CHEMICAL RECYCLING OF POLYURETHANE FOAMS FROM SHOE SOLES TO OBTAIN POLYOL AND USE IT AGAIN IN THE FOOTWEAR SECTOR

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Abstract

This paper is focused on closing rigid polyurethane (PUR) foams waste life cycle, come from shoe soles. First step is a chemical recycling of polyurethane foams, getting polyol with high efficiency and purity. Then, new recycled polyurethane foams are manufactured by reaction of the recycled polyol obtained previously with the appropriate amount of isocyanate and additives. Several factors that affect the recycling reaction have been studied following a factorial design of experiments to optimize the yield of polyol obtained. A polyol/PUR mass ratio of 0.80 has been achieved and this polyol obtained has been characterised to obtain the purity grade by means of GPC and FTIR. New polyurethane foams have been obtained using 20% of recycled polyol and 80% of virgin polyol, to manufacture new shoe soles with good properties which meet the minimum technical requirements necessary for both professional footwear and street shoes. So, the life cycle of the polyurethane foams is closed, giving an added value to these waste achieving manufacture new products used in the footwear sector.

Keywords: polyurethane, polyol, waste, recycling, footwear sector

1. INTRODUCTION

1.1. Polyurethane foams

PUR foams are thermostable polymers whose formulation is based on polyols of low hydroxyls number (-OH) combined with low content functional group isocyanates (NCO) [1].

There are several types of polyurethanes foams, although the most used are flexible and rigid foams. Flexible foams are composed of open cells and have a density between 12-25 kg/m^3 and a great resistance to deformation. Rigid foams are composed of closed cells and have a higher density between 30-50 kg/m^3. They have a great adhesion, high resistance to compression, good absorption of humidity and good dimensional stability. One of the main applications of rigid polyurethane foams is in the footwear sector [2, 3]. The use of PUR foams continues growing in the footwear sector year after year. The footwear production has increased over the past year to 13 pairs billion in 1995 to 16 pairs billion in 2000 and 20 pairs billion in 2005, increasing 50% since 1995 until nowadays. PUR is found in the sole principally, and represents 90% of the total polyurethane demanded in the footwear sector. It is expected, the total demand of PUR in the footwear market will be 2.000 kt in 2020 [4, 5].

Besides, PUR foams are used in various sectors and applications, such as thermal insulation, packaging materials, on supports, cushions, mattresses, covers, etc. [6]. This implies a huge amount of waste that nowadays are mainly landfilling without any treatment, causing negative impacts to the environment. In order to deal with the environmental problem caused by these waste, several methods to recover and recycling PUR foams have been investigated [7, 8].

· *Mechanical recycling* involves physical treatments in which the waste are clean and decontaminated to be reprocessed and the products obtained have lower quality than those of heading and only accept a maximum number of recycling cycles.

· *Feedstock recycling* consists of chemical treatments of depolymerisation to produce feedstock materials using chemical agents to enhance the reaction results. In this process, the monomer that composes the starting product is obtaining, which can be remanufactured with similar quality.

· *Energy recovery* involves thermal treatments, heating the waste material to use the thermal energy liberated as fossil fuel in other processes. This process is easy and fast but has environmental impacts due to the liberation of contaminants to the atmosphere.

- Nevertheless the most common final use of PUR waste is its deposition in *landfills*.

Moreover landfilling costs are increasing and environmental laws head for a reduction and a valorisation of the amount of generated waste. Due to this fact, PUR recycling is an interesting option to enhance the environmental protection, avoiding landfilling and recovering the polyol to manufacture new products [9].

So, the option of chemical recycling has been chosen in this study. It consists of the decomposition of polymers by chemical agents and catalysts to obtain the molecules that originated them, with high value potential applications such as chemicals, monomers or new polymers. Depending on the used agent, different types of chemical recycling can be carried out (hydrolysis, alcoholysis, glycolysis, etc.) [1]. In this research, the glycolysis is the process study and it is a chemical depolymerisation which breaks down the PUR chain with a glycol and a catalyst, obtaining better quality polyols for the production of new PUR material. It is by far the most widely used chemical recycling method for PUR foams [10-17]. There are several solvents which can be used (monoethylene glycol, 1,2-propylene glycol, dipropylene glycol, etc.). In this study the solvent used is diethylene glycol (DEG) because is the most suitable according to bibliography [11, 12, 15]. The catalysts more used are octoate salts and diethanolamine (DEA). In this study the last has been used due to its suitable catalytic effect in the process [12, 14, 16]. The reaction products obtained were analysed with standardised techniques such as Fourier Transform Infrared Spectroscopy (FTIR) or Gel Permeation Chromatography (GPC). Finally, the recycled polyol obtained will be used to manufacture new polyurethane foams to introduce in the shoe soles again.

