PRELIMINARY ANALYSIS OF POLYAMIDE-12 FOR STUDY OF PYROLYSIS IN FLUIDIZED BED

Fabio Nascimento da Silva, fabions@fem.unicamp.br
Caio Glauco Sánchez, caio@fem.unicamp.br
Elisabete Maria Saraiva Sanchez, bete@fem.unicamp.br
Laboratory of Combustion, DETF, Faculty of Mechanical Engineering, UNICAMP, P. O. Box 6088, Campinas/SP, Brazil

Abstract. *The technology of utilization of polyamide-12 (PA-12) in rapid prototyping (RP) processes for prototypes confection has been increasing in the last years. The PA-12 is a polymeric material derived from petroleum, containing twelve carbon atoms in its molecular structure and its functional group is the -CONH-. The process residue of RP consists in solid PA-12 free from contaminants. However, PA-12 residue is discarded as common waste, representing energetic and raw material losses and causing another environmental problems associated to this practice. The study of pyrolysis of PA-12 in fluidized bed becomes as a possible alternative to the discard, because it realizes the energetic recycling of the material, obtaining liquids and gaseous fractions that can be used as supplies or to generate energy for industries. The preliminary characterization consists in an important stage of pyrolysis processes, because it reveals fundamentals data about the origin and composition of material, permits to simulate the behavior during the pyrolysis process and estimates the products obtained. The preliminary analysis indicated that it has an excellent calorific value, higher than 40.0 MJ/kg, besides its be composed for 99 % of volatile matter and less than 1 % of moisture, evidencing the potential of utilization as fuel. Thermogravimetric analysis (TGA) shown that 98 % of the volatile matter is eliminated between the temperatures of 230 – 390 ºC and the material is composed by almost 75 % of carbon and 7.5 % of nitrogen.*

Keywords: *polyamide-12, characterization, recycling of polymers*

1. INTRODUCTION

According Pham and Gault (1998), the definition of Rapid Prototyping (RP) consists in a term which embraces a range of new technologies developed for the production of molds directly from CAD. This technologies permits the fabrication of parts in a few hours, with a little need for human intervention.

Many manufacture processes are subtractive, in that they modify the geometry of a mass of material by removing parts of the material until the final shape is achieved. By contrast, RP techniques are additive processes. RP are built-up gradually in layers until the final geometry is obtained (Upcraft and Fletcher, 2003).

Among the range of different existing technologies, the process called as Selective Laser Sintering (SLS) has been increasing its utilization in the market, mainly because the large kinds of materials that can be employed. The use of binder sacrificial materials (typically a polymer binder) to the basic powder allows to enlarge the pallets of laser sinterable materials. However, the range of materials (powders) that can be sintered without sacrificial binder is quite large as compared to other rapid prototyping processes (Kruth *et al*., 2003). Along with stereolithography and fused deposition modeling, SLS in one of the leading RP technologies (Dimov *et al*., 2001).

The SLS applications consists basically in the conformation of prototypes for automobile and aerospacial industries, besides another applications at medicine field as the fabrication of surgery prosthesis, conformation of bone structures in major scale, preoperative auxiliary and, more recently, as a support structure for growth of artificial skin for treatment of severe burn victims (Berry *et al*., 1997; Rosa *et al*., 2004; Lohfeld *et al*., 2005; Gibson *et al*., 2006).

The polyamide-12 (PA-12) is a material larger employed in SLS processes. According Kruth *et al*. (2003), it occurs as a function of good mechanical properties, resolution and surface roughness obtained, close to that projected before in CAD.

The obtaining of PA-12 occur trough a process knows as ring-chain scission that happens inside the dodecanolactam specie, a compound derived from butadiene (Welgos, 1895). PA-12 is a polymeric material derived from petroleum, containing twelve carbon atoms in its molecular structure and its functional group is -COHN-.

The PA-12 is classified as a degradable material under thermo and thermo-oxidative environments (TOD) as, for example, the SLS chambers. This characteristic does not permit to the residual material to be employed again in the SLS process before sintered once (Dickens, Jr. *et al*., 1994).

The discard of this material as common waste represents energetic and economical losses. Thus, is necessary the development of new PA-12 recycling and recuperation models to aim the finish of this discard directly in environment, minimize the environmental problems related at the practice of solid waste disposal and realize the energetic recovery of this material.

