Acta Scientiarum
http://www.uem.br/acta
ISSN printed: 1806-2563
ISSN on-line: 1807-8664
Doi: 10.4025/actascitechnol.v37i3.25056

Synthesis of carboxylate complexes and evaluation of their catalytic activities for polyesterification of castor oil (*Ricinum communis*) with terephthalic acid

Eduardo Ulisses Xavier Peres[1], Alexandre Perez Umpierre[2] and Paulo Anselmo Ziani Suarez[2*]

*[1]Instituto Federal de Educação, Ciência e Tecnologia de Brasília, Campus Taguatinga, Brasília, Distrito Federal, Brazil. [2]Universidade de Brasília, Instituto de Química, Cx. Postal: 4478, 70919-970, Brasília, Distrito Federal, Brazil. *Author for correspondence. E-mail: psuarez@unb.br*

ABSTRACT. The use of castor oil (Ricinus communis) has been pointed out as an interesting alternative to produce several polymers obtained from step-growth polymerization and are suitable to be used as resins and coatings. The ricinoleate metal complexes $Ni[C_{17}H_{34}(OH)COO]_2$, $Sn[C_{17}H_{34}(OH)COO]_2$, $Co[C_{17}H_{34}(OH)COO]_2$ and $Fe[C_{17}H_{34}(OH)COO]_2$ have been prepared and used as catalyst precursors for polyesterification of castor oil and terephthalic acid (TFA). The observed catalytic activity decreased in the order: $Fe[C_{17}H_{34}(OH)COO]_2 > Co[C_{17}H_{34}(OH)COO]_2 > Sn[C_{17}H_{34}(OH)COO]_2 > Ni[C_{17}H_{34}(OH)COO]_2$. The new polymeric materials did not show homogeneity in their chains, as indicated by their high polydispersity. Indeed, the polydispersity index value varied from 5.49 for the polymer produced in the presence of the nickel complex to 12.42 for these prepared with the cobalt compound. On the other hand, the final material presented high molecular weight, being the lower value (M_w = 13400 Da) observed for the polymer prepared with the nickel complex and the highest (M_w = 36400 Da) verified for the one obtained with the cobalt compound. It was observed only a glass transition temperature for all the materials, suggesting an amorphous structure of polymeric chains.

Keywords: polyester, step-growth polymerization, ricinoleate metal complexes, homogeneous Catalysis.

Síntese de complexos de carboxilatos e avaliação da atividade catalítica para poliesterificação de óleo de mamona (*Ricinum communis*) com ácido tereftálico

RESUMO. O uso de óleo de mamona (Ricinus communis) tem sido apontado como uma alternativa interessante para a produção de vários polímeros via polimerização em massa e são adequados para serem utilizados como resinas e revestimentos. Complexos metálicos de ricinoleato ($Ni[C_{17}H_{34}(OH)COO]_2$, $Sn[C_{17}H_{34}(OH)COO]_2$, $Co[C_{17}H_{34}(OH)COO]_2$ e $Fe[C_{17}H_{34}(OH)COO]_2$) foram preparados e usados como catalisadores para a poliesterificação do óleo de mamona e ácido tereftálico (TFA). Observou-se que a atividade catalítica decresce na seguinte ordem: $Fe[C_{17}H_{34}(OH)COO]_2 > Co[C_{17}H_{34}(OH)COO]_2 > Sn[C_{17}H_{34}(OH)COO]_2 > Ni[C_{17}H_{34}(OH)COO]_2$. O material polimérico produzido não apresenta homogeneidade em suas cadeias, indicado por sua alta polidispersidade. De fato, a polidispersidade variou de 5,49, para polímeros produzidos a partir de complexos de níquel, até 12,42 para polímeros produzidos com complexo de cobalto. Por outro lado, o material produzido apresenta alto peso molecular médio, sendo o menor valor (M_w = 13.400 Da) para materiais produzidos com complexo de níquel e maior valor (M_w = 36.400 Da) para materiais obtidos com complexos de cobalto. Observou-se apenas uma transição vítrea para todos os materiais produzidos, sugerindo estrutura amorfa para os polímeros produzidos.