Polyurethanes are obtained by the polycondensation reaction between the polyol and isocyanate. The most widely used technique to obtain polyurethanes is by reaction-injection moulding (RIM), where the polyol and isocyanate are mixed under high pressure and injected in a mould. Also, they are mixed with other additives such as amines, silicone and catalyst, which determine the reaction and the final product. The production process consists of a mixture of all these chemicals under controlled conditions. Then, the mixture is conducted to a mould where is expanded and hardened after a time. Depending on the mould, the foam needs to be cut or treated to obtain the desired final product of polyurethane foams.

2. EXPERIMENTAL

2.1. Materials

Rigid PUR foams waste used, came from the production cut-offs of shoe soles. These shoe soles waste were provided by the companies Garmaryga and Cauchos Ruiz Alejos. These PUR waste were on polyester base.

These waste were crushed before glycolysis process, to favour the reaction, by a crushing mill (Resthc 2000SM) with 1 cm mesh screen.

Reagents used for the glycolysis were diethylene glycol, DEG, (PANREAC) which was chosen as solvent because was the most favourable for the process; and diethanol amine, DEA, (PANREAC) which was selected as catalyst due to its suitable catalytic activity.

For the polymerisation and expansion reactions, isocyanate, fire retardant additives, thermal stabilizers and foaming agents were used.

2.2. Methods

2.2.1. Design of experiments: Taguchi optimization study

When an experiment has several factors that are relevant, the factorial experimental design should be used. Factorial experiments are the way to identify interactions between variables. So, the glycolysis of PUR foams experiments has been carried out using the Taguchi's parameter design methodology.

The main goal of the research was to find the higher yield of polyol with optimum purity. The operation variables (or control factors) considered as more influential were chosen based on previous studies and the experience of the research group in this field [18]. The variables and ranges used are the next:

- *Solvent to polymer mass ratio, DEG/PUR (w/w)*: The solvent has a great influence in the yield of the products obtained in the glycolysis process. In this sense, a greater amount of solvent above stoichiometric relationship is necessary to guarantee the success of the reaction [14-18]. On the other hand, the more solvent were used, the more expensive were the process, and less environmental friendly. Therefore it tried to use the minimum quantity to maximize the yield above the stoichiometric.

- *Reaction time, t (min)*: In a glycolysis process, the amount of oligomers that remains in the upper phase at 20 minutes from the beginning of the reaction are less than 10 wt%, confirming that the kinetic of the reaction has been very fast at the beginning of the reaction. Nevertheless, it has been necessary more than 120 minutes to finish the reaction completely. However, it has been reported that 90 minutes of reaction were enough to obtain a hydroxyl value constant in all of the performed experiments process [11-14].
- *Reaction temperature, T (ºC)*: As it was demonstrated in previous studies [11-14] reaction temperatures excessively high (above 220 ºC) induce the appearance of secondary products which are not interesting in the process. On the other hand, excessively low temperatures (below 170 ºC) decrease substantially the yield because it affects the kinetic of the reaction. In this study, several tests have been carried out showing that the shoe soles waste used have not been behave exactly as other PUR foams with the previous conditions. This is due to the fact that the rigid foams from the shoe soles contained many dyes and contaminants. This is the reason why it has been very complicated to attack and break them to obtain the polyol and separate from the rest of impurities and products. So the temperature range to study has been below 160 ºC. At higher temperatures, other reactions are triggered, making impossible the polyol obtaining.
- *Catalyst to polymer mass percentage ratio, DEA/PUR (%w/w)*: Products of low amine content can be obtained adding reagents in the glycolysis process [19-21]. The addition of catalyst reduced the time of reaction, i.e., while in reactions without catalyst before 150 minutes there was only a 50 wt% of polyol, in reactions with catalyst after 25 minutes, a 70 wt% of polyol is obtained. The quantity of catalyst has to be increased to counteract the low temperatures used in the reaction, to favor the kinetic of the reaction and to increase the yield of polyol.

In Table 1 appear the factors and levels used to perform an orthogonal array L_9 to carry out nine experiments combining the levels of each factor considered. Each experiment was repeated three times in order to observe the reproducibility on glycolysis process. After finishing the experiments, the results were analysed to find the optimal level of each variable and to obtain the optimal operational conditions.

