Introduction The use of renewable raw materials constitutes a significant contribution to a sustainable development in the plastics production. This strategy is based on the advantages given by Nature synthesis potential and Green Chemistry principles. In this sense, polymers obtained from renewable raw materials have raised some interest in the last years. The development of polymers synthesized from agricultural products, such as starch, cellulose, sugars or lignin has been considerably increased in the last two decades [1]. Amongst all the possible natural sources for polymers, vegetable oils are considered one of the cheapest and abundant in Nature [2]. They can be used as an advantageous chemical platform to polymer synthesis, by their inherent biodegradable condition and low toxicity to humans and the environment. In this context, many efforts are currently going on to propose a great variety of chemical methods to prepare thermoplastics and thermosets based on vegetable oils. This wide range of chemical methods applicable to these natural materials gives rise to many different monomers and polymers with many applications. Fatty acids are the major chemical entities present in vegetable oils. They are valuable compounds to design specific monomers in the search of polymers with particular properties without any need of important modifications in their native structure. This is an advantageous issue, not only in sustainability terms, but also in industrial applicability and competitiveness in terms of cost and properties [2-5]. Vegetable oils are mainly formed by triglycerols or triglycerides, mainly composed by three fatty acids bonded to a glycerol molecule. Fatty acids constitute 94-96 % of the total triglycerides weight in a vegetable oil and the number of carbon units in their structure is normally between 14 and 22, with zero to three double bonds by fatty acid molecule. The contents in fatty acids in some of the most common vegetable oils are indicated in Table 1. The use of fatty acids and vegetable oils either in polymer synthesis or as additives comes from some decades, not only by the raising interest in the search for alternatives to fossil fuels but also by the particular chemical characteristics that make them adequate for polymerization processes. Triglycerides are molecules with low reactivity and this fact is a disadvantage in their potential application in polymer synthesis. Nevertheless, the introduction of different functionalities in their reactive sites increases largely the synthetic possibilities of triglycerides [3]. At least three different uses of vegetable oils in polymer formulations can be proposed: (i) as polymer additives (plasticizers, stabilizers, etc); (ii) as building blocks to get polymers from them; and (iii) as units for the thermosets synthesis. Much work on the use of vegetable oils as additives [6-11] and as thermosets precursors [12-18] has been reported, but the development of thermoplastic polymer matrices is still in an early stage of research. Thermoplastics can be easily processed and recycled giving them possibilities in many different applications. The synthesis of thermoplastics from vegetable oils is still in an early stage of the study and development because of the experimental difficulties to be afforded to get reasonable yields in this process. It is known that thermosets obtained from vegetable oils have been largely studied with

many reported work [12-22]. This fact is partially due to the own composition of vegetable oils, formed by triglycerides containing different fatty acids with variable number of chain instaurations. Thus, seeds oils are rich in poly-unsaturated fatty acids, giving highly reticulated, rigid and temperature resistant materials [21]. The carbon chains forming the oils can be easily crosslinked by their double bonds. As indicated in Table 1, it can be concluded that most seed oils have fatty acids with 2 or 3 unsaturated bonds as the main component in their lipid profile, except castor, olive and rapeseed oils, which show a mono-unsaturated fatty acid as their main component. Therefore, thermosets can be easily synthesized from oils rich in poly-unsaturated fatty acids, such as those from soya, sunflower or linseed getting polymers with high mechanical and thermal resistance. Castor oil shows high content in ricinoleic acid (87.5 % in total oil weight) and the active site is occupied by an alcohol, while