Palavras-chave: poliéster, polimerização em massa, complexos metálicos de ricinoleato, catálise homogênea.

Introduction

Polymeric materials obtained from vegetable oils, particularly castor oil, have been used as binder in paints, coatings and inks for many years. Recently, the increasing cost of petrochemicals has raised the search for alternate raw materials to produce polymers (ERHAN; BAGBY, 1991; NIROOMAND et al., 1996) in special polymerization of vegetable oils (DUTTA et al., 2004; FERREIRA et al., 2007; SOMANI et al., 2003; SUAREZ et al., 2007; YEGANEH; MEHDIZADEH, 2004) or biomass processing residues (SUAREZ et al., 2008). These biopolymers have been described not only as binder for coatings (YEGANEH; REZA, 2007), but also for adhesives (SOMANI et al., 2003) and prosthesis (IGNÁCIO et al., 1997; REZENDE et al., 2001).

Vegetable oils are mainly composed by tri-esters of fatty acids and glycerin. The fatty acid chain of the ricinoleic acid contains 18 carbons and presents an hydroxyl group in the position 12 and a double bond in the position 9 and corresponds to ca. 90% of the composition of castor seeds oil (OGUNNIYI, 2006). Due to this composition, castor seed oil has a great potential as starting material to produce polymers (TRUMBO; TREVINO, 2002), which are suitable to be used as binder for paints, coatings and inks (PATEL et al., 2006; SOMANI et al., 2003; YEGANEH; REZA, 2007). The most of these studies describes the use castor oil as raw material for polyurethanes synthesis. However, interesting polyester materials have been reported using castor oil, such as: (i) resins after its transesterification with depolymerized post-consumer PET (PATEL et al., 2006); and (iii) co-polyesters suitable to use for drug delivery based on L- or DL-Lactic acid and castor oil (SOKOLSKY-PAPKOV; DOMB, 2008) or ricinoleic acid and poly-sebacic acid (KRASKO et al., 2003). Nonetheless, as far as our knowledge, no attempts have been done in order to use castor oil as tri-alcohol to obtain polyesters by its direct polyesterification with poly-acids.

In polycondensation is preferred catalyzed systems (ISHIHARA et al., 2002; LIGABUE et al., 1998; TAKASU et al., 2003). The most common methods for polyesterification use strong Bronsted or Lewis acid catalysts, usually using large excess of either carboxylic acid or alcohol monomer in order to achieve high reaction yields (OLAH et al., 1978). Because of their less corrosivity, Lewis acid catalysts are preferred. In this sense, several Lewis acid metal complexes have been utilized as catalysts for polyesterification (PARSHALL; ITTEL, 1992). An industrial examples are tin (IV) based compounds FASCAT® and LIOCAT®, which are largely used for the alcoholysis of vegetable oils with poly-alcohols to prepare alkyd resins (SUAREZ et al., 2007).

We have recently used castor oil fatty acids to obtain polyesters and also to produce composites using magnetic nanoparticules (PERES et al., 2014). Indeed, because of the presence of a hydroxi group and an acid group in ricinoleic acid, it was possible to obtain linear polyesters by its direct polyesterification. It is important to highlight that during this study we observed that there was a catalytic activity of the nanoparticles, probably due to the presence of iron cations.

In the present work, we describe the direct polycondensation of castor oil with terephthalic acid (TFA) catalyzed by different ricinoleate complexes using bi-valent Lewis metal cations in order to evaluate their catalytic activity. It was also studied some physical-chemical properties of the different polymeric materials obtained in order to evaluate their potential use in the paint and coating industry.

Material and methods

Solvents, terephthalic acid (TFA), metal halides and others chemicals were obtained either from Merck, Vetec or Acros, and used without further purification. Castor oil was obtained from Celtic LTDA (São Paulo State, Brazil) and used as received.

