

Mechanical and physical properties investigation of polyurethane material obtained from renewable natural source

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Properties

ABSTRACT

Purpose: The purpose of this paper is to investigate the influence of different polyol/diisocyanate ratios on the mechanical and physical behaviours of polyurethane based polymers.

Design/methodology/approach: Castor oil was mixed, as polyol, to diisocyanate in order to obtain polyurethane based polymers. Besides the ideal stoichiometry, polyol/ diisocyanate ratio, ratios with excess/lack of diisocyanates were provided. The mechanical behaviour was investigated by uniaxial tests. Differential Scanning Calorimetry (DSC) and Thermo gravimetric Analysis (TGA) were used to investigate the thermal behaviour. The various polymeric structures, obtained by the different ratios, were analysed and compared by Infrared Spectroscopy (IR).

Findings: Mechanical performance was increased proportionally to content of diisocyanate. High levels of diisocyanate have generated elongation decreasing and CO₂ formation during curing, damaging mechanical behaviour due to bubble presence. Analytical experiments have showed important changes on: polymeric structures, glass transition temperatures and behaviour at elevated temperatures.

Research limitations/implications: Free acid and water content were not taken into consideration by defining the ideal stoichiometry. The investigated formulations cannot be direct applied on practical applications; fillers and additives must be added to them, which were not taken in consideration.

Practical implications: The obtained results can support development of adhesives, engineering polymers and polymeric matrix for structural composites. Stabing the relation between component ratios to their behaviours is possible to define optimal performance ranges and to avoid excess of diisocyanate on polymers.

Originality/value: Deep investigation of PU based material, obtained from renewable natural source (castor oil). The results can orientate development of materials for industrial applications and researches using other oils as polyol.

Keywords: Engineering polymers; Mechanical properties; Polyurethanes; Castor oil

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1. Introduction

Polyurethanes are versatile materials, which show different behaviours by varying the ratio of their components. Their behaviour can vary from a soft (elastomeric) to a rigid (brittle) behaviour. They diversify widely in composition and can be designed to possess either soft or stiff mechanical characteristics according to the intended end-use with the proper control of their molecular structure. Besides their versatility, polyurethanes have moderate price. Some examples of market segments in which polyurethanes are found are construction, flexible packaging, footwear, synthetic leather and automotive industry [1].

Basically, polyurethanes are a broad group of polymers that contain a common urethane linkage, obtained by the reaction of polyol with isocyanate. Petroleum based polyols are usually applied on industrial applications, but many papers have presented the possibility of applying vegetal oils as polyol [2]. Due to concerns over the depletion of petroleum resources, extensive research has been concentrating on developing bio-based polyols and PU products from renewable sources [3]. Castor oil-based polyurethane is a useful, versatile material and widely used as an individual polymer possessing network structure because of its good flexibility and elasticity [4]. It contains about 90% (wt/wt) of ricinoleic acid. This triglyceride contains hydroxyl groups in its chain which react with isocyanate groups to form urethane links [5].

Different types of polyols are also available, allowing the development of many polyurethane polymers. The material studied on this paper was composed by castor oil, as polyol, and MDI as diisocyanate. MDI is a molecule with two aromatic isocyanate groups of equal reactivity. It is used where high tensile strength, toughness and heat resistance is required and its lower volatility makes easier to handle [3].

The aim of this study is to investigate the influence of four polyol / diisocyanate ratios on the mechanical and physical behaviour of polyurethane based polymers. The investigation was carried out using IR spectroscopy, in order to verify the chemical group changing caused by the NCO/OH ratio variation. Uniaxial tensile experiments have shown the mechanical behaviour improvement, which was generated by increasing the ratio, mainly represented by the tensile strength increasing and by elongation decreasing. DSC results allowed identifying different glass temperature transitions (T_g) for the different ratios. Small changes on the mass losses at high temperatures could be investigated by analysing TGA results.

The polymer characterization, provided by studying the experiment results, can orientate new developments of engineering polymers, adhesives, based on renewable source materials.

2. Materials and methodology

2.1. Material

The polyurethane samples were obtained by mixing castor oil with diisocyanate (MDI) considering different NCO/OH ratios. The reference sample presumes a ratio of 1 between both groups,

it means, any available NCO group should be able to react with the respective OH group.