olive and rapeseed oils show a main content in mono-unsaturated oleic acid (71.1 and 60.9 % in total oil weigh, respectively). It is known that the potential monomers or polymer building blocks should have at least one (in the case of addition polymerization) or two double bonds in their structure (in the case of condensation polymerization) to get thermoplastic materials. Therefore, triglycerides should be modified of functionalized before polymerization. Nevertheless, there are some examples of thermoplastic biomaterials obtained from naturally functionalized castor oil with homogeneous composition and acceptable polymerization yields. The main thermoplastic materials already synthesized from vegetable oils are thermoplastic polyurethanes (TPUs), polyamides (PA), thermoplastic polyesters, polyesteramides and polyanhydrides. TPUs: chemistry, structure and properties Polyurethanes are generally synthesized by addition polymerization between a polyalcohol and a poly-isocyanate. This is an exothermic reaction caused by the release of a proton from the alcohol group followed by a general molecular rearrangement by the formation of the urethane bond. [23]. If both reagents are bi-functional linear polyurethanes are obtained, while if functionalities are increased some crosslinked chains are formed, with the formation of reticulated structures. In summary, one of the most common synthesis routes for TPUs consists basically of the reaction of three main components. 1. Polyols with polyester or polyether functionalities with hydroxyl end groups. 2. Di-isocyanate 3. Short-chain diol or diamine used as chain extender. The clear differences in the structure of all these components are essential to get the final properties of the synthesized thermoplastic polyurethanes. TPUs are block copolymers with (AB)n segmented structure formed by hard and soft blocks. Soft segments correspond to the elastomeric part of the polymer (polyester chains from the polyol) and they are characterized by a glass transition temperature much lower than ambient, which gives them high flexibility. This is the reason why these parts of the polyurethane are known as the soft block. On the other hand, hard segments are formed by the di-isocyanate and the chain extender forming a rigid structure, mainly formed by the urethane group bonded to aromatic rings. Therefore, some heterogeneity between both blocks in

polyurethanes, the hard segment (with high polarity and melting point) and the soft segment (non-polar and low melting point), should be expected, leading to phase separation in the copolymer structure, as presented in Figure 1 [24,25]. However, the phase separation is not complete in TPUs at the molecular scale, and it is possible to find soft segments inside the hard region and vice-versa (Figure 2), as was reported by Tawa et al. [26]. They indicated that urethane groups from neighbour chains could form hydrogen bonds very easily. This inter-molecular bonding leads to the formation of aggregates acting as physical reticulation nodes with crystalline regions dispersed into the soft area in the polymer structure. This would lead to crosslinking with the final result of the increase in the overall rigidity in the TPU. The phase separation between hard and soft segments depends on, among other factors, their affinity, their relative mobility, the chain extender and the isocyanate structural symmetry [25]. Fig. 1 - Segmented structure of a thermoplastic polyurethane TPU structures are generally linear, since the relative amount of hard segments is small. Therefore, the most relevant properties of these polymers are conditioned by the secondary and inter-molecular interactions (mainly Van der Waals) between the soft segments [24,27]. The elastic properties of polyurethanes mainly depend on the polyol chains mobility, which is dependent on their chemical nature and length of the soft segments. The higher the molar mass of the soft segments, the higher tensile strength and elongation to break and consequently the more flexible TPU [24,25]. Fig. 2 - Polyurethane biphasic structure at molecular scale [26], with permission On the other hand, when the hard segment content is high, the plastic deformation and the polymer general softening are observed after the application of mechanical stresses at high temperature. The thermal stability of polyurethanes is determined by the temperature range where the rigid segments start to melt and