Synthesis of the complexes

A fatty acids mixture containing up to 90% of ricinoleic acid was obtained through saponification of castor oil followed by acidification with hydrochloridric acid. The mixture was washed three times with water, dissolved in dichloroetane, dried with magnesium sulfate, filtered and the final fatty acids isolated by flash distillation to remove the volatiles (MELLO et al., 2011).

The ricinoleic acid (0.01 mol) and sodium or potassium hydroxide (0.01 mol) were added to a 30 mL of distilled water to produce an aqueous solution of the corresponding salt. This mixture was dropped to distilled water solutions of tin (II), iron (II), nickel (II) or cobalt (II) chlorides (0.0125 mol) and kept stirring for 2h at 343 K producing different insoluble complexes. These compounds were filtered and washed with distilled water to take out the starting soluble salts and then dried until constant weigh. The resulting reaction yields for ricinoleate metal complexes were: 65.10% for Sn, 47.43% for Fe, 55.85% for Ni and 40.43% for Co. The metal content of the final complexes were checked by Thermogravimetry (Shimadzu DTG-60) and were in very good agreement with the theoretical value. Infrared analysis (KBr pellets): (i) Sn: 3397.06 (νO–H), 1550 ($\nu\mathrm{C}\overset{\cdots}{-}\mathrm{O}$), 3009.85 (ν =C–H); (ii) Fe: 3448.57 (νO–H), 1560.51 ($\nu\mathrm{C}\overset{\cdots}{-}\mathrm{O}$), 3010.45 (ν =C–H); (iii) Ni: 3448.57 (νO–H), 1561.13 ($\nu\mathrm{C}\overset{\cdots}{-}\mathrm{O}$), 3009.42 (ν =C–H); (iv) Co: 3417.63 (νO–H), 1563.12 ($\nu\mathrm{C}\overset{\cdots}{-}\mathrm{O}$), 3009.41 (ν =C–H).

Polymerization reactions

Polymerization was carried out in a 1 L reactor system consisting of a five necked round-bottom flask. The flask was equipped with a mechanical stirring, a thermocouple, nitrogen inlet tube and adjacent partial reflux condenser. The monomers TFA and castor oil in the proportion 3:2, respectively, and the ricinoleate metal complex were added to the flask and heated using an electrical heating mantle connected to the automatic controller setted at 523 K and connected to a Pt 100 thermocouple inserted in the reaction bulk. It is important to highlight that according to the literature, the thermal degradation of the castor oil occurs above 623 K (LIMA et al., 2004). The stirrer is adjusted to 100 RPM. Samples were collected every two hours and their acid index (AI) was determined according to ASTM D 465-9 (1996). The reaction was stopped when the acid index stabilized and then dropped to a glass tray.

Material analysis

Fourier Transformer Infra-Red (FTIR): The FTIR-ATR, spectra was obtained on an Equinox 55 Fourier transform instrument from Bruker. The FTIR-ATR spectra were recorded using a NaCl cell, using a DTGS detector. Each spectra data were obtained using a 4 cm^{-1} of nominal resolution and it was a averaging of 32 scans.

Nuclear Magnetic Resonance (NMR): The ^1H (300 MHz) NMR spectra was recorded in a Varian Mercury Plus M300 spectrophotometer using $CDCl_3$ as solvent.

Differential scanning calorimetry (DSC): Determinations were performed in a TA Instruments DSC-2010 (T_{star}: – 100°C, T_{end}: + 100°C, heating rate: 20°C $min.^{-1}$ in N_2).

Size exclusion chromatography (SEC): The molecular weights were measured using the equipments Waters 410 Differential Refractometers, operating at 45°C, equipped with a ultra tyragel linear column (7.8 x 300 mm) from Waters using THF as solvent with 1.0 mL $min.^{-1}$ flowing rate.

Results and discussion

Catalytic polymerization

Four complexes of the type $M^{+2}(ricinoleate^{-1})_2$ were prepared and their catalytic activity in cartor oil polyesterification with TFA was evaluated, and the results are summarized in Table 1.

