_{max}$) and for the onset temperature (T_i). Furthermore, nanosilica in TPUs decreases the kinetics of decomposition due to more interactions among the polyurethane soft segments. The silanol groups on the silica surface enhance phase separation and improve its thermal properties. In fact, PU0 has the lowest temperature of the maximum rate for weight loss and onset temperature, and the highest degradation rate constant.

Fig. (9). Comparison of the reaction order obtained from the kinetic standard equation.

In the comparison of TPU-nanosilica samples, PU15 shows the smallest rate constant. PU100 and PU57.5 exhibit a similar rate constant. Therefore, an increase of silanol groups in the nanosilica surface enhances the polymer thermal degradation rate.

Finally, at low temperatures the reaction order was unaffected in samples with nanosilica. When the temperature approaches that of degradation (420°C), the reaction order increases up to 1.5. In addition, PU0 sample shows a reaction order of 2. Therefore, fumed nanosilica in TPU-nanocomposites changes the thermal degradation mechanism.

Another isothermal technique is the so-called *stationary point method* or Klatic method [24, 25]. The decomposition ratio (α) was redefined as shown in equation 7.

$$\alpha = \frac{w_i - w(t)}{w_i} \quad (7)$$

The stationary point is defined on the curve of da/dt versus t as the point where the rate V reaches a maximum value (V_{max}). The activation energy can be obtained from equation 8 with respect to V_{max} . Fig. (10) shows the linear dependence in the Klatic method used for TPU-silica nanocomposites.

$$\frac{d \ln V_{max}}{d \left(\frac{1}{T} \right)} = \frac{d \ln k}{d \left(\frac{1}{T} \right)} = -\frac{E_a}{R} \quad (8)$$

Fig. (10). Linear dependence in the Klatic method used for TPU-silica nanocomposites.

Table 4 shows the activation energy obtained from Klatic method. The values of the activation energies shown in Table 3 are roughly twice those found using the Arrhenius method. This discrepancy between the E_{act} values can be attributed to the assumptions used during treatment of data. It is difficult to determine maxima points at the lowest temperatures using the Klatic method.

MacCallum develop another method for analysis of isothermal degradation. The decomposition fraction (α) was redefined as show in equation 7. MacCallum proposed a function F and a first-order reaction modelled by equation 9 [27, 28].

Table 4. Activation Energy for TPU-Silica Nanocomposites (Klaric Method)

Sample	E_a (kJ/mol)
PU0	173.4
PU15	133.9
PU57.5	168.1
PU100	172.5

$$\frac{d(1-\alpha)}{dt} = kF(1-\alpha) \quad (9)$$

Then, integrating equation 9 and using equation 4 equation 10 is obtained.

$$F(1-\alpha) = Ae^{-\frac{E_a}{RT}t} \quad (10)$$

Over some temperature range, $F(1-\alpha)$ should be constant for a given value of α . Rewriting equation 10 leads to equation 11.

$$\frac{E_a}{R} + \ln[F(1-\alpha)] - \ln A = \ln t \quad (11)$$

Plotting $\ln t$ against $1/T$ (for fixed values of α) yields a straight line with slope proportional to E_a . Moreover, plotting intersections at several temperatures against α and extrapolating to zero yields the value of A (equation 12).

$$\text{Intersection} = \ln[F(1-\alpha)] - \ln A \quad (12)$$

Fig. (11) shows the linear dependence in the MacCallum method used for characterizing TPU-silica nanocomposites. In order to compare the kinetic parameters, the results of the MacCallum method have been summarized in Table 5. Comparing with the results of the Klaric method (Table 4), the tendency and values obtained are similar. In both cases, activation energy and A change depending on the silanol groups content on the nanosilica surface.

Fig. (11). The linear dependence in the MacCallum method used for TPU-silica nanocomposites.