consequently their phase separation and their segmented structure. Polyurethanes will show thermoplastic behaviour at higher temperatures than the melting point of the hard regions [28]. Another important feature of the hard/soft ratio in TPUs is the decrease of molar masses and low phase separation in polymers with high values of that ratio, conditioning their rheological and mechanical properties, giving rise to more rigid materials. In addition, the isocyanate structure also influences the final TPU properties. High-volume di-isocyanates lead to polyurethanes with high elastic modulus and tensile strength [25]. The development of TPUs from vegetable oils is the main goal of this study. In the next sections some work performed by our research group for TPUs synthesized from rapeseed oil dimer fatty acids is presented. Experimental Materials The bio-based polyester polyol used in this study was kindly supplied by Croda (Yorkshire, UK) and it is based on dimmer fatty acids from rapeseed oil, with purity higher than 98 % and weight average molar mass (Mw) around 3000 g mol-1. Hydroxyl and acid values are 40 mg KOH g-1 and 0.253 mg KOH g-1 respectively, as given by the supplier. 4,4’-diphenylmethane di-isocyanate (MDI) was supplied by Brenntag (Rosheim, France). 1,4-butanediol (BDO), dibutylamine, toluene and hydrochloric acid were purchased from Sigma Aldrich (Lyon,

France). All reagents were used without any further purification step. TPU Synthesis Four different TPUs were prepared with a NCO/OH ratio equal to 1 and increasing HS content (10-40 wt%, named TPU10–TPU40, respectively), by the two-step prepolymer process for TPU polymerization (Table 2). In a first step, the polyol reacted with an excess of MDI (ratio 2:1) for 2 h in a five-necked round-bottom flask having the provision for nitrogen flushing, mechanical stirring and temperature control at 80 ^{0}C. During the synthesis, samples were extracted each 30 min in triplicate and diluted in 20 mL of a standard solution of dibutylamine 0.05 M in toluene for the reaction between the residual di-isocyanate and the amine, to control the NCO consumption during the reaction. Each solution was then stirred at room temperature for 10 h to ensure the complete reaction of NCO groups with dibutylamine. The excess amine was titrated back with standard aqueous HCl 0.05 M solution using bromophenol green as indicator. For each titration, 25 mL of isopropyl alcohol were added to the solution to ensure compatibility between dibutylamine and the HCl solution. It was calculated from these experiments that 56.1 % of NCO groups were consumed at the end of the prepolymer synthesis. This result was used for the addition of the precise amount of diol groups in the processing step. The prepolymer was further melt-blended in a second step by reactive processing with the adequate amount of polyol and chain extender, depending on the HS content targeted in the final TPUs. The prepolymer synthesized in the first step and the calculated amount of polyol for a NCO/OH = 1 ratio were directly introduced in the feeding zone of an internal mixer (counter-rotating mixer Rheocord 9000, Haake, USA) equipped with a pair of high-shear roller-type rotors, at 80 °C, with a rotation speed of 50 rpm and 15 min processing time. Then, the adequate amount of BDO chain extender was added and the temperature was immediately increased to 180 °C for 8 min, without any catalyst. After polymerization, all systems were cured overnight in an oven at 70 °C to ensure the complete reaction of NCO groups, which was further checked by attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR). TPUs were subsequently compression-molded in a hot press at 200 °C by applying 200 MPa pressure for 5 min and further quenched between two steel plates for 10 min to obtain sheets with 1.5 mm thickness for each system. The expected HS length for each TPU sample was calculated from data in Table 2 by following a protocol already described by Petrovic et al. [29] to determine the average polymerization degree in segmented polyurethanes. This method was applied to the TPUs synthesized in this study resulting in an HS average polymerization degree of 5-7, 7-9, 11-13 and 19-21 units for TPU10, TPU20, TPU30 and TPU40, respectively. These results could give an estimation of the length of HS for each TPU. Table 2 - Calculated hard segment (HS) percentage and reactants amounts for each TPU blend [30], with permission Sample HS (wt%) Polyol (g) MDI (g) BDO (g) TPU10 10 49.5 5.1 0.36 TPU20 20 44.0 9.1 1.94 TPU30 30 38.5 13.0 3.52 TPU40 40 33.0 16.9 5.11 Materials characterization ATR-FTIR Spectroscopy ATR-FTIR was used to screen the complete reaction between NCO and OH groups and, consequently, to