The reference stoichiometry has not taken acid and water contents in consideration, which probably are present in both components. Samples with lack (ratios of 0.6 and 0.8) and excess (ratio of 1.2) of diisocyanate were provided.

All samples were cured at room temperature into a glass mould, coated with permanent mould release, in order to make them able to be removed from the mould.

Polymers sheets with dimensions of 100 mm x 100 mm x 2 mm were obtained by curing them at room temperature for 72 hours. The polymers sheets were released and cut according to the required geometry for each experimental method.

2.2. Infrared spectroscopy

The 2 mm polyurethane films had their surfaces investigated by Fourier Transform Infrared (FTIR) using a PerkinElmer – Spectrum One equipment. The spectra were collected through Attenuated Total Reflectance (ATR) method, starting from 650 cm^{-1} up to 4000 cm^{-1} . ATR method is indicated to investigate polymeric films and planar sheets with good results [6-7]. Five different surface points of each condition were analysed to ensure a material homogeneity and data reliability.

A statistical analysis was carried out using the COMPARE™ toll, in order to quantify the similarity between the collected spectra concerning chemical groups. Peaks with relevant different highs were analysed in details to understand the polymerization dynamic on the surface.

2.3. Uniaxial tests

Uniaxial tensile tests were carried out in order to study the mechanical behaviour under tensile. Specimens were cut from the polymer sheet, according to a multinational OEM standard/specification. The choice of using a car manufacturer specification was based on fact that automobile industry can be one of the segments where renewable sources of PU can be applied. Five specimens of each condition were tested. The materials were stretched under constant speed of 50 mm/min, using a 100 N load cell of EMIC universal test equipment.

2.4. Thermogravimetric analysis

Thermogravimetric analysis has generated mass loss curves using a PerkinElmer – Pyris Diamond. The specimens, cut from the 2 mm sheets, were heated under inert atmosphere (N_2) following an isothermal process until 50°C during 1 minute. After finishing the first heat stage, the specimens were heated at a rate of 20°C / minute up to 750°C. An isothermal process at 750°C during 1 min has ended the experiment. As output, the method has provided mass losses curves.

2.5. Differential scanning Calorimetry

Differential Scanning Calorimetry technique is widely used to study the thermal transition T_g of the polymers [8-9], on this tests they were heated from -90°C to 90°C , at the rate of $20^{\circ}\text{C}/\text{min}$. The equipment used was Diamond DSC – PerkinElmer.

The glass transition temperature, T_g , is a phenomena widely study and its determination has countless application in polymers characterization. Therefore, T_g enables, for example, the identification of unknown polymers or the presence of plasticizers by its decreasing. The calorimetric curves obtained have shown the T_g of each NCO/OH ratio, besides other second transitions.

3. Results and discussion

3.1. Infrared spectroscopy results

Infrared microscopy is a widely used technique to investigate chemical groups, which are present, for example, in polymeric structures. The Fig. 1 shows the collected spectra related to the different NCO/OH ratios, analysed on this work. The COMPARE™ tool, has quantified the similarity among spectra and has found a similarity level superior than 95%. This analysis has neglected the relevant changes, noted on ranges of 1.217 cm^{-1} , 1.525 cm^{-1} e 1.722 cm^{-1} , respectively related to the presence of urethane, urethane + phenylene and urethane + uretoneimine.

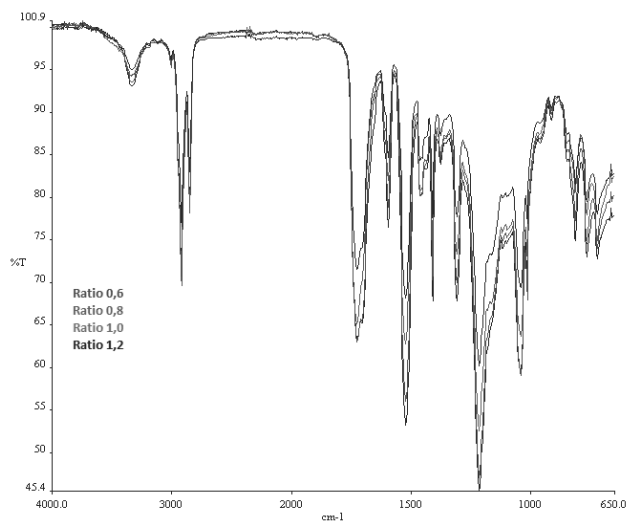


Fig. 1. IR spectra for different NCO/OH ratios

The excess of diisocyanate, present on condition 4, should theoretically cause a diisocyanate peak on the IR spectra at 2.260 cm^{-1} , which has not occurred, Figure 2. Such result requires some considerations: the theoretical excess of diisocyanate can be reacted with; (i) water presents in the polyol; (ii) air humidity, remembering that the specimens were not cured under dry conditions or; (iii)