PA-12 recycling by pyrolysis represents an alternative to final disposal. Pyrolysis consists in submit the material into an inert atmosphere and high temperature (above 800 and 1000 °C), converting the original material in three products: gas, liquid and char (almost pure carbon) (Bridgewater and Bridge, 1991). The study of PA-12 pyrolysis processes in bubbling fluidized bed aims to evaluate the utilization of polyamide as supplies or industrial fuel.

Herrera *et al.* (2001) made the thermal degradation of PA-12 by pyrolysis way and shown that one of the principals products obtained is the cyclic monomer lauril-lactam, and so another sub product as toluene, C_4 – C_{12} nitriles and polynuclear aromatic hydrocarbons (PAH). These results were so observed by Czégéni and Blazsó (2001) that classified the hydrocarbons as *n*-alkenes, *n*-alkenenitriles and *n*-decanenitrile.

The preliminary characterization of the material before the realization of tests in bubbling fluidized bed reactor in pilot scale consists in an important step of recycling process, because it permits to optimize the reactor operation parameters, preview in qualitative and quantities manner the products obtained and a better comprehension of kinetics and reaction parameters of the employed material.

This work aims to divulgate the results obtained during the PA-12 characterization, discarded as residue from SLS process, increasing the number of available data on literature and pre-evaluating its application in bubbling fluidized bed pyrolysis reactor.

2. EXPERIMENTAL

The PA-12 characterization evaluated the particle average diameter (d_p), proximate analysis, ultimate analysis, higher heating value (HHV) and thermogravimetric analysis (TGA) for evaluation of thermal degradation parameters, as show as follow.

2.1. Materials

The PA-12 is obtained from two different fabricants: EOS GmBH – produces the PA2200 (PA2200) and 3D Systems – produces DuraForm (DF12). It was obtained as residue of SLS process from Renato Archer Research Center (CenPRA), localized in the city of Campinas, São Paulo state, Brazil.

The analysis was done with each different polyamides without mix of materials.

2.2. Particle average diameter (d_p)

Particle average diameter measurements was carried out by screening 50 g of each material for 60 minutes in sieves of Tyler-Mesh series (with 88 μm, 75 μm, 63 μm, 53 μm and 45 μm of wire cloth opening) in a 60 Hz and ½ HP equipment of Produtest. It was made 3 tests for each type of PA-12.

The particle average diameter was calculated following the equation developed by Howard (1989), described in Eq. (1).

$$d_p = \left[\sum_{m=1}^{N} \frac{x_p}{d_{p,m}} \right]^{-1} \tag{1}$$

Where:
N: number of sieves.
x_p: mass fraction of particles with diameter equal as $d_{p,m}$.
$d_{p,m}$: Sauter's average diameter of particles retained in a sieve and its subsequent (μm), given by Eq. (2).

$$d_{p,m} = \frac{d_{pi} + d_{pi-1}}{2} \tag{2}$$

2.3. Scanning electron microscopy (SEM)

Scanning electron microscopy of PA-12 powder was obtained in JEOL JXA-840A microscopy after the material was sputtered with a gold layer.

2.4. Proximate analysis

Proximate analysis was carried out following standards methods of American Society for Testing Materials (ASTM) for the determination of moisture average proportion (ASTM D-3173), ash (ASTM D-3174), volatile matter (ASTM D-3175) and fixed carbon (ASTM D-3172). It was made 10 tests for each material and obtained its average value.

2.5. Ultimate analysis

The ultimate analysis of PA-12 gives the mass fractions of chemical elements that arrange the material. In the case of polyamides these elements are carbon, hydrogen, nitrogen and oxygen.

2.6. High heating value (HHV)

The determination of HHV was done in calorimetric bomb following the standard method ASTM D-2015. In this work was used around 0.6 g of material for each sample. It was made 3 tests for any type of polyamide and obtained its averages value.

2.7. Thermogravimetric analysis (TGA)

The studies of thermal degradation of polyamides were used for determination of thermal decomposition parameters. These parameters were conversion optimum temperature (T_O) and range limits temperatures of volatiles elimination (T_E).

The tests were made utilizing a thermogravimetric equipment developed by BP Engineering, as so the data acquirement system.

After parameters adjustment of the samples treatment, 3 tests were made for each type of PA-12. The thermal degradation was performed under inert atmosphere of nitrogen, flow rate of 7 L min^{-1}, sample mass of 5.0 g, heating rate of 10 ºC min^{-1} and heated from ambient temperature up to 700 ºC.