evaluate the adequate curing of the TPUs. Infrared spectra were collected on a TA Instruments SDT Q600 (Thermo-Nicolet, New Castle, DE, USA) at a resolution of 4 cm-1 and 64 scans per run. The ATR accessory was equipped with a Germanium (n = 4) crystal and it was used at a nominal incidence angle of 45°, yielding 12 interval reflections at the polymer surface. Thermogravimetric analysis (TGA) The four TPU systems as well as the bio-based polyol were analyzed in dynamic mode by using a TGA/SDTA 851e Mettler Toledo (Schwarzenbach, Switzerland) equipment. Approximately 7 mg samples were weighed in alumina pans (70 µL) and they were heated from 30 ºC to 700 ºC at 10 ºC min-1 under nitrogen atmosphere (flow rate 30 mL min-1). In the case of TPUs, the initial degradation temperature was calculated as the temperature where 5 wt% of the initial mass was lost (T5%). Differential Scanning Calorimetry (DSC) Thermal and structural characterization of TPUs and the polyol was carried out by using a TA Instruments Q2000 (New Castle, DE, USA) equipment. Approximately 5 mg of each sample were weighed in aluminum pans (40 □L) and they were subjected to a first heating stage from 30 ºC to 240 ºC, with a further cooling from 240 ºC to -90 ºC and a subsequent heating from -90 ºC to 240 ºC. All steps were carried out at 10 ºC min-1 under nitrogen (flow rate 50 mL min-1). All tests were performed in duplicate. Glass transition temperatures (Tg) were determined on the second heating scan. Tg of the polyol was determined by using modulated differential scanning calorimetry (MDSC) during a cooling scan from 30 ºC to -90 ºC at 2 ºC min-1, with 60 s period and heat-only mode. Uniaxial mechanical tests Tensile properties of TPUs were determined with an Instron tensile testing machine (model 4204, USA), at 25 ºC and 50 % relative humidity at a rate of 20 mm min-1, using dumbbell specimens (dimensions: 30 x 10 x 1.5 mm3). For each formulation at least five samples were tested. Results and discussion ATR-FTIR Spectroscopy The adequate curing of all TPUs is a key-point prior to the materials characterization, since the presence of residual NCO groups in the final polymer gives an indication of an incomplete synthesis. In this work ATR-FTIR was used to confirm the complete reaction between NCO and OH groups. TPUs spectra are shown in Figure 3 and they could be used to highlight the main structural differences between them. No peak was found at 2270 cm-1 (NCO stretching band) suggesting that the reaction was complete in all cases. As expected, the main variations are related to the increasing content in HS and consequently the higher concentration in urethane groups (-NH-CO-O). In Figure 3, vibrations at 3335 and 1550 cm-1 corresponded to -NH stretching and bending, respectively. Besides, the peak for the C=O stretching from the urethane group could be observed at ≈1700 cm-1 [31-33]. All these bands, assigned to the urethane groups, increased in their intensity from TPU10 to TPU40, with confirmation of the higher concentration in carbamate groups at higher HS contents. Nevertheless, the absorption band at 1735 cm-1 was assigned to the C=O group stretching in the polyol, and it was similar for all TPUs, except for TPU10 where this band was broader and almost no discernible from the band at 1700 cm-1, certainly due to the lower content in urethane groups in this

material. Fig. 3 - ATR-FTIR spectra of TPU 10-40 wt% of HS and main peak assignments (cm-1) [30], with permission Thermogravimetric analysis (TGA) The thermal stability of the polyol and all bio-based TPUs were studied by dynamic TGA. Figure 4 shows their mass percentage and derivative curves. The bio-based polyol showed a narrow derivative peak (Figure 4b, left) due to its purity, while Figure 4b (right) clearly shows the derivative curves of TPUs with lower intensity peaks. It is known that degradation of polyurethanes is a complex and multistep process, as observed in Figure 4. An important parameter, the degradation onset, is dependent on the thermal stability of the less thermally stable part on the polyurethane chains [34,35]. Initial degradation temperatures (T5%) of each step