

**Synthesis and Use of Glycerol Based Hyperbranched Biopolyesters as Impact Modifiers for  
Poly (Butylene Succinate) Matrix**

**by**

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## Abstract

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Glycerol sources of different purity and succinic acid were employed for the synthesis of hyperbranched polyesters. Biobased polymers termed poly (glycerol succinate) (PGS) were obtained by polycondensation. The aim of this research was to determine the influence of impurities of glycerol source on the chemical and mechanical properties of PGS. It was found that the presence of free fatty acid residues in glycerol source is increasing the glass transition temperature of polyesters and decreasing their cross-linking density due to the incorporation of fatty acid residues to PGS structure. By these reasons, only high purity glycerol (>98% glycerol content) based PGS could effectively improve impact properties of poly (butylene succinate) (PBS) showing a 3-fold increment on impact strength while tensile strength was reduced to half original value of virgin PBS. These results show that efficient biobased impact modifiers for bioplastics can be obtained using biodiesel derived glycerol purified to high extent.

## **Acknowledgements**

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## List of abbreviations and defined terms

- 1) ASTM: American society for testing and materials
- 2) CG: Crude glycerol
- 3) DMA: Dynamical mechanical analysis
- 4) DSC: Dynamic scanning calorimetry
- 5) FAME: Fatty acid methyl esters, a.k.a. biodiesel
- 6) FFA: Free fatty acid
- 7) HBP: Hyperbranched polymer
- 8) LDPE: low density polyethylene
- 9)  $M_w$  : Molecular weight
- 10) PBAT: Poly (butylene adipate – co – terephthalate)
- 11) PBS: Poly (butylene succinate)
- 12) PCL: Poly (caprolactone)
- 13) PDLA: Poly (D – lactic acid)
- 14) PDLLA: Poly (DL – lactic acid)
- 15) PE: Polyethylene
- 16) PEO: Poly (ethylene oxide)
- 17) PG: Pure glycerol
- 18) PGS: Poly (glycerol succinate)
- 19) PHA: Poly (hydroxyalkanoate)
- 20) PHB: Poly (hydroxybutyrate)
- 21) PHBV: Poly (hydroxyl butyrate – co – hydroxyvalerate)
- 22) PLA: Poly (lactic acid)
- 23) PP: Polypropylene
- 24) PTT: Poly (trimethylene terephthalate)
- 25) PVC: Poly (vinyl chloride)
- 26) PVF: Poly (vinylidene fluoride)
- 27) RG: Refined glycerol
- 28) SEM: Scanning electron microscopy
- 29) TG: Technical glycerol
- 30) TGA: Thermogravimetric analysis
- 31) USD : United States dollars
- 32) wt: weight

## List of units of measurement and abbreviations

- 1) °C = degrees Celsius
- 2)  $\mu\text{m}$  = micrometers
- 3) cm = centimeters
- 4) g = grams
- 5) h = hours
- 6) Hz = hertz
- 7) J = Joule
- 8) kg = kilograms
- 9) kV = kilovolts
- 10) lb = pounds
- 11) m = meters
- 12) M = molar concentration
- 13) min = minutes
- 14) mm = millimeters
- 15) MPa = mega pascal
- 16) N = newton
- 17) Pa-s = pascal seconds
- 18) rad = radians
- 19) rpm = revolutions per minute
- 20) s = seconds

## **1. Introduction**

### **1.1. Bioproducts: the key for shifting to a sustainable biobased economy**

We currently live in an economic system based in fossil resources, which are being extracted from the environment without the possibility for being naturally renewed in a human time scale. Petroleum appears nowadays as the key resource in our economy, from which fuels, chemicals and materials are obtained. Since the industrial revolution in the 19<sup>th</sup> century, mankind has enjoyed the endless benefits of the power contained in every barrel of oil that has been drilled out from deep earth reservoirs. Nevertheless, petroleum is a finite resource, and several studies have shown the possibility of its depletion in a near future, suggesting that petroleum reservoirs will be emptied in the next 50 to 100 years [1]. We as humanity have come to a point where our dependence on petroleum is compromising the environmental sustainability of the development of nations.