Table 5. Activation Energy for TPU-Silica Nanocomposites (MacCallum Method)

Sample	E_a (kJ/mol)	$\ln A$
PU0	177.4	31.4
PU15	140.6	25.2
PU57.5	163.3	31.8
PU100	176.9	33.6

CURRENT & FUTURE DEVELOPMENTS

Isothermal decomposition kinetics of the thermal degradation process in thermoplastic polyurethanes (TPUs) with hydrophilic nanosilicas was studied by thermogravimetric analysis. Addition of nanosilicas improved the thermal properties of thermoplastic polyurethanes due to the creation of hydrogen bonds among the soft segments of polyurethane. Nanosilica disrupted the compatibility between the hard and soft segments, favouring the degree of phase separation in the polyurethanes. The highest silanol content in the nanosilica produced a maximum degree of phase separation.

Kinetic parameters from TGA data yield additional insight about the mechanism of thermal degradation. In order to analyze isothermal thermogravimetric data, some models of thermal degradation were used. An increase of the temperature in isothermal analysis produced an increment in the rate constant. Furthermore, nanosilica in TPUs decreases the kinetics of decomposition due to the increase of the interaction between the polyurethane soft segments. Nevertheless, an increase of the silanol groups in nanosilica surface enhanced the polymer thermal degradation rate. Also, these studies showed an increment in E_a and A values produced by the increase of the content of silanol groups in the silica surface. However, TPUs without nanosilica showed higher E_a and A values. This suggests that although it degrades at a higher rate with lower initial degradation and at a maximum rate within decomposition temperatures, it needs higher activation energy for degradation. The latter has been explained as a smaller segregation of the phases in TPUs without silica, enhancing the interaction among the hard and soft segments of TPUs through hydrogen bonds. It was necessary to apply more energy for their thermal degradation.

The study of the interaction between different polymers and nano-particles is a common task in the process of improving materials for different target applications, in this particular case for producing an enhanced adhesive. Another area that might benefit from this technology is car painting and painting in general due to the principle behind the interactions between polymers and the silanol groups, leading to significant improvements in the properties of paints.

REFERENCES

- [1] Oertel G. In: Polyurethane Handbook 2nd, Hanser: New York, 1993, 7; Chapter 2.
- [2] Maciá-Agulló TG, Fernández-García JC, Pastor-Sempere N, Orgilés-Barceló AC, Martín-Martínez JM. Addition of Silica to Polyurethane Adhesives. J Adhesion 1992; 38: 31-53.