were also studied in TPUs and, together with mass loss percentages, allowed to study the differences between samples depending on their HS content. It was noted that the T5% value of the pure rapeseed oil-based polyol was higher than in the case of TPU systems, as it was expected, but also higher than the T5% value reported for castor oil [36] and cashew nut shell liquid-based polyols [37]. TPUs also showed higher thermal stability than polymers with similar structures [38]. It has been reported that their first degradation stage is related to urethane bond decomposition into isocyanate and alcohol with possible formation of primary and secondary amines [39,40]. Nevertheless, the complexity of this stage is also related with the HS content. In this way, when this content increases T5% decreases, making those materials more susceptible to degradation and suggesting that the starting point of degradation takes place predominantly within hard segments. Differential Scanning Calorimetry (DSC) The structure of TPU samples was investigated by DSC while the bio-based polyol was studied both by DSC and MDSC. The main results of this study are shown in Table 3 and Figure 5. This technique is valuable for a precise determination of Tg and from these values it is possible to estimate the real amounts of HS in the unorganized and organized microphases. It has been indicated that HS in TPUs do not fully belong to the hard domains, since some of them can be found in the soft regions and vice versa. Moreover, when MDI is not bonded to the chain extender but to the polyol, presumably in systems with high polyol amount [42], such as in the case of TPU10, this trend is more clearly observed. This phenomenon was also clearly evidenced in the thermal stability of the TPUs, since the initial degradation temperatures (T5%) of TPU30 and TPU40 fell significantly with respect to those obtained for TPU10 and TPU20. This behavior could be associated to the higher HS content. Moreover, it should be mentioned that the mass loss associated with this first degradation stage could be also correlated with the HS content. In samples with higher HS content, such as TPU30 and TPU40, a peak and a shoulder in their derivative curves were observed, both associated with the first stage of the thermal decomposition of urethane bonds (Figure 4b). Table 3 - Glass transition temperatures (Tg) and hard segment content (%) for TPUs Sample Tgs SS (ºC) Tgh HS (ºC) TPU10 -47.0 --- TPU20 -47.8 122.8 TPU30 -50.0 120.7 TPU40 -51.3 118.1 In a preliminary step the bio-based polyol was studied by conventional DSC but the glass transition was not clearly

observed since some melting transitions were superposed in this temperature range, probably associated to the crystalline polymorphism of some oils and fats, such as the case of rapeseed oil. Modulation of DSC data (MDSC) is a powerful tool to separate transitions and to get higher resolutions in particular thermal events. In the case of the polyol, MDSC was used during the cooling cycle and the Tg transition was determined in the reversing phase curve at -61.8 ºC. It was also observed that glass transition temperatures of the SS for all TPUs were higher than that of the polyol (Table 3). Tg values of SS were slightly lower with increasing HS concentrations, as it was reported by Xu et al. [43]. Soft domains have higher mobility when larger HS are present, and this fact could be related with a better microphase separation at high HS content. Besides, the TPUs with lower molar masses and the highest concentrations in HS could contribute to the decrease in Tg values. Higher amount of end chains could result in higher free volume, increasing the mobility of the amorphous phase. Moreover, as it is shown in Figure 5, Tg transition of the MDI-BDO HSs was very difficult to detect due to their stiffness and low mobility [42]. Tg of HS of TPUs slightly increased when their concentration decreased. This result could be attributed to the higher concentration in HS inside the soft domains, as previously explained. Moreover, the intensity of the glass transition of HS is larger at higher HS content but the Tg value is lower, suggesting some interactions between hard and soft phases, that is the low Tg of SS observed for TPU40 which was previously attributed to the microphase separation, could also help to the decrease in Tg of HS in this material due to the higher interaction of soft domains in the hard