3. RESULTS AND DISCUSSION

3.1. Particle average diameter

The particle average diameter of PA-12 is represented in Tab. 1. Figure 1 shows the particle size of materials. It is important to describe that the founded values (69.2 μm for PA2200 and 68.3 μm for DF12) are higher than that informed by materials datasheets. According datasheet of PA2200 fabricant, the particle average diameter is 60 μm (EOS GmBH, 2007) and the datasheet of DF12 fabricant informs a particle average diameter of 58 μm (3D Systems, 2001).

A possible reason to this increasing in particle diameter is due the utilization of the PA in SLS processes. Both materials were submitted at a laser heating and, consequently, had some of its fraction sintered. So, according Dickens, Jr. *et al*. (1994), even if the particles themselves are not degraded, overheating the part bed to crystallization temperature, the temperature that which the particles agglomerate, causes high enough interparticle bonding. This bonding turns the materials inappropriate to reuse in others SLS process, because it may compromise some characteristics of final product as surface roughness and full density.

Table 1. Particle average diameter and standard deviation of PA-12.

	PA2200	DF12
d_p (μm)	69.2 ± 2.7	68.3 ± 4.6

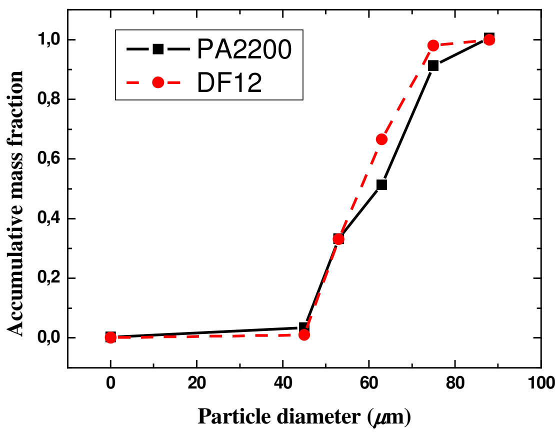

Figure 1. Particle size of PA-12.

3.2. Scanning electron microscopy

The images obtained by SEM (Fig. 2 and Fig. 3) confirmed the results obtained for particle diameter average. It can be observed that occurs a superficial rupture in the PA-12 particle and the dilatation of its interior after sintered. This event also helps to a better comprehension of the powder properties losses and the less quality of the prototype made with PA-12 recycled.

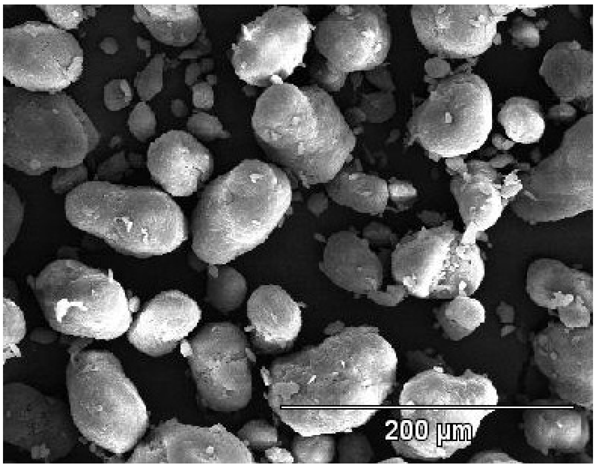

Figure 2. Image of PA-12 virgin obtained by SEM.

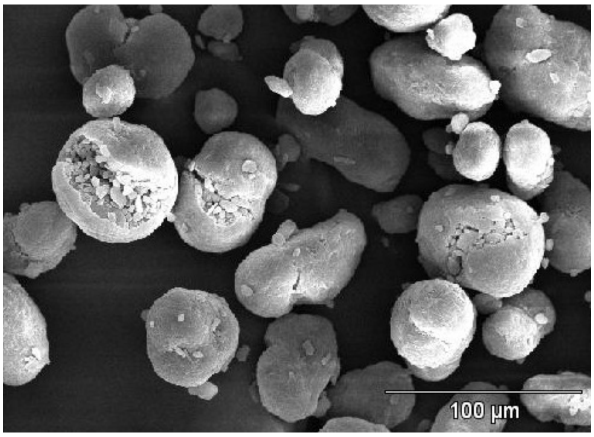

Figure 3. Image of PA-12 recycled obtained by SEM.