Table1. Castor oil and terephthalic acid direct and assisted by different $M^{+2}(ricinoleate^{-1})_2$ complexes polyesterification.

Entry	Catalyst	Reaction time (min.)	Acid value*	Water (g)
1	No catalyst	840	145	5.0
2	$Ni^{+2}[C_{17}H_{34}(OH)COO^{-1}]_2$	480	143	5.2
3	$Sn^{+2}[C_{17}H_{34}(OH)COO^{-1}]_2$	360	132	5.1
4	$Co^{+2}[C_{17}H_{34}(OH)COO^{-1}]_2$	240	124	3.9
5	$Fe^{+2}[C_{17}H_{34}(OH)COO^{-1}]_2$	240	118	4.6

*Starting acid value (at t = 0 min.): 245.22. Reaction conditions: temperature 523 K; Castor oil /terephthalic acid/complex = 200 g / 50 g / 0.57 g.

As can be depicted from Table 1, in the absence of metal complex (entry 1 of Table 1), it was observed the formation of esters in low reaction yield, evidencing a self-catalyzed reaction promoted by TFA probably because of its weak Bronsted-Lowry acidity. Nonetheless, except for the nickel complex, the use of metal complexes leaded to better yields when compared to the auto-catalyzed reaction, indicating their catalytic activity. This results can be better visualized in Figure 1, where is plotted the acid values for different times during the polymerization. It is worth to mention that the observed catalytic activity of the metal increases in the same order of their Lewis acidity (PARSHALL; ITTEL, 1992).

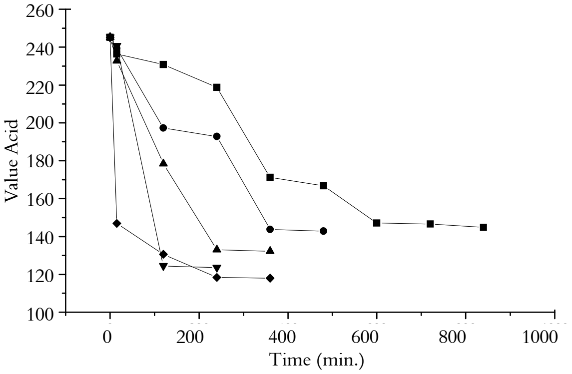

Figure 1. Acid value versus reaction time during polyesterification of castor oil with TFA in the absence (■) and presence of ricinoleate complexes of Ni II (●), Sn II (▲), Co II (▼) and Fe II (◆).

Resin characterization

A comparison of the infrared spectra of castor oil, TFA and the different obtained materials is showed in Figure 2. TFA spectra shows broad band in the region between 2500 and 3300 cm^{-1}, characteristic of carboxylic acids and attributed to O-H stretching (LIMA et al., 2004), and a band in 1701 cm^{-1} related to the C=O stretching. After the polyesterification, this broad band disappears and the band in 1701 cm^{-1} was dislocated to 1720 cm^{-1}. It is also possible to note that the O-H stretching related to the hydroxyl group of castor oil observed in 3422 cm^{-1} seems to have also disappeared from the spectra after the polymerization. Other important new band in the polymer spectra appears in 1266 cm^{-1}, probably related to C–O stretching in aromatic esters (SILVERSTEIN et al., 2000). These observations strongly indicate the esterification of TFA with hydroxyl groups from castor oil. In the castor oil spectra appears in 1750 cm^{-1} a strong stretching of the C=O related to fatty acids and glycerol ester groups. After the reaction, this band is maintained and a shoulder appears in low wavenumber, suggesting that the original acil esters are maintained and a new different ester group was formed.

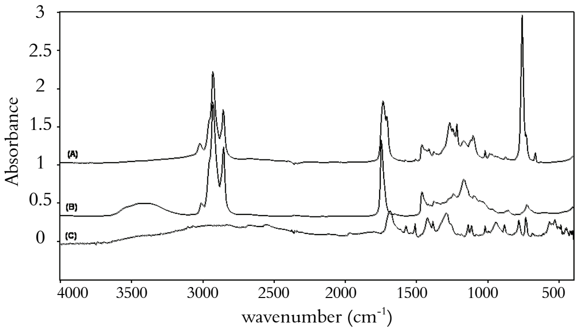

Figure 2. Infrared spectra of the Polymer (A), Castor oil (B) and TFA (C).