other chemical groups present into the structure, causing the phenomena classified as parasite reaction. In sum, in the four analysed ratios, all diisocyanate has reacted with other chemical groups, avoiding the presence of free diisocyanate.

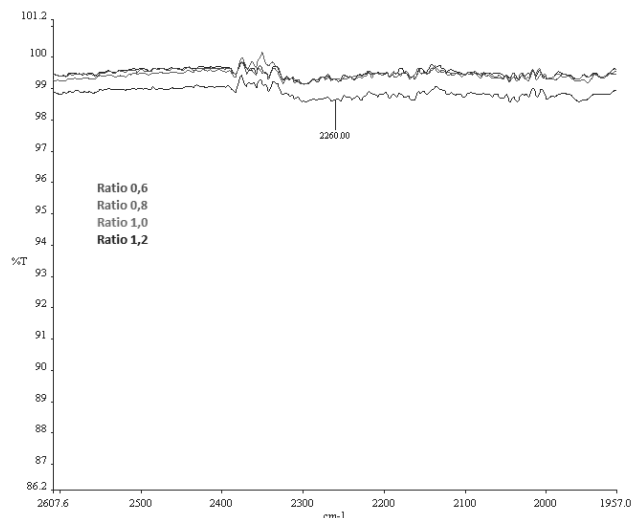


Fig. 2. Peak absence at 2.260 cm^{-1} (diisocyanate groups) for different NCO/OH ratios

Figure 3 presents the spectra at 1217 cm^{-1} (urethane group) [10]. An increasing of the urethane groups, mainly verified between 0,6 and 0,8 ratios, has indicated a large amount of OH available to react on the condition 1. The ratios 1.0 and 1.2 have an insignificant difference between their urethane group peaks, which suggests a similar quantity of reactions between NCO and OH groups in both conditions.