This pressing challenge has created awareness in consumers and producers around the world, about the need of transforming gradually our fossil based economy into a new renewable based one, where the feedstocks for the industrial processes can be harvested and renewed in a time span that ensures the sustainability of the economic growth. Thus, a new economic paradigm is emerging, called bioeconomy, promoting the use of feedstocks that are renewable and include agricultural crops, crop – derived by-products, forestry resources, and other forms of renewable biomass in gradual substitution of petroleum based feedstocks [2]. This new bioeconomy paradigm has been highlighted as the new dominant economy for the next decades to come, where biotechnology will play a fundamental role, providing tools for developing bioproducts that can perform equal or better than existing petro – based products available in the

market, comprising biofuels, biochemicals and bioplastics. It is expected that in this way, the petroleum dependence will be gradually diminished and eventually substituted with biomass dependence, which will promote the development of domestic supply chains and the development of rural economies. The Organization for Economic Co-operation and Development (OECD) has elaborated a list of several biotechnologies with high probability of reaching the market by 2030 as part of this new bioeconomy concept development and implementation (Table 1).

**Table 1.** Biotechnologies with a high probability of reaching the market by 2030. Modified after ref. [55]

Agriculture	Health	Industry
More diagnostics for genetic traits and diseases of livestock, fish and shellfish.	Improved drug delivery systems from convergence between biotechnology and nanotechnology	Greater market share for biomaterials such as bioplastics, especially in niche areas where they provide some advantage.
Improved varieties of major food and feed crops with higher yield, pest resistance and stress tolerance developed through GM, MAS, intragenics or cisgenesis	Extensive screening for multiple genetic risk factors for common diseases such as arthritis where genetics is a contributing cause	High energy-density biofuels produced from sugar cane and cellulosic sources of biomass.
Major staple crops of developing countries enhanced with vitamins or trace nutrients, using GM technology	Low-cost genetic testing of risk factors for chronic diseases such as arthritis, Type II diabetes, heart disease, and some cancers.	Improved micro-organisms that can produce an increasing number of chemical products in one step, some of which build on genes identified through bioprospecting
Cloning of high-value animal breeding stock	New nutraceuticals, some of which will be produced by GM micro-organisms and others from plant or marine extracts	Improved enzymes for a growing range of applications in the chemical sector
Widespread use of marker assisted selection (MAS) in plant, livestock, fish and shellfish breeding	Regenerative medicine providing better management of diabetes and replacement or repair of some types of damaged tissue.	Biosensors for real-time monitoring of environmental pollutants and biometrics for identifying people.
GM plants and animals for producing pharmaceuticals and other valuable compounds	Greater use of pharmacogenetics in clinical trials and in prescribing practice, with a fall in the percentage of patients eligible for treatment with a given therapeutic	
Genetically modified (GM) varieties of major crops and trees with improved starch, oil, and lignin content to improve industrial processing and conversion yields	Many new pharmaceuticals and vaccines, based in part on biotechnological knowledge, receiving marketing approval each year.	
	Improved safety and efficacy of therapeutic treatments due to linking pharmacogenetic data, prescribing data, and long term-health outcomes.	

The transition from the petro-based economy to a renewable based bioeconomy will be realized gradually, with the introduction to the market of bioproducts that can be comparable to petro-based alternatives on a cost/performance basis. In 2005, the global chemical market (excluding pharmaceuticals) was evaluated in \$1.2 trillion, with a presence of bioproducts reaching \$21.2 billion (1.7% of total). The global chemical market is expected to grow to over \$2 trillion per year in 2025, with bioproducts replacing petro-based products to a further extent, reaching a market value of more than \$500 billion (22% of total) as detailed in Table 2.