The formation of the polyesters was also confirmed by ^{1}H-NMR analysis. It was observed a peak at δ = 8.0-9.0 ppm, indicating the presence of aromatic hydrogens related to TFA. It was also observed a peak at δ = 1.25-1.30 ppm and at δ = 5.33-5.35 ppm aliphatic C-H stretching and at δ = 4.1-4.3 ppm corresponding to glycerol C-H stretching, usually observed for vegetable oils [4].

The average molecular weight values were determined for the different materials by SEC and were listed in Table 2. A high polydispersity were observed in all cases and an important M_w variation was observed according to the catalyst used. Indeed, the M_w varied from 24300 Da when no catalyst was used to 36400 Da for the polymer prepared in the presence of Co(ricinoleate)$_2$.

Table 2. The average molecular weights, polydispersity and glass transition temperature of the different materials prepared after polyesterification of TFA with castor oil in the absence (A) and presence of Ni^{+2} (B), Sn^{+2} (C), Co^{+2} (D) and Fe^{+2} (E) ricinoleate complexes.

Material	M_n (Da)	M_w (Da)	Polydispersity	T_g (°C)
A	2,700	24,300	9.07	– 49,23
B	2,700	33,700	12.43	– 79,83
C	3,600	32,500	8.95	– 57,47
D	2,900	36,400	12.42	– 79,54
E	2,500	34,100	13.60	– 79,09

The polymers were also analyzed by Differential Scanning Calorimetric (DSC). For all polymers were obtained similar profiles and, as an example, Figure 3 shows the results obtained for the materials prepared in the presence of Ni(ricinoleate)$_2$ (Figure 3A) and in the absence of any complexe (Figure 3B). As can be depicted from Figure 3, no melting point were observed, but only glass transitions in the temperature range from – 80 and – 40°C, suggesting a no-crystalline structure.

The glass transition temperatures for the different materials are listed in Table 2. It becomes clear from Table 2 that, as observed for the average molecular weights, the catalyst used in the process has a great influence in glass transition temperature. It is also clear that there is a good correlation between the glass transition temperature and the average molecular weights and polydispersity of the polymer, indicating that the noncrystallinity of the material increases with the average molecular weight and the dispersity of the chains size. A good explanation for these results is the relation between the polymeric chain growth and its molecular organization. The smaller and less polydisperse polymers are easily organized and for a better molecular organization of the biggest chains is necessary more energy release. On the other hand, polymeric chains will have less movement with less temperature. This result was particularly expected due to the crosslink in the chains during the polyester formation using a tri-alcohol and a di-carboxylic acid.

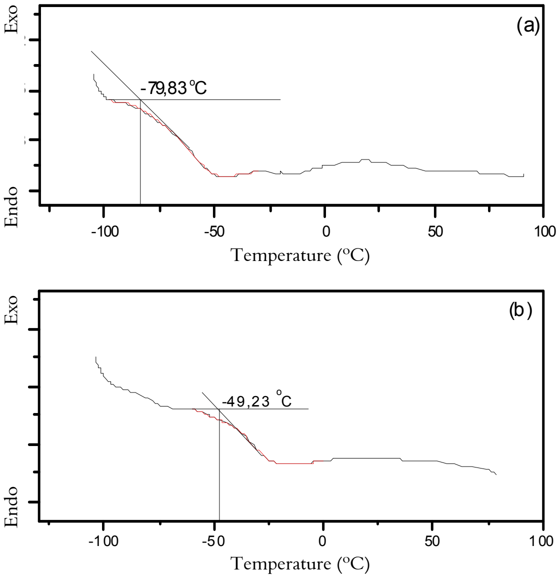

Figure 3. DSC analysis of the polymers obtained with Ni(ricinoleate)$_2$ (a) and without catalyst (b).