3.3. Proximate analysis

The average values of proximate analysis are described in Tab. 2. The obtained values for moisture and ash proportion signalizes for the applicability of residual PA-12 in thermal processes. The high proportion of volatile matter means a large conversion of this material in gas and tar, in the same way, the low value for ash means that, after the thermal degradation of polyamides, will remain just a few, or almost nothing, solid residue. These characteristics are fundamental to evaluate the behavior of PA-12 during the thermal treatment.

Table 2. Results of proximate analysis and standard deviation of PA2200 and DF12.

	Moisture[1] (%)	**Volatile matter (% d.b.)**	**Fixed carbon (% d.b.)**	**Ash (% d.b.)**
PA2200	0.77 ± 0.48	99.47 ± 0.11	0.17 ± 0.04	0.36 ± 0.08
DF12	0.85 ± 0.59	99.47 ± 0.11	0.19 ± 0.04	0.34 ± 0.08

[1]: Values calculated in wet basis. May change according local humidity and temperature.

3.4. Ultimate analysis

The results from ultimate analysis of PA-12 (Tab. 3) confirmed the homogeneity of the materials. The values of elementary fractions (C, H, N and O) obtained for PA2200 and DF12 shown insignificants variances.

Realizing a comparison between the obtained results of PA-12 and another synthetic polymer, as unsatured polyester (UP) studied by Da Silva (2005), can be observed that the element carbon constitutes around 75 % of the polyamides, in other way, the carbon represents around 40 % of UP. Even the UP having the others masses fractions bigger than PA-12, the UP has a fraction of inert material (ashes). By contrast, it does not happen with the polyamides (Fig. 4).

Table 3. Results and standards deviation of elementary analysis obtained for PA2200 and DF-12.

	C	H	N	O(1)
PA2200	72.26 ± 0.08	12.08 ± 0.06	7.14 ± 0.07	8.53 ± 0.08
DF12	72.21 ± 0.15	12.22 ± 0.01	7.19 ± 0.13	8.40 ± 0.01

(1): Calculated by difference.

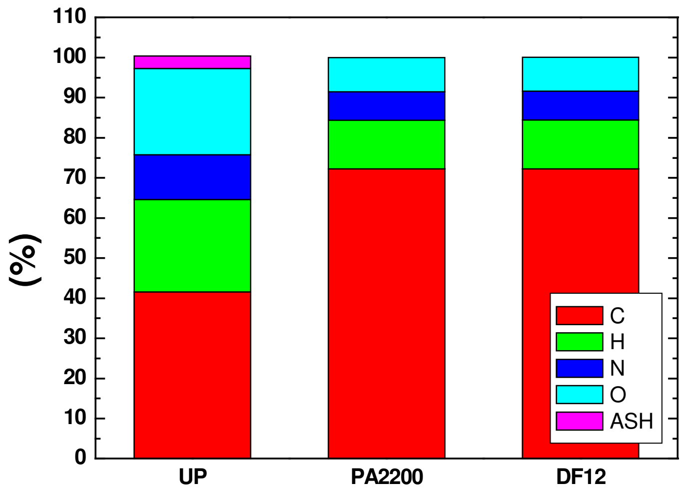

Figure 4. Comparison between ultimate analysis of unsatured polyester and polyamides.

3.5. High heating value

Table 4 shows HHV values found for polyamides. The obtained numbers are substantially elevated and very close to that found by others authors for different types of synthetics materials, as shown in Fig. 5.

However, even it having a good HHV, the thermal degradation of PA-12 may produce toxics gases as NH_3, HCN, CO, CO_2 and N_2, according Nielsen *et al*. (1995). The occurrence of these substances could mean the necessity of some kind of gas treatment during the process, if probed the applicability of PA-12 as industrial fuel.

Table 4. High heating value of polyamides and standard deviation.