2.2.2. Glycolysis process

Glycolysis experiments were carried out in a 2L stainless steel batch reactor. It has an electrical resistance to heat, a temperature control and a stirrer to ensure good mixing. An initial purge of nitrogen was used to prevent possible oxidation of the reaction products. DEG has been used as solvent and DEA as catalyst.

Temperature was maintained constant during the whole reaction. Once reaction has finished, the products obtained were cooled and poured into a decanter to separate the phases in order to obtain the maximum amount of polyol. There were obtained three phases. The upper phase is composed of the recovered polyol, in the bottom phase were deposed the heavy fraction constituted by the excess of solvent and the isocyanates, and the third phase (in the middle) which is formed by a solid product (un-reacted polyurethane).

2.2.3. Manufacturing PUR foams process

Once the polyol has been obtained, the next step has been the production of new PUR foams to manufacture shoe soles. To obtain the best formula, several trials have been carried out with the addition of different amounts of isocyanates, retardant additives, thermal stabilizers and foaming agents, necessary to carry out the foaming process.

Regarding the behaviour of the recycled polyol, it has been behave differently from the industrial polyol, having to modify the theoretical reaction with polyol isocyanate, taking into account the quantity of hydroxyl characterised in the recycled polyol. The work relation between the recycled polyol and the isocyanate was altered, having to add a bigger quantity of isocyanate to obtain the perfect curing.

These tests have been carried out with different proportions of recycled and virgin polyol to find the best percentage which fulfil with the necessary technical requirements.

2.2.4. Analysis of products

Polyol obtained was characterised by Gel Permeation Chromatography (GPC, Polymer Lab, PL-120) in order to determine the molecular weight distribution.

A Fourier Transform Infrared Spectrophotometer (FTIR, Varian 670-IR with ATR Pike accessory) was used to identify the chemical structure of the polyol.

Virgin polyol was used for calibration purposes, in order to compare with the recovered polyol.

To analyse the morphological and mechanical behaviour of PUR foams obtained with recycled polyol, several analyses were carried out according to the next procedures: hardness (UNE-EN ISO 868:2003), density (UNE 53526:2001, method A), abrasion resistance (UNE-EN 12770:2000), tensile strength (UNE-EN 12803:2001), elongation at break (UNE-EN 12803:2001), tear strength (UNE-EN 12771:2000) and bending resistance (UNE-EN ISO 17707:2005).

3. RESULTS AND DISCUSSION

3.1. Glycolysis of rigid polyurethane foams from shoe soles

An analysis of variance of the results, using the ANOVA® commercial software, was completed to obtain the contribution of the factors and their interactions over the response variable (polyol obtained), and to determine the levels that maximize the polyol production. This ANOVA® was made mixing the contributions of no significant factors according to significance test of Fisher with a confidence level of 99%.

According to the analysis of variance carried out, it was obtained that DEG to PUR mass ratio has been the most significant factor with an influence of 28.60%. Temperature and DEA/PUR mass percentage ratio presented similar values with an influence of 23.07% and 22.49% respectively. Finally, time reaction had an influence of 18.42%. The contribution of the experimental and analysis error was low, 7.42%. These percentages have showed that all factors studied had a great influence on the polyol obtained, so all of them must be taken into account separately to optimise the glycolysis.

The Fig1 shows the influence of these factors or conditions studied separately to act on them directly to increase the polyol yield.

For the most influential factor, DEG/PUR mass ratio, the best level to obtain more polyol as it was expected, was in which more solvent was used, corresponding to the third level. The more solvent is used, the poliol yield will be greater, but the process economy will be decreased, making the process will not be viable and will not worth it. So, it is necessary to look for an intermediate point between economy and yield of the process.

The temperature factor offered the highest quantity of polyol with the second level tested. As has been explained previously, it can be seen that above 150 ºC the polyol yield decreases sharply due to the complexity of the shoe soles PUR and the amount of impurities which are released from the process and are mixed with the polyol.

The first level for time factor had the optimum quantity of polyol, so it was not necessary more time due to the amount of oligomers increase, decreasing the polyol yield.

By last, for the least influential factor, DEA/PUR mass percentage ratio, the best level was the first, in which the catalyst used was the lowest but was enough to favour the kinetic of the glycolysis reaction.