**Table 2.** Projected global markets of chemical sectors. Modified after ref. [56]

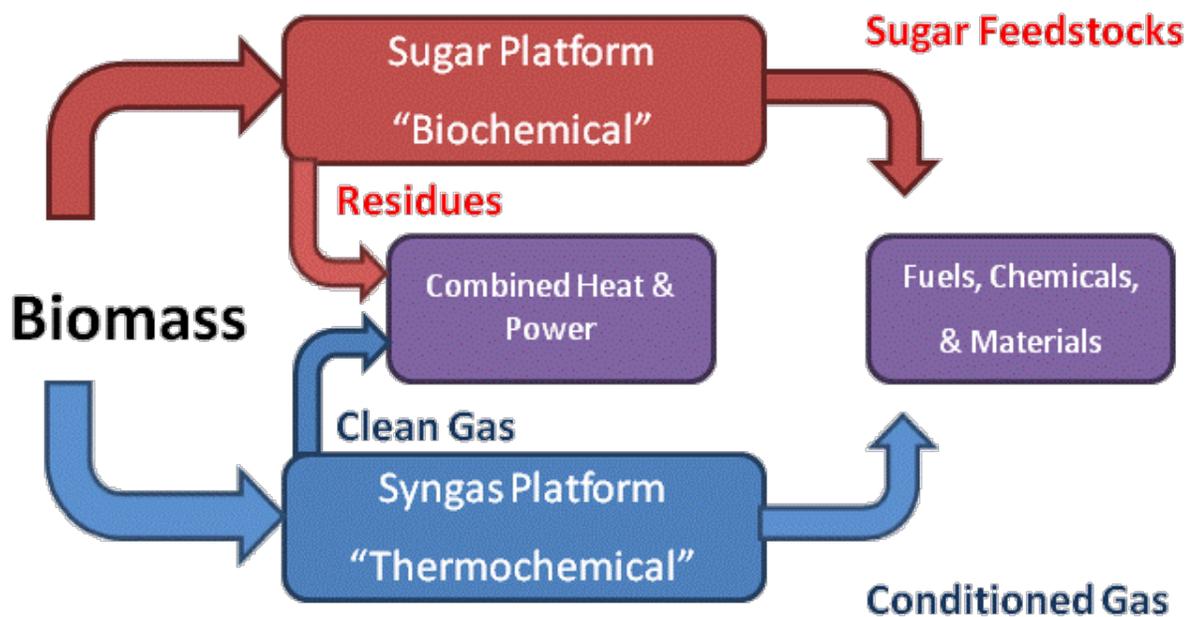
(Billion U.S. dollars)

Chemical sector	2005		2012		2025	
	Total	Biobased	Total	Biobased	Total	Biobased
Polymer	250	0.3	290	15 - 30	452	45 - 90
Commodity	475	0.9	550	5 - 11	857	50 - 86
Fine	100	15	125	25 - 32	195	88 - 98
Specialty	375	5	435	87 - 110	679	300 - 340
<b>Total</b>	<b>1200</b>	<b>21.2</b>	<b>1400</b>	<b>132 - 183</b>	<b>2183</b>	<b>483 - 614</b>

The key strategy for the realization of this new paradigm in the industrial area is to be able to set an integrated biorefinery concept, where renewable biobased feedstocks can be processed to obtain biofuels, biochemicals and biomaterials, as the analogous of the classic petroleum refinery concept, and co-products or waste streams of the main production steps can be used as inputs for subsequent processes, aiming to set a zero waste production [2, 3].

According to United States National Renewable Energy Laboratory (NREL), two main concepts for biorefinery can be adopted: the biochemical route, also called “Sugar Platform”, involving fermentations of the sugars present in biomass as the main transformative steps of the biorefinery, and the thermochemical route, also termed “Syngas Platform”, where the biomass is subjected to thermochemical transformative processes aiming to produce mainly syngas through biomass gasification, which can be further converted to other bioproducts in the biorefinery.

Figure 1 shows schematically these two biorefinery approaches.



**Figure 1.** Schematic representation of two biorefinery concepts. Redrawn after ref. [57].

Bioproducts, comprising biofuels, biochemical and biomaterials are the next generation of products that will realize the transition from a fossil based economic growth, to a renewable, sustainable biobased economy [4]. This will be done through a gradual introduction to the market of biobased products that can be comparable with petro-based products already available in the market in a cost-performance basis. The change has already started and a dramatic

expansion of biobased industries will be observed in the next 20 years, decreasing drastically the use of fossil based resources and increasing the use of biomass as the building block for the economic growth of the society.

## **1.2. Biofuels as an alternative to substitute fossil fuels**

The usage of fossil fuels is compromising the long term sustainability of the global economies in several ways. One side of the problem concerns the reduction of crude oil reserves and difficulties in their extraction and processing, leading to increased prices of petroleum derived fuels. On the other hand, transportation and energy sectors using fossil fuels contribute with more than 20% and 60% of the emissions of CO<sub>2</sub> and greenhouse gases in developed countries, rising concerns about its effect in global warming [5]. It is widely accepted that using fossil fuels as a source of energy should be gradually substituted with renewable, clean energy sources to reduce carbon dioxide and greenhouse gas emissions [6].