	PA2200 (MJ/kg)	DF12 (MJ/kg)
Average HHV	**41.0 ± 0.5**	**43.8 ± 3.5**

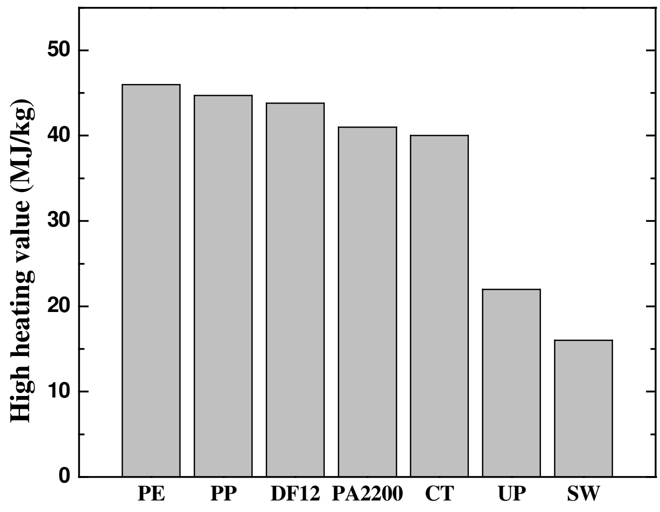

Figure 5. HHV of some synthetics materials: polyethylene (PE), Pinto *et al*. (2002); polypropylene (PP), Xiao *et al*. (2007); polyamides (DF12; PA2200); car tires (CT), Cunliffe e Williams (1998); unsatured polyester (UP), Da Silva (2005); solid waste (SW), Matsuzawa *et al*. (2007).

3.6. Thermogravimetric analysis

The thermal degradation of DF-12 and PA2200, obtained by TGA (Fig. 6), show that the mass losses, which represents the elimination of volatile matter (T_E), occurs between the temperature range of 230 °C and 390 °C and the DTA curves (Fig. 7), show that the conversion optimum temperature (T_0) is around 320 °C and 340 °C. The T_O temperature obtained for both polyamides are lower than that observed in the virgin material. It demonstrates the material properties losses when submitted to a heat. The polyamides DF12 and PA2200 showed similar behavior when submitted to heating. Herrera *et al*. (2001) described the conversion range between 350 °C and 475 °C. This discrepancy is probably due the heating rates used in each work (1, 5 and 10 °C min^{-1}, used by Herrera *et al*., 2001). They described that, in air atmosphere, the degradation of material occurs around temperatures of 400 °C and 480 °C and the weight loss is 2 %, higher than the degradation under nitrogen atmosphere.

Da Silva (2005) evaluating the thermal degradation of unsatured polyester with fiber glass obtained T_O between the range of 270 ºC and 380 °C, as function of heating rates employed. For the heating rate corresponding to 10 °C min^{-1}, the author found T_O of 300 °C, which is lower than the values obtained for PA-12. However, the corresponding T_E temperatures are more distant, as shown in Tab. 5. It means that the PA-12 are more thermally stable when compared to UP, needing more quantities of energy to realize its thermal degradation.

Table 5. Conversion optimum temperature (T_O) and volatile elimination limits temperature (T_E) of UP, PA2200 and DF12.

Material	T_O **(ºC)**	T_E **(°C)**
Unsatured Polyester	300	177 – 527
Polyamide PA2200	332	227 – 386
Polyamide DF12	333	237 – 395

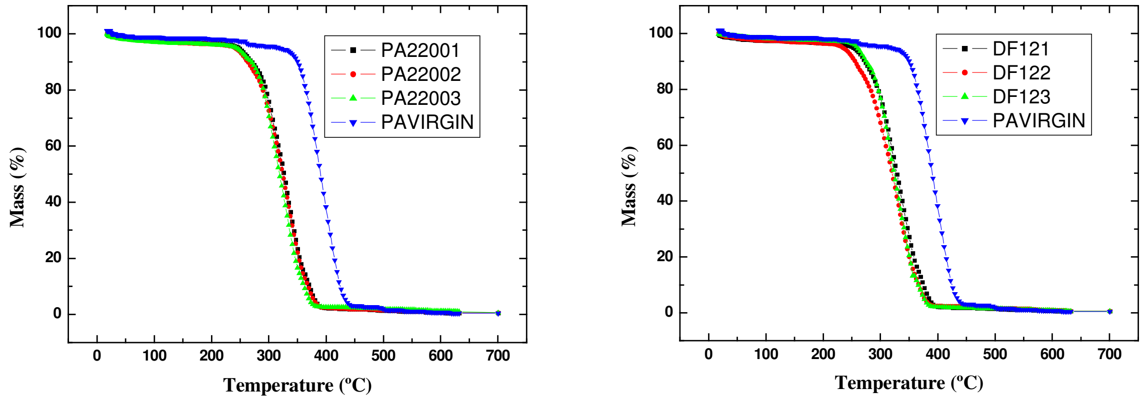

Figure 6. TGA of PA2200 e DF12.