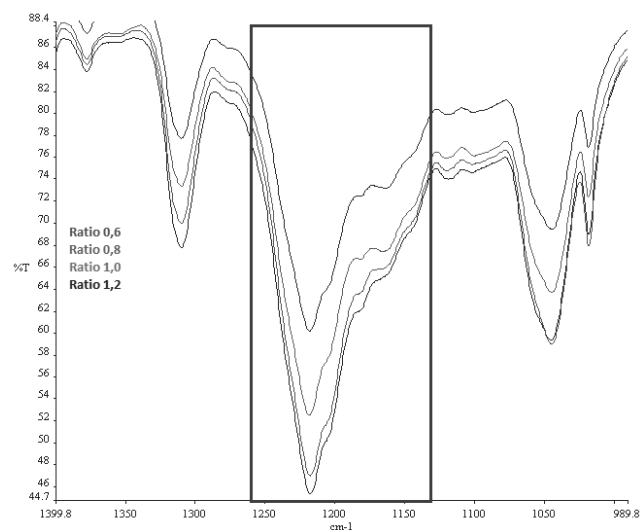


Fig. 3. Peak at 1.217 cm^{-1} (urethane groups) for different NCO/OH ratios

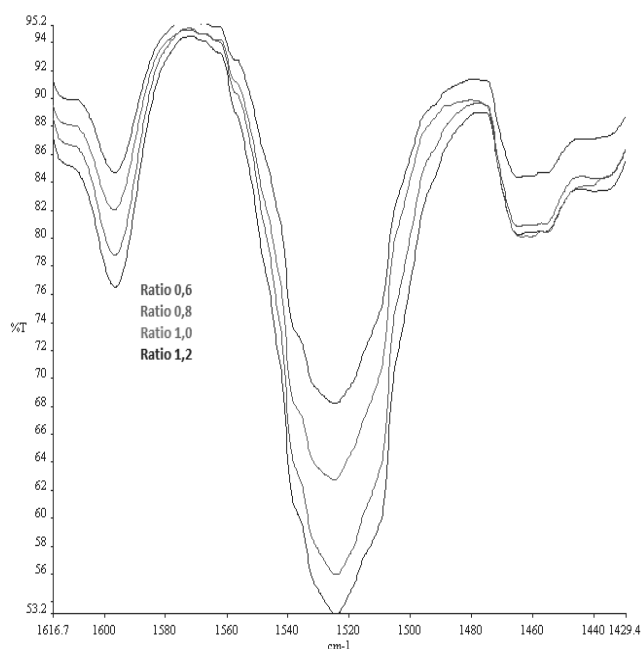


Fig. 4. Peak at 1.525 (urethane + phenylene groups) cm^{-1} for different NCO/OH ratios

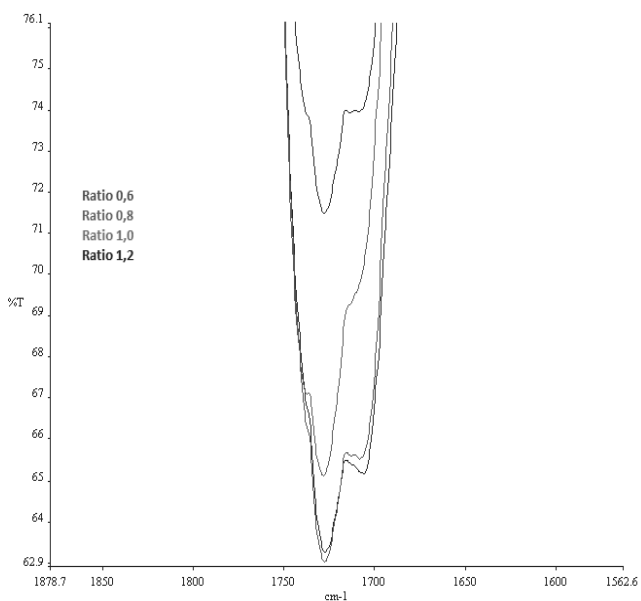


Fig. 5. Peak at 1.722 (urethane + uretoneimine) cm^{-1} for different NCO / OH ratios

After verifying the similar consumption of NCO / OH groups in the conditions 3 and 4, based on peaks at 1.217 cm^{-1} , a significant peak difference must be noted in other region, in order to justify the consumption of diisocyanate with 1.2 ratio. Such peak difference is noted at 1.525 cm^{-1} , Figure 4, showing the increased amount of urethane + phenylene groups in the condition 4,

probably caused by diisocyanate excess, reaction classified by many authors as parasite reaction, which has their causes based on reaction with other groups present on the structure.

Figure 5 presents an increasing of urethane + uretoneimine groups between conditions 1 and 2, while the peak keeps constant between conditions 3 and 4.

A more precise analysis requires an improved specimens preparation technique or condition. A dry air or argon atmosphere has to be used in order to avoid parasite reactions. The surface contact with humidity allows different mechanism reactions on the polymer surface, in comparison to the middle region. The collected spectra on this work were taken from the material surface. The collected spectra on this work, was taken from the material surface.

A depth measurement depends on equipment features [11], it means, the collected spectra are probably different to spectra collected on a region, which was not affected by environmental influence.

3.2. Mechanical tests

A complete elastomeric material characterization requires three mechanical experiments [8, 12-13], but in many cases uniaxial experiments can provide data for an initial mechanical behaviour analysis. The Table 1 shows the strength at rupture changes, which were caused by the NCO/OH ratio variation concerning all tested ratios.

Table 1.

Experimental results of strength at rupture

	Strength at rupture (MPa)	Standard deviation (MPa)
1	1.18	0.25
2	2.26	0.69
3	10.19	0.83
4	13.21	1.36

The samples obtained with 0.6 ratio of NCO/OH, which means a lack of diisocyanate, has presented the lowest strength at rupture. Such low strength behaviour can be related to the low crosslinking density, it means, a "large" distance between urethane groups into the polymeric structure, which allows the chains to deform, when submitted to a force and to recover the original shape by unloading the force, typical rubber-like or large strain material behaviour.