Among existing renewable energies, liquid biofuels have the potential to become the short time alternative for gradually diminishing crude oil usage since through blending with traditional gasoline, its introduction to the market could be done without requiring any major step in redesigning transportation and industrial systems already operating. Bioethanol and biodiesel have been traditionally the most widely produced biofuels, and its introduction to the market is already a reality in many countries. The world annual production of bioethanol and biodiesel reached 83.1 and 22.5 billion liters respectively in 2012 [7]. The introduction of these biofuels to the market represents great environmental and economic advantages. Unfortunately, nowadays these biofuels are produced mainly from food grade feedstocks, and cultivable soil is being used for providing feedstocks for their production (corn and sugarcane for bioethanol,

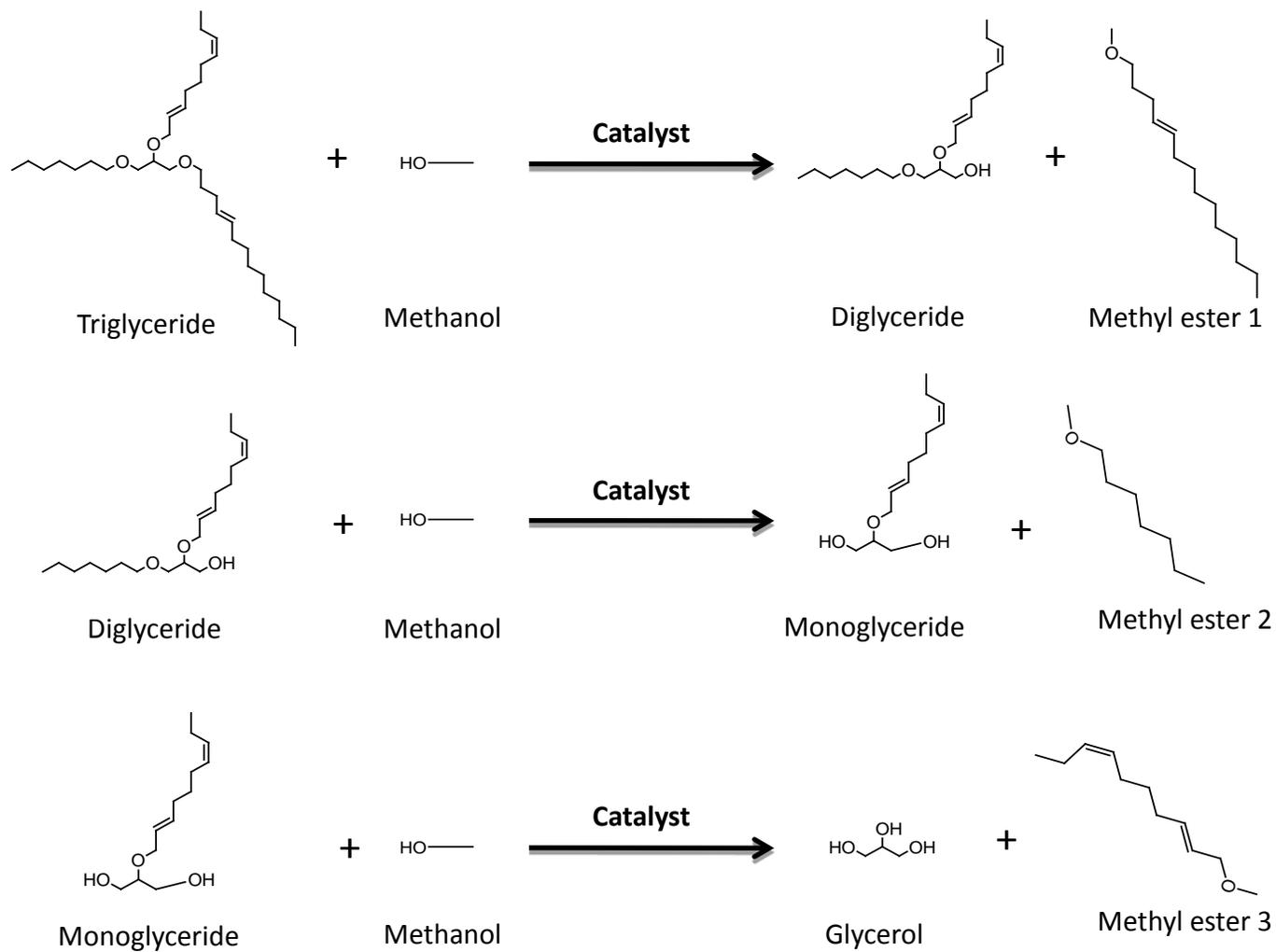
vegetable oil for biodiesel) [8]. A major challenge for making liquid biofuels a realistic alternative to substitute petroleum in the long term is the availability of a renewable, sustainable and non-food grade feedstock for biofuel production that ensures the production of enough biofuels for satisfying world demand annually. Much research has been done in this field and remarkable examples of new and promising non-food feedstocks for the biofuel industry, such as lignocellulosic biomass for bioethanol and algae for biodiesel production, have been reported in the existing literature [9] making possible to think about a renewable and sustainable source of liquid biofuels for the next generations.