Conclusion

We prepared polyesters from castor oil and terephthalic acid in the presence and absence of different ricinoleate metal complexes and the ester formation was confirmed by IR and NMR spectroscopy. It was observed that in the presence of the complexes the reaction velocity was increased and that the iron II complex has more active. The materials prepared showed none crystallinity, high molecular weight and a high polydispersity and only a glass transition (T_g). It is important to emphasize that these properties make these polymers suitable to be used when no rigid materials are desired, such as coatings, sealings, and others.

Acknowledgements

Procad-CAPES and INCT-Catálise for financial support. PAZS thanks CNPq for research fellowship.

References

DUTTA, N.; KARAK, N.; DOLUI, S. K. Synthesis and characterization of polyester based on Nahar seed oil. **Progress in Organic Coating**, v. 49, n. 2, p. 146-152, 2004.

ERHAN, S. Z.; BAGBY, M. O. Lithographic and letterpress ink vehicles from vegetable-oils. **Journal American Oil Chemists Society**, v. 68, n. 9, p. 635-638, 1991.

FERREIRA, P.; PEREIRA, R.; COELHO, J. F. J.; SILVA, A. F. M.; GIL, M. H. Modification of the biopolymer castor oil with free isocyanate groups to be apllied as bioadhesive. **International Journal of Biological Macromolecules**, v. 40, n. 2, p. 144-152, 2007.

IGNÁCIO, H.; BARBIERI, C. H.; MAZZER, N.; CHIERICI, G. Uso da poliuretana derivada do óleo de mamona para preencher defeitos ósseos diafisários segmentares do rádio. **Revista Brasileira de Ortopedia**, v. 32, n. 10, p. 815-821, 1997.

ISHIHARA, K.; NAKAYAMA, M.; OHARA, S.; YAMAMOTO, H. Direct ester condensation from a 1:1 misture of carboxylic acids and alcohols catalyzed by hafnium(IV) or zirconium(IV) salts. **Tetrahedron**, v. 58, n. 41, p. 8179-8188, 2002.

KRASKO, M. Y.; SHIKANOV, A.; EZRA, A.; DOMB, A. J. Poly(ester anhydride)s prepared by the insertion of ricinoleic acid into poly(sebacic acid). **Journal of Polymer Science Part A: Polymer Chemistry**, v. 41, n. 8, p. 1059-1069, 2003.

LIGABUE, R. A.; MONTEIRO, A. L.; SOUZA, R. F.; SOUZA, M. O. Catalytic properties of Fe(acac)(3) and Cu(acac)2 in the formation of urethane form a diisocyanate derivate and EtOH. **Journal of Molecular Catalysis A: Chemical**, v. 130, n. 1-2, p. 101-105, 1998.

LIMA, G.; SOARES, V. C. D.; RIBEIRO, E. B.; CARVALHO, A. D.; CARDOSO, E. C. V.; RASSI, F. C.; MUNDIM, K. C.; RUBIM, J. C.; SUAREZ, P. A. Z. Diesel-like fuel obtained by pyrolysis of vegetable oils. **Journal of Analytical and Applied Pyrolysis**, v. 71, n. 2, p. 987-996, 2004.

MELLO, V. M.; POUSA, G. P. A. G.; PEREIRA, M. S. C.; DIAS, I. M.; SUAREZ, P. A. Z. Metal oxides as heterogeneous catalysts for esterification of fatty acids obtained from soybean oil. **Fuel Processing Technology**, v. 92, n. 1, p. 53-57, 2011.

NIROOMAND, A.; SCHUMAN, T. P.; THAMES, S. F. Hydroxylated guayule rubber in powder coatings. **Journal of Coating Technology and Research**, v. 68, n. 863, p. 15-20, 1996.

OGUNNIYI, D. S. Castor oil: industrial raw material. **Bioresource Technology**, v. 97, n. 9, p. 1086-1091, 2006.