According to the analysis of variance carried out, if these best levels of control factors are chosen and are applied in the glycolysis process, a maximum mass ratio of polyol/PUR injected would be obtained whose value would be 0.81 ± 0.02.

However, the best levels were chosen less in the case of DEG/PUR which second level was selected due to economic aspects. This supposes that the quantity of polyol obtained theoretically decrease, but only in a 3.7% (0.78 ± 0.02), considering this percentage acceptable because of the environmental benefits obtained and because of the economy of the process will be improved.

In order to demonstrate the results obtained in the ANOVA analysis were right, a confirmatory experiment was carried out with the levels chosen, obtaining 0.80 polyol/PUR mass ratio. So, the glycolysis process of shoe soles has been optimised and demonstrates its technical viability.

3.2. Characterisation of recycled polyol

A GPC chromatography and a FTIR spectrophotometer were used to determine the molecular weight distribution and to identify chemical structure respectively. Virgin polyol was used for calibration purposes, in order to compare with the recovered product.

GPC chromatograms of the virgin and recycled polyol obtained in the glycolysis are shown in Fig2. As can be observed, both chromatograms show several peaks. The first peak, at lowest retention time (between 17-18 minutes), corresponds to polyol, indicating that molecular weight of both polyols is quite similar. The next peak, around 20 minutes, corresponds to the glycol, that indicates, as was mentioned above, that the full extraction of polyol from the mass of the reaction is quite hard due to the similar viscosity of the products, leaving some glycol in this phase. Finally, the peak at 22 minutes and almost 23 minutes corresponds to the solvent employed in the GPC analysis, tethrahydrofuran (THF).

Through these chromatograms it can be stated that the glycolysis has been optimised properly because the length of the chains in the recycled polyol is quite similar to virgin polyol. In this sense, the only precaution to be considered is the effect of possible impurities on the additivation of recycled polyol and their effect in the foaming.

The Fig3 shows the comparison between the recycled polyol phase and glycol phase obtained in the glycolysis. The main difference is the intermediate peaks between 18 and 19,5 minutes presents in the glycol chromatogram which corresponds to impurities formed in the glycolysis process.

In order to add more information to the polyol obtained, FTIR analysis was done. The FTIR spectra of both polyols, virgin and recycled, are presented in Fig4. As can be observed, both polyols have shown the same peaks indicating that both materials were similar. It demonstrates that the upper phase is formed by polyol, but there is a group of additional signals which are attributed to impurities (the same results as in GPC analysis). The new absorption bands in the recycled polyol are produced for the presence of excess of glycolysis compound (an increase in absorption bands due to stretching vibrations of hydroxyl end groups, -OH, around 3.420 cm^{-1}), trans-esterification carbamates (bands assigned to stretching vibrations of the C=O bond, found around 1.690-1750 cm^{-1} and linked to a band at 1.500-1.550 cm^{-1}) and the urethane group glycolysis product (presence of a band around 1.620 cm^{-1} assigned to bending vibrations of NH in primary amines).

3.3. Characterization of recycled PUR foams

Once the best formulation to obtained PUR foams was chosen, the shoe soles were performed following the industrial manufacturing line facilities of Garmaryga and Cauchos Ruiz Alejos. The behaviour in the use of an injection moulding machine was suitable. The mixture with the virgin polyol, the final viscosity in the circuits of the machine and the dosage in the injection head and in the moulds was correct.

Finally, 20% of recycled polyol and 80% of virgin polyol was the best ratio obtained in the formulation of PUR foams to obtain the required properties of the PUR foams.

In order to do comparisons, the shoe soles with virgin polyol and the shoe soles with recycled polyol were analysed.

A complete characterization of the new polyurethane foams manufactured with 20% of recycled polyol and 80% of virgin polyol, were carried out to determine the recycled polyol effect on the final properties of the foams. The mechanical properties analysed were hardness (UNE-EN ISO 868:2003), density (UNE 53526:2001, method A), abrasion resistance (UNE-EN 12770:2000), tensile strength (UNE-EN 12803:2001), elongation at break (UNE-EN 12803:2001), tear strength (UNE-EN 12771:2000) and flex resistance (UNE-EN ISO 17707:2005). The results obtained are presented in Table 2 and show that the incorporation of 20% recycled polyol into the virgin polyol mixture has not modified any of the tested properties necessary for the good use in footwear.

The rigidity as well as the density of the foams were the main parameters involved in the mechanical behaviour of the foams. The value of the hardness in the recycled foam was higher than in the original. This is because of the isocyanate excess in the recycled mixture, but this has not affected the quality of the foam. Therefore, the differences found in the density may be associated to the differences achieved in the size of the cells in the foams.