#### **1.4. Biodiesel: Synthesis, characteristics and co-products**

Biodiesel is defined by ASTM D6751 standard as an “n-fuel comprised of monoalkyl esters of long chain fatty acids derived from vegetable oils or animals fats, designed as B100”. Biodiesel has been pointed out as the most promising liquid biofuel because it presents several technological and environmental advantages, such as high biodegradability, low CO<sub>2</sub> emissions and lack of transportation and storage problems, which had lead its large scale production and distribution in many countries using animal fats and vegetable oils as the main feedstocks [6]. Also, due to the easiness of production, many small scale producers have installed biodiesel production facilities, often using waste cooking oil as the feedstock for transesterification reaction [7]. Biodiesel synthesis is performed by contacting an alcohol (usually methanol) with a source of triglycerides, such as vegetable oil or animal fat in the presence of a catalyst. This causes a transesterification reaction to occur, also called alcoholysis, where fatty acid residues are cleaved from glycerol backbone and end capped by methyl group from methanol, giving rise to methyl esters of fatty acids (FAMES) and glycerol in a sequential mechanism as shown in Figure 1 [10]. In a typical transesterification reaction 90 wt% of the oil feedstock is converted to

biodiesel, and remaining 10 wt% is recovered as crude glycerol, with a variable glycerol content which can range from 20 to 80 wt% [11].

World biodiesel production reached 22.5 billion liters in 2012 [7]. In Canada, about 110 million liters of biodiesel were produced in 2011, using animal fat as the main feedstock followed by soy and canola oil [12]. The production of biodiesel in Canada is distributed across the territory, with 22 plants operating or under construction, and a total nominal capacity installed of 1.2 billion liters [13]. For meeting 2% biofuel usage recommendation of Canadian Renewable Fuel Association, biodiesel production in Canada should be increased to 600 million liters and in Ontario, 160 million liters of biodiesel would be required [12,14]. As a result of this 6 - fold expansion in biodiesel production in the incoming years in Canada to meet 2% biofuels usage, a drastic increment in the production of crude glycerol from biodiesel sources will be seen. The lack of direct value added applications on the market for this crude glycerol appears as a huge barrier for the economic and environmental sustainability of this biodiesel expansion. It is therefore absolutely necessary to find new alternative value added uses of crude glycerol, both to ensure economic sustainability of such a dramatic biodiesel production increment and also for allowing the biodiesel industry to expand under the biorefinery concept, aiming to find value added uses to all of its co – product to maximize benefits and minimize waste production.