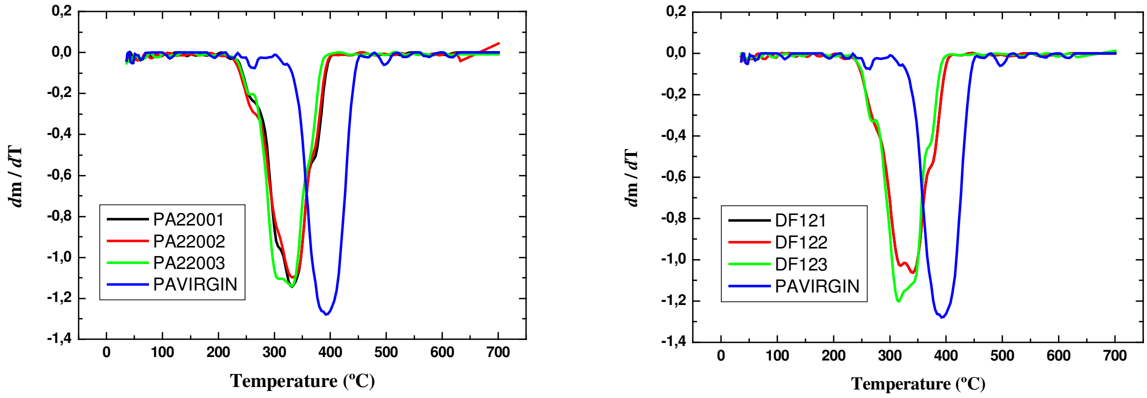

Figure 7. DTA of PA2200 e DF12.

4. CONCLUSIONS

The results obtained for volatile matter proportion, ash and HHV of polyamides makes them susceptible to thermal degradation. In all analyses the samples presented a similar behavior and were not observed several discrepancies between the results. It proved the homogeneity of PA-12, even when made-up for different companies and after submitted at SLS process. The characterization of investigated polyamides showed that the materials have a possible application as fuel in thermal processes. The next step consists in realize the pyrolysis of materials in bubbling fluidized bed, characterizing the gaseous and liquids products obtained and evaluating the applicability of these products, creating a cyclic process for utilization of the PA-12.

5. ACKNOWLEDGEMENTS

The authors wish to express their gratitude to CenPRA for the samples, to Capes for the financial support and Environmental Chemical Group of Chemical Institute of UNICAMP (DQA/IQ).

6. REFERENCES

3D Systems, 2001. “DuraForm PA and GF: Materials for SLS Systems”, Material Datasheet. 18 January, 2008 <http://www.3dsystems.com/products/datafiles/datasheets-1007/SLS/DS-DuraForm_PA_plastic_1207.pdf>.

ASTM Standard D2015. “Test Method for Gross Calorific Value of Coal and Coke by Adiabatic Bomb Calorimeter”. American Society for Testing and Materials, Philadelphia, USA.

ASTM Standard D3172-07a. “Standard Practice for Proximate Analysis of Coal and Coke”. American Society for Testing and Materials, Philadelphia, USA.