The values of tensile strength, abrasion resistance, elongation at break and tear strength have not varied in a significant percentage, fulfilling the quality standards necessary for both professional and urban footwear.

In parallel, the samples were subjected to hydrolysis resistance tests (7 days at 95% RH) and several samples were tested by tear strength before and after immersion. The results have not varied more than 20%, considering it suitable for use in safety footwear and urban footwear. In addition, the results of the hydrocarbon resistance for professional footwear are not modified using the recycled polyol.

Finally, it is important to notice that the presence of urethane groups was higher in the postconsumer PUR foam followed by the virgin and recycled polyol foam. These differences in the content of urethane groups among PUR from virgin or recycled polyol are due to the different index employed in the formulation of the foam.

As in the characterization of the polyol, a FTIR analysis were carried out to the foams showing no important difference among the materials as could be seen in Fig5. As can be observed, both samples have shown the same peaks indicating that both PUR foams were quite similar. New bands are detected in the recycled PUR foams at 3.279-3.340 cm^{-1} correspond to -NH group, which occupy the same position of -OH bands presents in the polyol. The -NH bands are narrower and less intense than the -OH band. The diisocyanate band is not observed and the carbonyl group, C=O, band appears at 1.705-1.772, indicating the possible formation of the urethane group. Besides, bands at 1.600 cm^{-1} correspond to the ring aromatic of 2,4-toluene diisocyanate.

4. CONCLUSIONS

In this research, an optimization of the chemical recycling process of PUR foams come from shoe soles waste have been carried out. An analysis of variance of the results, using the ANOVA® commercial software, was completed to obtain the conditions which maximize the polyol production. According to the results obtained by the analysis of variance, it was observed that DEG to PUR mass ratio was the most significant factor. The most suitable operating conditions were: T = 150 ºC, t = 90 min, DEG/PUR = 1.5 w/w, DEA/PU = 5 %w/w, to obtain a polyol/PUR mass ratio of 0.80. GPC and FTIR analysis verified that the recycled polyol was equivalent to virgin polyol with a high purity. So, the results have shown that glycolysis is an efficient process of recycling polyurethane rigid foams presents in shoe soles. It is important to point out the behaviour of rigid PUR foams in the glycolysis process were very different from that of flexible foams.

Furthermore, with the recycled polyol, new polyurethane foams were obtained to manufacture shoe soles again. The incorporation of 20% recycled polyol into the pure polyol, does not modify any of the tested properties necessary for good use in footwear. Once the new recycled shoe soles have been obtained, their physical and mechanical properties were analyzed, comparing them with the original ones. The values of tensile strength, abrasion, elongation and tear, did not vary in a significant percentage, achieving the quality standards necessary for both professional footwear and street shoes.

5. ACKNOWLEDGEMENTS

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TABLES

Table 1 Factors and levels used in the factorial design of experiments in the glycolysis

Factors	**Levels**		
	1	**2**	**3**
Temperature (ºC)	140	150	160
Time (min)	90	120	150
DEG/PUR (w/w)	1.0	1.5	2.0
DEA/PUR (%w/w)	5.0	7.5	10.0

Table 2 Characterization of the soles manufactured with recycled PUR vs.the reference value which is necessary fulfill

TEST	**Mean value of Recycled PUR foam sole**	**Reference value**
Hardness (ºShore A)	58 – 65	37
Density (g/cm^3)	0,55 – 0,70	0,52
Abrasion resistance (mm^3)	150 80	Max. 250 Max. 180
Tensile strength (N/mm^2)	5	3-7
Elongation at break (%)	425 – 459	Min. 400
Tear strength (N/mm)	5,6 7,6	Min. 5 Min. 7
Bending strength (30.000 cycles / increase of mm)	30.000 1 2	30.000 < 4 < 10