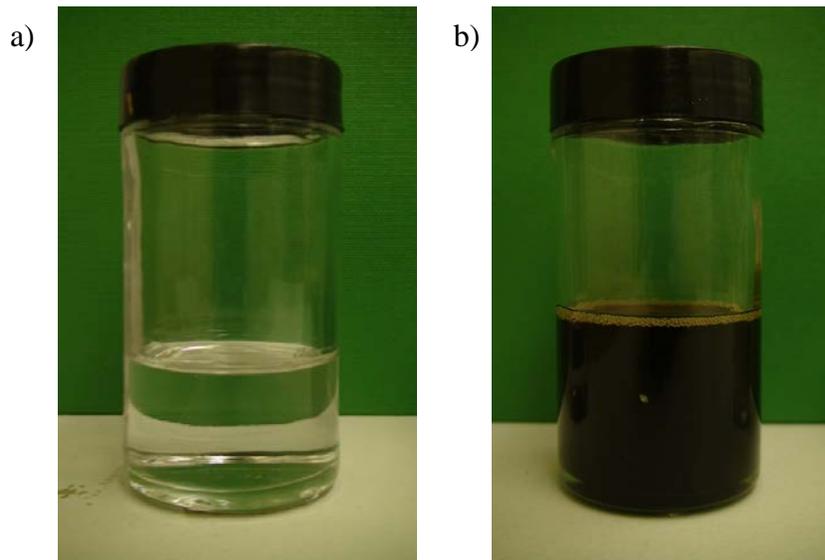


**Figure 2.** Schematics of transesterification reactions for a model triglyceride.

## **1.5. Crude glycerol as a sustainable feedstock for bioproducts development**

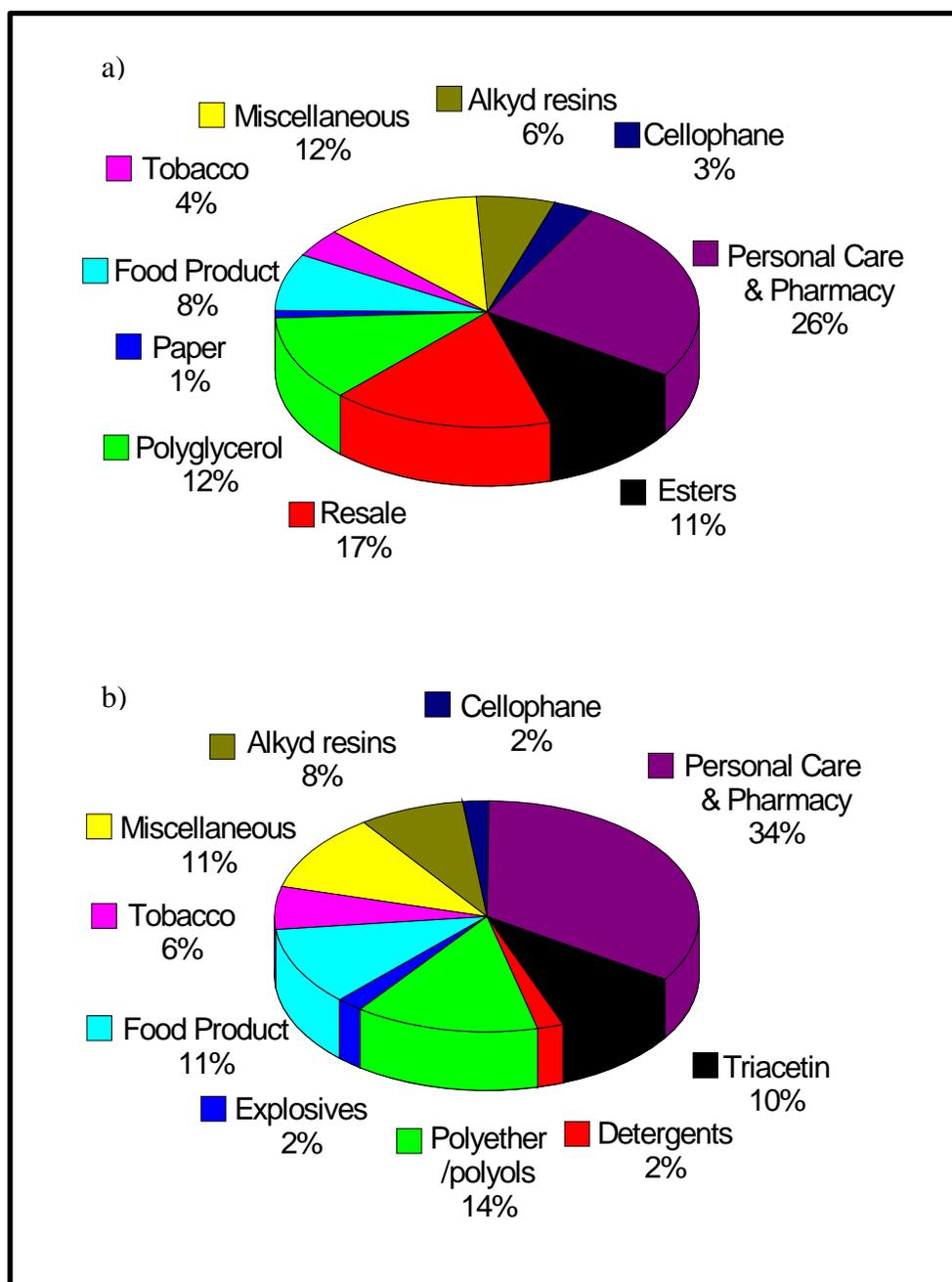
Crude glycerol is the co – product of biodiesel production, which is commonly performed by means of a transesterification reaction of an oil source (usually animal fat or vegetal oil) with an alcohol (usually methanol) in presence of a basic or acid catalyst. This reaction involves the scission and esterification of fatty acid molecules from the glycerol backbone in mono, di and triglycerides present in oil, giving rise to fatty acid alkyl esters (FAAE) (0.9 g FAAE/g oil), which after easy purification can be used as fuel (biodiesel), and to crude glycerol (0.1 g crude glycerol/g oil), which can be composed of glycerol, methanol, soap, fatty acids, glycerides, water and ash.