phase. Uniaxial mechanical tests Tensile properties were determined by uniaxial tensile tests and data are summarized in Table 4 and Figure 6. Results showed that the increase in HS content lead to a brittle material with higher tensile modulus and lower elongation at break (around 25 % for TPU40), as expected, while this material showed lower tensile strength than TPU30 and TPU20. This behavior could be attributed to the fragility provided by the crystalline macro-structures with sizes between 20 and 30 µm that were observed in a previous morphological study [30]. The presence of these macro-structures in TPU40 increased the segregation phase size and may promote points of stress concentration, due to their boundary impingement, which could influence properties such as tensile strength and elongation at break [43]. As expected, TPU40 also exhibited the higher modulus (11.1 MPa), leading to the conclusion that the HS higher crystallinity has a significant effect on the mechanical properties of these TPUs. Table 4 - Uniaxial tensile properties of TPUs [41], with permission Sample Tensile strength (MPa) Elongation at break (%) Young modulus (MPa) TPU10 1.3 ± 0.1 > 600 0.7 ± 0.0 TPU20 3.7 ± 0.1 > 600 2.5 ± 0.1 TPU30 5.6 ± 0.3 430 ± 40 8.6 ± 0.5 TPU40 1.5 ± 0.4 25 ± 7 11.1 ± 1.2 Figure 6 shows the elastomeric behavior of those TPUs with lower HS content, as demonstrated by their lower moduli. It was also observed in Figure 6 that TPU20 was the only material with a yield point in the range of deformation 250-300 %. This particular behavior, presented as a rubbery region in Figure 6, could be related to a good

resistance to the permanent deformation. Fig. 6 - Stress-strain curves of TPUs [41], with permission Conclusions Bio-based TPUs were synthesized from a di-functional dimmer fatty acid-based polyol obtained from rapeseed oil, MDI and BDO at four HS contents, i.e. 10-40 wt%. The polyol characteristics determined the structure and properties of TPUs. FTIR-ATR spectra confirmed that all the isocyanate groups reacted with hydroxyl groups (from polyol or BDO) during the TPUs synthesis. Thermal studies carried out by TGA, DSC and MDSC revealed some interactions between hard and soft domains for all TPUs and a degradation behavior closely linked to their HS concentration. Stress-strain uniaxial tests showed that the increase in HS content in TPUs lead to higher tensile modulus and lower elongation at break. TPU10 and TPU20 showed a strong elastomeric behavior with very high elongation at break (>600 %) and very low elastic modulus. In summary, TPUs partially synthesized from vegetable oils are very promising materials in good agreement with the current tendency for sustainable development, making them very attractive since they are expected to show specific properties which can be easily tailored by selecting the appropriate HS concentration. These materials could also fulfil many industrial requirements for different fields, such as construction, automotive, textile, adhesive and coatings. Table 1 - Fatty acid distribution in vegetable oils (g fatty acid/100 g oil) Fatty acid C:DB Cotton Rapeseed Sunflower Linseed Corn Olive Palm Castor Soybean Myristic 14:0 0.7 0.1 0.0 0.0 0.1 0.0 1.0 0.0 0.1 Myristoleic 14:1 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 Palmitic 16:0 21.6 4.1 6.1 5.5 10.9 13.7 44.4 1.5 11.0 Palmitoleic 16:1 0.6 0.3 0.0 0.0 0.2 1.2 0.2 0.0 0.1 Stearic 18:0 2.6 1.8 3.9 3.5 2.0 2.5 4.1 0.5 4.0 Oleic 18:1 18.6 60.9 42.6 19.1 25.4 71.1 39.3 5,0 23.4 Linoleic 18:2 54.4 21.0 46.4 15.3 59.6 10.0 10.0 4.0 53.2 Linolenic 18:3 0.7 8.8 1.0 56.6 1.2 0.6 0.4 0.5 7.8 Ricinoleic 18:1 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 87.5 0.0 Arachidic 20:0 0.3 0.7 0.0 0.0 0.4 0.9 0.3 0.0 0.3 Gadoleic 20:1 0.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 Eicosadienoic 20:2 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 Behenic 22:1 0.2 0.3 0.0 0.0 0.1 0.0 0.1 0.0 0.1 Erucic 22:1 0.0 0.7 0.0 0.0 0.0 0.0 0.0 0.0 0.0 Lignoceric 24:0 0.0 0.2 0.0 0.0 0.0 0.0 0.0 0.0 0.0 DB/triglyceride 3.9 3.9 4.7 6.6 4.5 2.8 1.8 2.7 4.6 Iodine index (I) 104-117 91-108 110-143 168-204 107-120 84-86 44-58 82-88 117-143 C, number of carbon atoms; DB, number of C = C double bonds. Fig. 4 - TGA curves for mass percentage (a) and derivative (b) vs. temperature for bio-based polyol and TPUs [41], with permission Fig. 5 - DSC curves from TPU samples and zoom in the zone of Tg of HS [30], with permission