FIGURES

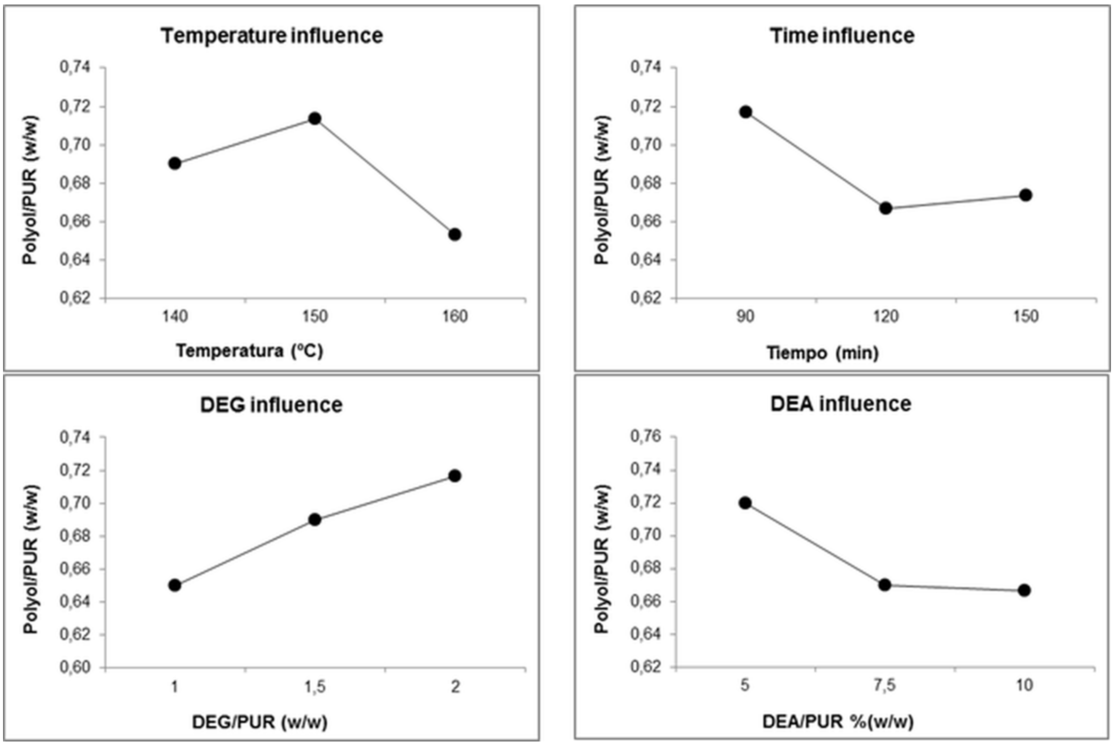

Fig1 Influence of factors in PUR glycolysis

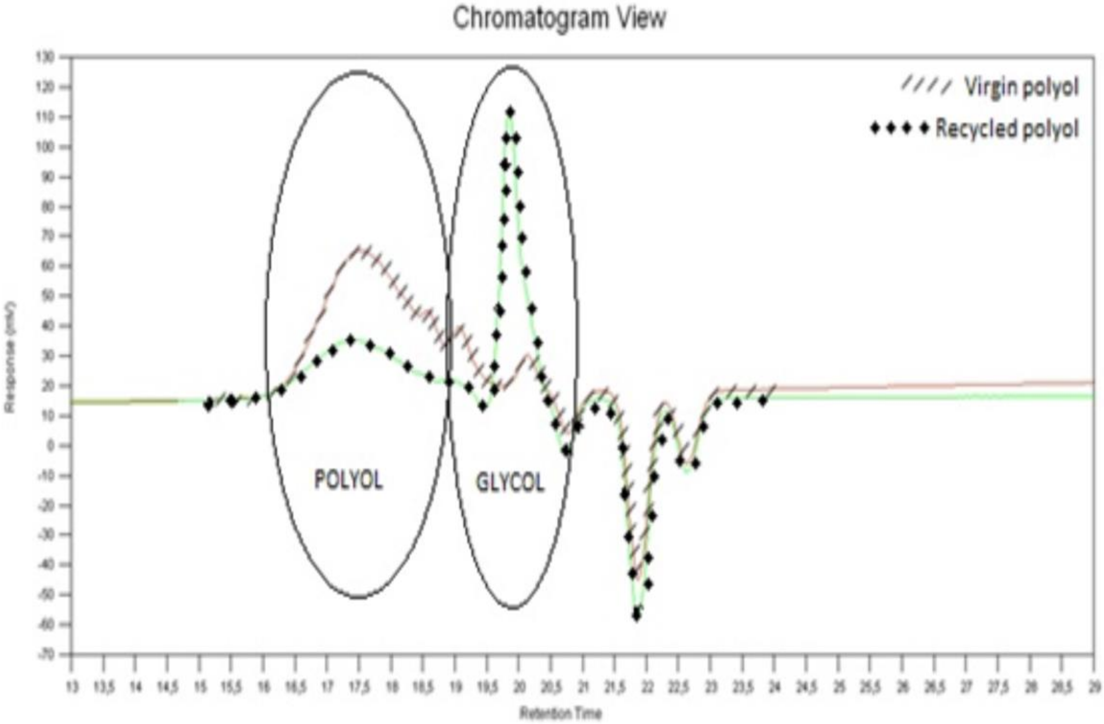

Fig2 GPC chromatograms (recycled polyol vs. virgin polyol)