The exact composition of crude glycerol is variable according to the feedstock employed and the production method in the biodiesel synthesis, as has been reported by several studies [11, 17, 18]. The glycerol content in crude glycerol can range from 20 to 80 wt%, whereas pure glycerol has a glycerol content of 99.9 wt% (Figure 3). The remaining percentage in crude glycerol samples can be comprised of any combination of methanol, soap, fatty acids, glycerides, water and ash coming from transesterification process.



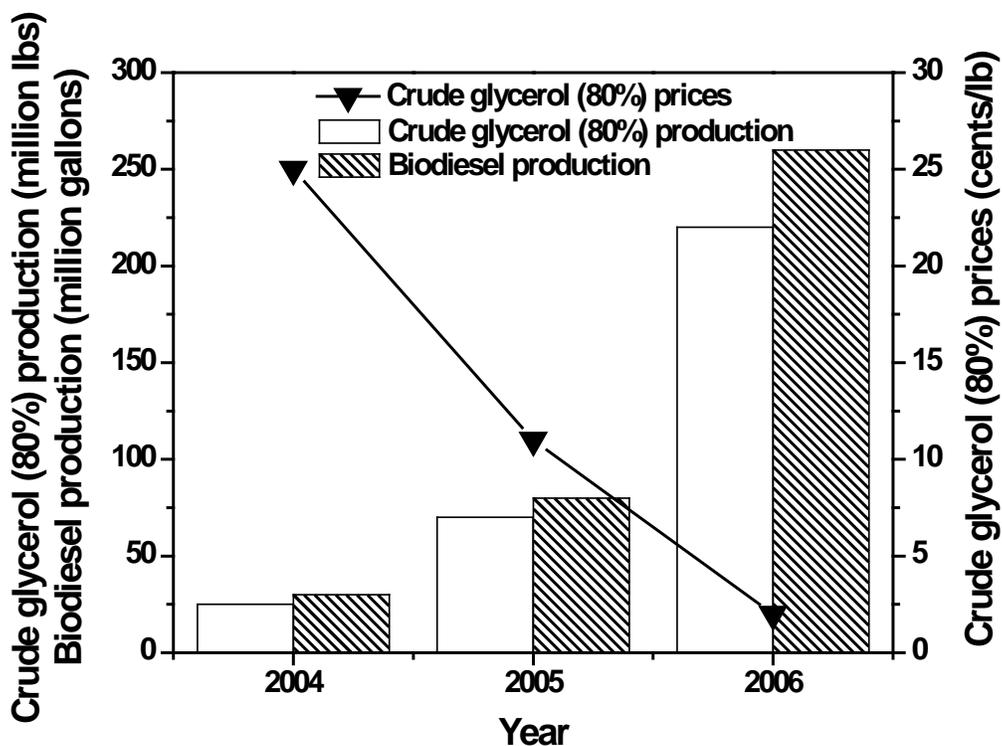
**Figure 3.** Example of a) pure glycerol sample, b) crude glycerol sample.