The strength at rupture has increased by increasing the NCO/OH ratio, along the studied ratio range. The most relevant gain was verified from 0.8 to 1.0 ratio, where the strength at rupture was increased from 2.29 MPa to 10.19 MPa. Figures 6, 7, 8 and 9 enable to identify an elongation decreasing by increasing the ratio. Closer to the theoretical balance of NCO/OH, concerning stoichiometry, more brittle has become the obtained polymer. As known, the crosslinking density level is directly proportional to the material modulus [8, 14]. The increased tensile at rupture, associated to the decreased elongation, results into an increasing of elastic modulus of the polymer, consequently an increasing of crosslinking density level.

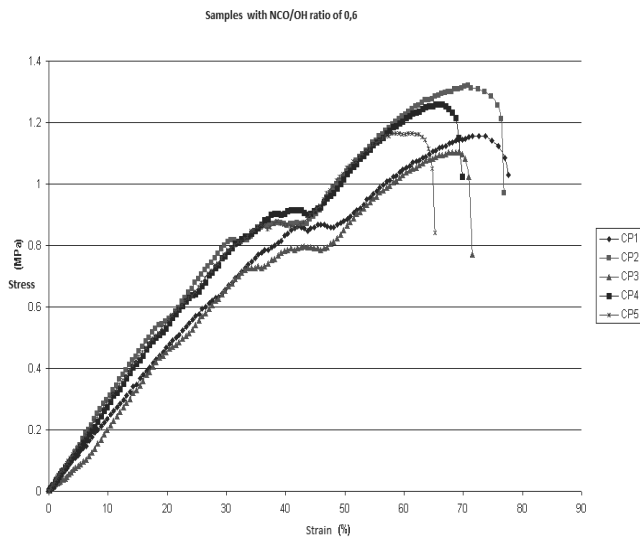


Fig. 6. Uniaxial test results of 0.6 ratio samples

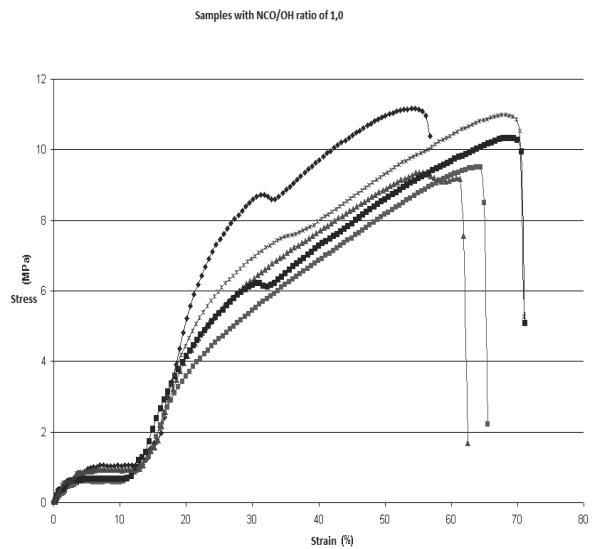


Fig. 8. Uniaxial test results of 1.0 ratio samples

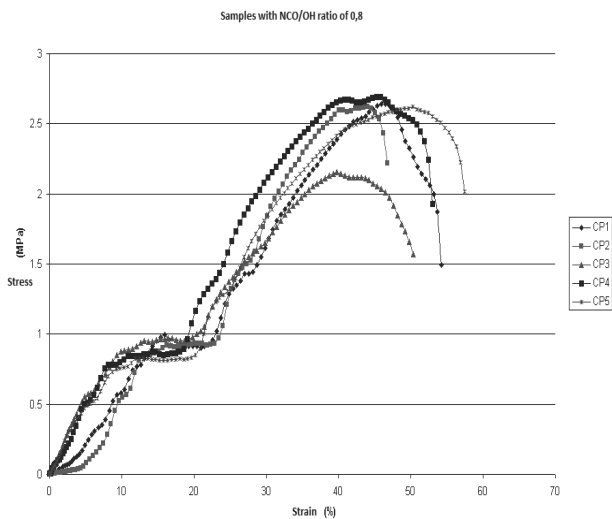


Fig. 7. Uniaxial test results of 0.8 ratio samples

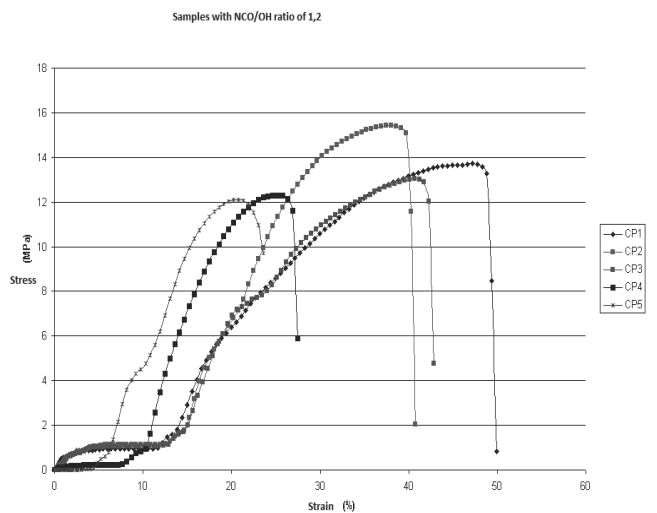


Fig. 9. Uniaxial test results of 1.2 ratio samples

A simple visual analysis was needed to identify bubble formation into 1.2 NCO/OH ratio samples. These bubbles were probably composed by by-product polymerization, it means, CO₂ bubbles as effect of diisocyanate excess. The condition named 4 in Table 1 shows a slight strength increasing comparing to condition 3, respectively ratios 1.2 and 1.0. This slight increasing does not represent an improved material behaviour. The polymer performance improvement was higher than represented by these results. The mechanical results were damaged by the presence of bubbles, concerning the 1.2 ratio samples. To avoid such bubbles, the samples must be prepared at a controlled or inert atmosphere.

3.3. Thermogravimetric analysis