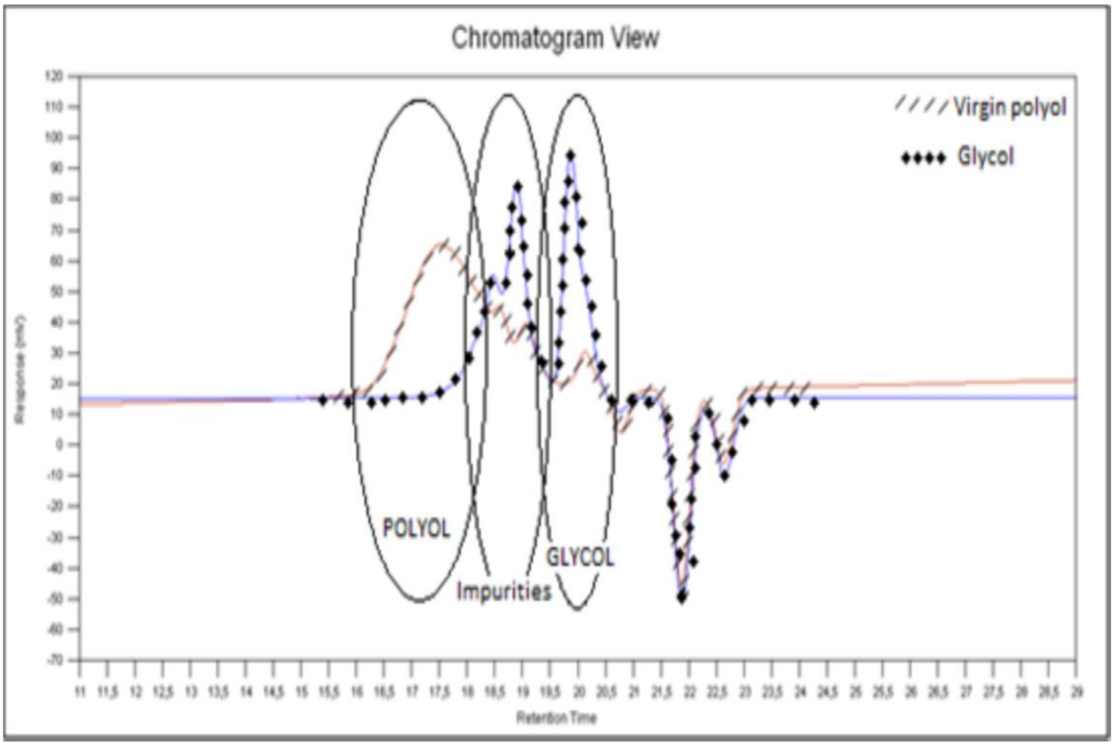

Fig3 GPC chromatogram (virgin polyol vs. glycol phase)