- [3] Jaúregui-Beloqui B, Fernández-García JC, Orgilés-Barceló AC, Mahiques-Bujanda MM, Martín-Martínez JM. Thermoplastic polyurethane-fumed silica composites: Influence of the specific surface of fumed silica on the viscoelastic and adhesion properties. *J Adhes Sci Technol* 1999; 13: 695-711.
- [4] Jaúregui-Beloqui B, Fernández-García JC, Orgilés-Barceló AC, Mahiques-Bujanda MM, Martín-Martínez JM. Rheological properties of thermoplastic polyurethane adhesive solutions containing fumed silicas of different surfaces areas. *Int J Adhes Adhes* 1999; 19: 321-328.
- [5] Torró-Palau A, Fernández-García JC, Orgilés-Barceló AC, Martín-Martínez JM. Characterization of polyurethanes containing different silicas. *Int J Adhes* 2001; 21: 1-9.
- [6] Pérez-Limiñana MA, Torró-Palau AM, Orgilés-Barceló AC, Martín-Martínez JM. Rheological properties of polyurethanes adhesives containing silica as filler; influence of the nature and surface chemistry of silica. *Macromol Symp* 2001; 169: 191-196.
- [7] Limerkens, D., Lindsar, C., Mijls, C., Wouters, S.: WO07144292A1 (2007).
- [8] Sánchez-Adsuar MS, Papón E, Villenave J. Influence of the prepolymerization on the properties of thermoplastic polyurethane elastomers. Part I. Prepolymerization characterization. *J Appl Pol Sci* 2000; 76: 1596-1601.
- [9] Tien Y and Wei K. Hydrogen bonding and mechanical properties in segmented montmorillonite/polyurethane nanocomposites of different hard segment ratios. *Polymer* 2001; 42: 3213-3221.
- [10] Nunes RCR, Fonseca JLC, Pereira MR. Polymer-filler interactions and mechanical properties of a polyurethane elastomer. *Polym Test* 2000; 19: 93-103.
- [11] Nunes RCR, Pereira RA, Fonseca JLC, Pereira MR. X-ray studies on composition of polyurethane and silica. *Polym Test* 2001; 20: 707-712.
- [12] Lin, J.: WO07146353A2 (2007).
- [13] Lin, J.: US20070292623A1 (2007).
- [14] Vega-Baudrit J, Sibaja-Ballester M, Vázquez P, Torregrosa-Maciá R, Martín-Martínez JM. Properties of thermoplastic polyurethane adhesives containing nanosilica with different specific surfaces area and silanol content. *Int J Adhes Adhes* 2006; 27: 469-479.
- [15] Navarro-Bañón V, Vega-Baudrit J, Vázquez P, Martín-Martínez JM. Interactions in nanosilica-polyurethane composites evidenced by plate-plate rheology and DMTA. *Macromol Symp* 2005; 221: 1-10.
- [16] Ravey M and Pearce EM. Flexible polyurethane foam. I Thermal decomposition of a polyether-based, water-blown commercial type of flexible polyurethane foam. *J App Polym Sci* 1997; 63: 47-74.
- [17] Semsarzadeh MA and Navarchian AH. Effects of NCO/OH ratio and catalysis concentration on structure, thermal stability and crosslink density of poly(urethane-isocyanurate). *J Appl Pol Sci* 2003; 90: 963-972.
- [18] Araújo RCS, Pasa VMD. Thermal study of polyurethane elastomers based on biopitch-PEG-MDI system. *J Ther Anal Cal* 2002; 67: 313-319.
- [19] Criado JM, González M, Ortega A, Real C. Some consideration regarding the determination of the activation energy of solid-state reaction from a series of isothermal data. *Thermochim Acta* 1984; 29: 243-250.
- [20] Vlase T, Vlase G, Chiriac A, Doca N. The influence of concentration and anion nature on the support effect. *J Therm Anal Cal* 2003; 72: 847-853.
- [21] Liu N, Zong R, Shu L, Zhou J, Fan W. Kinetic compensation of effect in thermal decomposition of cellulosic materials in air atmosphere. *J Appl Pol Sci* 2003; 89: 135-141.
- [22] Pelichowski K, Kulesza K, Pearce E. Thermal degradation studies on rigid polyurethanes foams blown with pentane. *J Appl Pol Sci* 2003; 88: 2319-2330.
- [23] Chuang FS, Tsen WC, Shu YC. The effect of different siloxane chain-extenders on thermal degradation and stability of segmented polyurethanes. *Pol Deg Stab* 2004; 84: 69-77.
- [24] Klarić I, Roje U, Stipanelov N. Kinetic investigation of thermooxidative degradation of poly (vinyl chloride)/acrylonitrile-butadiene-styrene blends by isothermal Thermogravimetric analysis. *J Appl Pol Sci* 1999; 71: 833-839.
- [25] Klarić I, Roje U, Kovacic T. Kinetic of thermal degradation of PVC/ABS blends. *J Therm Anal* 1995; 45: 1373-1380.
- [26] Duwenhorst, J., Malz, H., Scheffer, K., Flug, T., Vallo, M.: EP1877460 (2008).
- [27] O'Sickey M. PhD Thesis Characterization of structure-property relationships of poly(urethane-urea)s for fiber applications, Virginia Polytechnic, Virginia, 2002; Chapter 1-2.
- [28] De Britto, Campana-Filho S. A kinetic study on the thermal degradation of *N,N,N*-trimethylchitosan. *Pol Deg Stab* 2004; 84: 353-361.