OLAH, G. A.; KEUMI, T.; MEIDAR, D. Synthetic method and reactions. Convenient and improved method for esterification over nafion-H2. A superacidic perfluorinated resinsulfonic acid catalyst. **Synthesis-Stuttgart**, v. 12, p. 929-930, 1978.

PARSHALL, G. W.; ITTEL, S. **Homogeneous Catalysis**: the applications and chemistry of catalysis by soluble transition metal complexes. 2nd ed. New York: John Wiley and Sons, Inc., 1992.

PATEL, M. R.; PATEL, J. V.; SINHA, V. K. Glycolyzed PET waste and castor oil-based polyols for two-pack coating systems. **Polymer International**, v. 55, n. 11, p. 1315-1322, 2006.

PERES, E. U. X.; JUNIOR, F. G. S.; SILVA, F. M.; CHAKER, J. A.; SUAREZ, P. A. Z. Biopolyester from Ricinoleic Acid: Synthesis, Characterization and Its Use as Biopolymeric Matrix for Magnetic Nanocomposites. **Industrial Crops and Products**, v. 59, p. 260-267, 2014.

REZENDE, C. M. F.; SILVA, M. C.; LARANJEIRA, M. G.; BORGES, A. P. G. Estudo experimental do poliuretano de óleo de mamona (*Ricinus communis*) como substituto parcial do tendão calcâneo comum em coelhos (Oryctolagus cuniculus). **Arquivo Brasileiro de Medicina Veterinária e Zootecnia**, v. 53, n. 6, p. 695-700, 2001.

SILVERSTEIN, R. M.; BASSLER, G. C.; MORRIL, T. C. **Spectrometric Identification of Organic Compounds**. 6th ed. New York: John Wiley and Sons, Inc., 2000.

SOKOLSKY-PAPKOV, M.; DOMB, A. J. Stereoisomeric effect on in vitro drug release from injectable poly(lactic acid co castor oil) polyesters. **Polymers for Advanced Techologies**, v. 19, n. 6, p. 671-679, 2008.

SOMANI, K. P.; KANSARA, S. S.; PATEL, N. K.; RAKSHIT, A. K. Castor oil based polyurethane adhesives for wood-to-wood bonding. **International Journal of Adhesion and Adhesives**, v. 23, n. 4, p. 269-275, 2003.

SUAREZ, P. A. Z.; MENEGHETTI, S. M. P.; MENEGHETTI, M. R.; WOLF, C. R. Transformation of triglycerides into fuels, polymers and chemicals: Some applications of catalysis in oleochemistry. **Química Nova**, v. 30, n. 3, p. 667-676, 2007.

SUAREZ, P. A. Z.; EINLOFT, S.; BASSO, N. R. S.; FERNANDES, J. A.; MOTTA, L.; AMARAL, L. C.; LIMA, D. G. The use of crude tall oil as feed-stock for alkyl resins. **E-polymers**, v. 8, n. 1, p. 662-669, 2008.

TAKASU, A.; OISHI, Y.; IIO, Y.; INAI, Y.; HIRABAYASHI, T. Synthesis of aliphatic polyesters by direct polyesterification of dicarboxylic acids with diols under mild conditions catalyzed by reusable rare-earth triflate. **Macromolecules**, v. 36, n. 6, p. 1772-1774, 2003.

TRUMBO, D. L.; TREVINO, A. S. Acetoacetylated castor oil in coatings applications. **Progress in Organic Coating**, v. 44, n. 1, p. 49-54, 2002.

YEGANEH, H.; MEHDIZADEH, M. R. Synthesis and properties of isocyanate curable millable polyurethane elastomers based on castor oil as a renewable resource polyol. **European Polymer Journal**, v. 40, n. 6, p. 1233-1238, 2004.

YEGANEH, H.; REZA, M. H. Novel polyurethane electrical insulator coatings based on amide-ester-ether polyols derived from castor oil and re-cycled poly(ethylene terephthalate). **High Performance Polymers**, v. 19, n. 1, p. 113-126, 2007.

Received on September 24, 2014.
Accepted on January 23, 2015.