ASTM Standard D3173-03. “Standard Test Method for Moisture in the Analysis Sample of Coal and Coke”. American Society for Testing and Materials, Philadelphia, USA.
ASTM Standard D3174-04. “Standard Test Method for Ash in the Analysis Sample of Coal and Coke”. American Society for Testing and Materials, Philadelphia, USA.
ASTM Standard D3175-07. “Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke”. American Society for Testing and Materials, Philadelphia, USA.
Berry, E., Brown, J.M., Connell, M., Craven, C.M., Efford, N.D., Radjenovic, A. and Smith, M.A., 1997, “Preliminary Experience with Medical Applications of Rapid Prototyping by Selective Laser Sintering”, Medical Engineering and Physics, Vol.19, No. 1, pp. 90-96.
Bridgwater, A. V. and Bridge, S. A., 1991. “Biomass Pyrolysis Liquids Upgrading and Utilisation”. Ed. Elsevier, New York, 377p.
Cunliffe, A.M. and Williams, P.T., 1998. “Composition of Oils Derived from the Batch Pyrolysis of Tyres”, Journal of Analytical and Applied Pyrolysis, Vol.44, pp.131-152.
Czégény, Zs and Blazsó, M., 2001. “Thermal Decomposition of Polyamides in the Presence of Poly(Vinyl Chloride)”, Journal of Analytical and Applied Pyrolysis, Vol.58-59, pp. 95-104.
Da Silva, G.F., 2005. “Kinetic Study of the Pyrolysis of Unsatured Polyester with Fiberglass using Thermogravimetric Analysis and Bubbling Fluidized Bed”, Doctoral Thesis, Faculty of Mechanical Engineering, Campinas State University, Campinas, São Paulo, Brazil.
Dickens Jr., et al., 1994. “Method of Recovering Reciclable Unsintered Powder from the Part Bed of a Selective Laser-Sintering Machine”, U.S. Patent, No. 5,304,329.
Dimov, S.S., Pham, D.T., Lacan, F. and Dotchev, K.D., 2001. “Rapid Tooling Applications of the Selective Laser Sintering Process”, Assembly Automation, Vol.21, No. 4, pp. 296-302.
EOS GmBH, 2007, “Fine Polyamide PA2200 for EOSINT P”, Material Datasheet. 18 January 2008 <http://www.eos.info/products/plastic-laser-sintering/materials.html?L=1#c361>.
Gibson, I., Cheung, L.K., Chow, S.P., Cheung, W.L., Beh, S.L., Savalani, M. and Lee, S.H., 2006. “The use of Rapid Prototyping to Assist Medical Applications”, Rapid Prototyping Journal, Vol.12, No. 1, pp. 53-58.
Herrera, M., Matuschek, G. and Kettrup, A., 2001. “Main Products and Kinetics of the Thermal Degradations of Polyamides”, Chemosphere, Vol.42, pp. 601-607.
Howard, J.R., 1989. “Fluidized Bed Technologies: Principles and Applications”, Adam Hilger Publishers, Bristol, England, 214p.
Kruth, J.P., Wang, X., Laoui, T. and Froyen, L., 2003. “Lasers and Materials in Selective Laser Sintering”, Assembly Automation, Vol.23, No. 4, pp. 357-371.
Lohfeld, S., Barron, V. and McHugh, P.E., 2005. “Biomodels of Bone: A Review”, Annals of Biomedical Engineering, Vol.33, No. 10, pp. 1295-1311.
Matsuzawa, Y., Mae, K., Hasegawa, I., Suzuki, K., Fujiyoshi, H., Ito, M. and Ayabe, M., 2007. “Characterization of Carbonized Municipal Waste as Substitute for Coal Fuel”, Fuel, Vol.86, pp. 264-272.
Nielsen, M., Jurasek, P., Hayashi, J. and Furimsky, E., 1995. “Formation of Toxic Gases during Pyrolysis of Polyacrylonitrile and Nylons”, Journal of Analytical and Applied Pyrolysis, Vol.35, pp. 43-51.
Pham, D.T. and Gault, R.S., 1998. “A Comparision of Rapid Prototyping Technologies”, International Journal of Machine Tools & Manufacture, Vol.38, pp. 1257-1287.
Pinto, F., Franco, C., André, R.N., Miranda, N., Gulyurtlu, I. and Cabrita, I., 2002. “Co-gasification Study of Biomass Mixed with Plastic Wastes”, Fuel, Vol.81, pp. 291-297.
Rosa, E.L.S., Oleskovicz, C.F. and Aragão, B.N., 2004. “Rapid Prototyping in Maxillofacial Surgery and Traumatology: Case Report”, Braz. Dent. J., Vol.15, No. 3, pp. 243-247.
Upcraft, S. and Fletcher, R., 2003. “The Rapid Prototyping Technologies”, Assembly Automation, Vol.23, No. 4, pp. 318-330.
Welgos, R.J., 1985. “Polyamides, Plastics”, Encyclopedia of Polymer Science and Engineering, 2ed., John Willey and Sons, Vol.11, pp. 445-475.
Xiao, R., Jin, B., Zhou, H., Zhong, Z. and Zhang, M., 2007. “Air Gasification of Polypropylene Plastic Waste in Fluidized Bed Gasifier”, Energy Conversion and Management, Vol.48, pp. 778-786.

7. RESPONSABILITY NOTICE

The authors are the only responsible for the printed material included in this paper.