Thermoset polymer, like the studied PU, usually starts to lose their mass after being affected by a high energy quantity, which should be enough to cause chain scission [15]. An opposite dynamic can be identified if some low molecular weight structures are dispersed into the polymer, which would start to be eliminated by a lower level of applied energy, like non cured component or additives.

The following curves, Figure 10, shows homopolymer behaviour, for all analysed conditions, which begin to lose their mass at 254.1°C, 243.97°C, 251.93°C and 251.25°C, respectively from ratio 0.6 to 1.2. The difference of loss initial temperature

among the ratios is not significant. As exposed, the analysed PU is composed by mixing two components, castor oil (as polyol) and MDI diisocyanate, which is not usually applied as industrial product. The usual industrial materials are composed by plasticizers, additives and fillers, which add some mechanical features and provide material cost reduction. The high loss initial temperature indicates the absence of some additives and of non-cured products. The usual maximum working temperature for PU based adhesives, for example, is around 120°C. At this first step, the condition 1 has the highest loss percentage, because of low crosslinking density level in comparison to the other conditions. Such low crosslinking density level was confirmed by the inferior elastic modulus condition in comparison to the others.

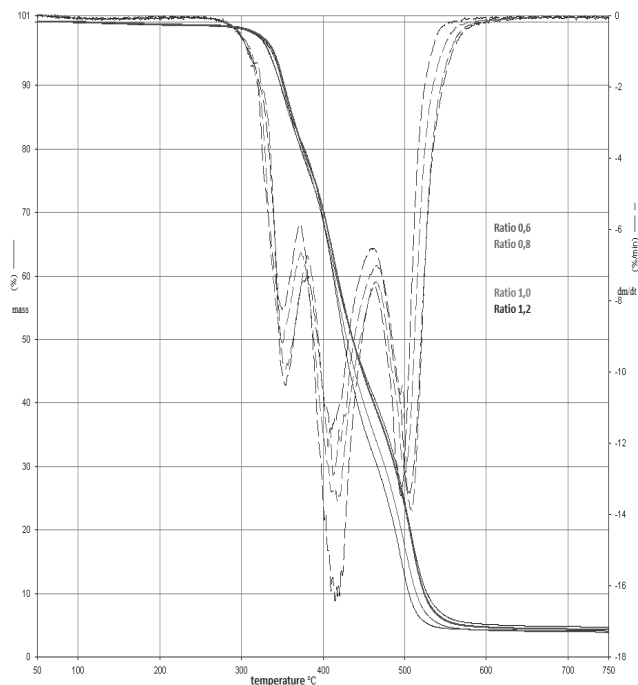


Fig. 10. Curves of mass losses in function of temperature and their second order derivatives (dm^2/dt)

A second temperature range was also identified, where a peak of mass loss has occurred. Such temperature regions have varied according to each condition from 371.08°C up to 381.12°C. At this stage the same behaviour was verified, the lowest crosslinking density material has presented the highest loss of mass.