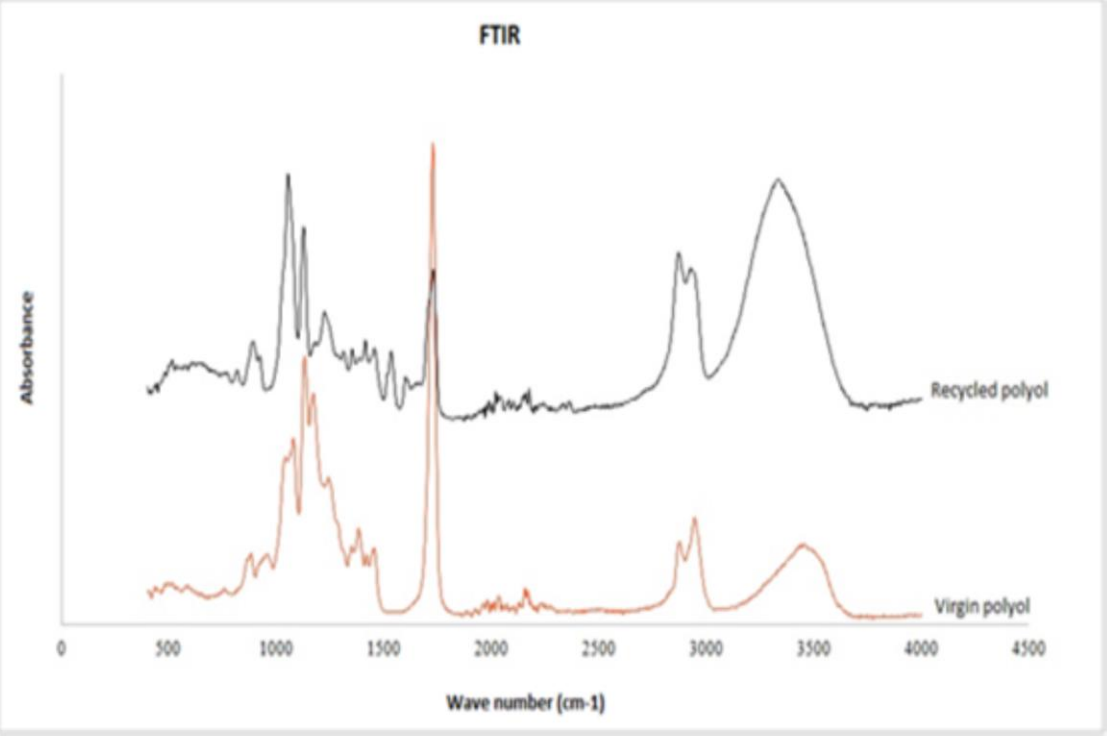

Fig4 FTIR chromatograms (recycled polyol vs. virgin polyol)

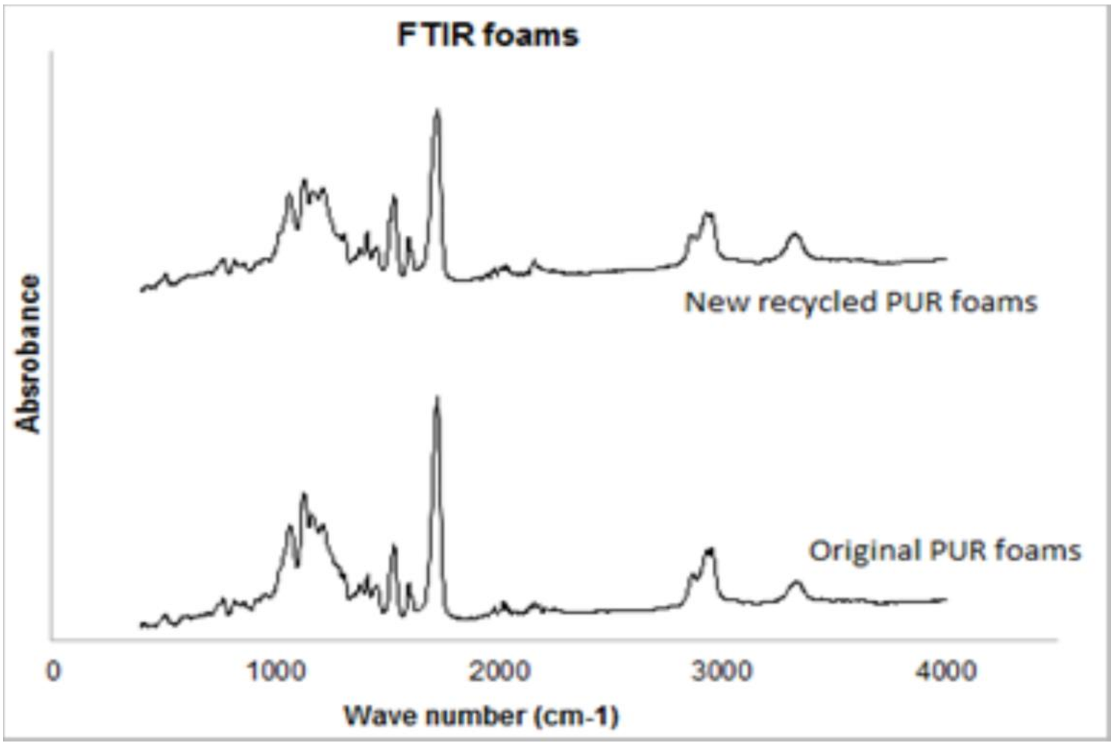

Fig5 FTIR chromatograms (recycled PUR foams vs. original PUR foams)