The third stage, where peak or maximum mass losses have occurred, has shown temperature variation from 461.10°C to 463.20°C. The main difference, as expected, was the highest mass, which was lost by materials with higher crosslinking density levels, obviously because they have kept their mass along the temperature range.

At 750°C the conditions have presented 95.30%, 95.36%, 95.01% and 94.56% of mass loss. The curves analysis have shown a slightly improvement on the temperature resistance for the conditions 3 and 4, where an increased ratio of NCO/OH was applied.

3.4. Differential Scanning Calorimetry

Differential Scanning Calorimetry analysis was carried out in order to identify possible changes on the glass transition temperatures, Figure 11. For elastomers it is desirable for the T_g to be below room temperature to ensure good flexible behaviour under ambient conditions. For 0.6 and 0.8 ratios the verified T_g are negatives, respectively -15.25°C and -9.71°C, which explain their soft or elastomeric mechanical behaviour. The soft domains have the highest resilience, there appears to be an optimum level of hard block. Apparently, a specific amount of hard block is required for an elastomer to resist permanent deformation.

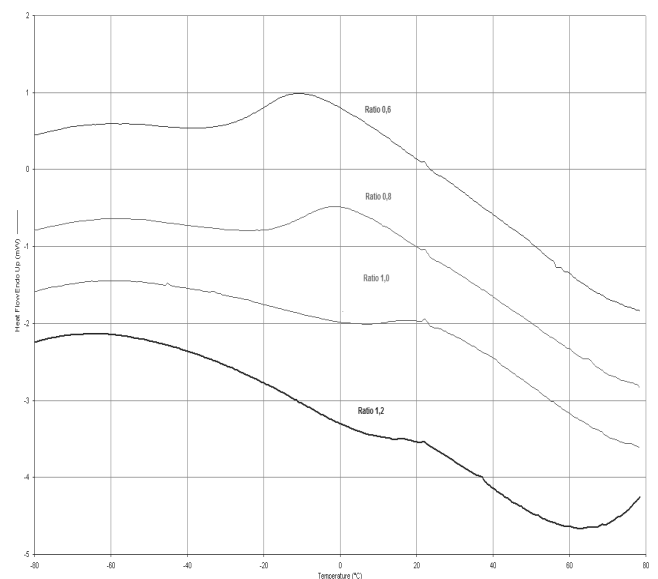


Fig. 11. Differential scanning calorimetry curves

The positives T_g obtained from the measurements of 1.0 and 1.2 ratios, 13.70°C and 17.94°C, have shown an elastomeric behaviour with the highest hard block content indicating increasing mechanical properties. These behaviours have their causes in below room temperature T_g . Comparing the found T_g for 0.6 and 0.8 with 1.0 and 1.2 ratios, it is easily verified that all conditions have provided materials with elastomeric behaviour, but the 1.0 and 1.2 ratios surely present improved mechanical properties. The polyol structure, the soft domain, affects polyurethane polymers in several ways starting with the influence on the type and degree of hard block aggregation.

4. Conclusions

The increasing of diisocyanate groups, in relation to polyol amount, has increased the strength at rupture of the obtained polymers and has decreased the polymers elongation, which has resulted into a modulus increasing.

No free diisocyanate was found into the formed polymeric structures after curing, even in the condition with theoretical diisocyanate excess.

The theoretical stoichiometric balance has agreed with experimental results.

A controlled environment condition is required to avoid reactions between diisocyanate and humidity or parasitic reactions.

The first mass loss has not differed among the various tested ratios. The increasing of diisocyanate has increased the second level of mass losses, indicating a superior thermal resistance at such temperature range.

Higher glass transition temperatures were found for conditions with higher level of diisocyanates. This feature was increased from -15.25°C (0.6 NCO/OH ratio) to 14.94°C (1.2 NCO/OH ratio).

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