The highest industrial usage of pure glycerol is found in personal care and pharmacy, food and tobacco products. These are also the markets which have shown the highest expansion on glycerol demand in the past few years (Figure 4). Food, cosmetic and pharmaceutical applications require high purity ingredients, and their quality is strictly regulated by governmental agencies such as FDA in the United States for example. This is the main reason causing crude glycerol not to be used as a direct substitute of pure glycerol without incurring in extensive purification steps to increase the glycerol content at least up to 99.5 wt% for meeting quality requirements to be used in cosmetic, personal care, pharmaceutical, and other value added products [15]. Traditional low value uses of crude glycerol have been animal feeding and low grade burning fuel [16]. This has created a big challenge for biodiesel producers who have to manage to upgrade crude glycerol or dispose it properly, impacting negatively the sustainability of biodiesel production especially for small scale producers.



**Figure 4.** Comparative end use of glycerol during a) 1995 and b) 2006. Redrawn after ref. [15] with permission.

The world production of crude glycerol in 2004 was of 1.1 billion lb (500,000 ton) and it is expected that by 2020 the production would be increased up to 5.8 billion lb (2.6 million ton) [15, 16]. This dramatic increment of the glycerol stock, led by the expansion of biodiesel industry has made its price drop considerably in the past few years (Figure 5), setting its price to around 0.1 USD/kg [16]. In the United States, in a 2 year period (2004 – 2006), the biodiesel production was incremented 10 times, leading to a 10 fold increment in crude glycerol production with 80% of glycerol content. As a result, the price of crude glycerol dropped drastically, forcing many glycerol refineries to stop operations [58].



**Figure 5.** U.S. biodiesel production and its impact on glycerol prices on 2004 – 2006 period.

Redrawn after ref. [58] with permission.

The sustainability of the biodiesel production process could be greatly enhanced regarding economic and environmental aspects if new value added applications were developed for using crude glycerol directly or semi refined glycerol, which doesn't meet the quality requirements for being used in food and pharmaceutical industries but still present a high glycerol content, as a feedstock for the synthesis of bioproducts (biofuels, biochemicals or biomaterials). In fact, crude glycerol components glycerol, methanol, fatty acids, soaps, and glycerides present either hydroxyl or carboxyl functionalities which make them candidates for reactive processes in order to synthesize bioproducts. Moreover, glycerol, fatty acids, soaps, and glycerides are organic carbon molecules, which also make them suitable to be used as feedstocks for fermentative processes, where microorganisms can obtain energy from metabolizing these molecules. This makes crude glycerol an ideal building block for bioproducts development which could set a biorefinery concept around biodiesel production and help to establish the new biobased economy concept in the biodiesel market. A recent survey showed that many value added application of crude glycerol have been researched in the past few years, which highlights both the multifunctional nature of this co-product as a feedstock for chemical and biotechnological processes and the awareness and effort of scientific community for finding solutions to this bottleneck in biodiesel industry expansion (Table 3).

**Table 3.** Potential uses for crude glycerol. Reprinted from ref. [19] with permission

Product name	Process Method/Nature	Researchers/Scientists
1,3 - propanediol	Continuous and batch microbial fermentations ( <i>C. butyricum</i> , <i>K. pneumoniae</i> )	Himmi et al (1999), Papanikolaou and Aggelis (2003), Zeng (1997), Xiu et al. (2004), Menzel et al (1997), Wang et al (2001), Wang et al (2003)
	Selective hydroxylation technique	
Hydrogen	Continuous microbial fermentation ( <i>E. aerogenes</i> HU-101)	Ito et al (2005), Wood (2002), Hirai et al (2005), Huber et al (2003), Valliyappan (2001)
	Catalytic reforming operation at moderate temperatures and pressures	
	Steam reforming of glycerol with metal catalysts	
	Aqueous phase reforming over a tin promoted Raney-nickel catalyst.	
	Pyrolysis and steam gasification of glycerol	
Succinic acid	Microbial fermentation ( <i>A. succiniciproducens</i> )	Lee et al (2001)
1,2-propanediol	Low pressure hydrogenolysis in multi clave reactor pressurized with Hydrogen	Dasan et al (2005), Perosa and Tundo (2005)
	Selective hydrogenolysis with Raney nickel catalyst in an autoclave with hydrogen	
Dihydroxyacetone	Chemoselective catalytic oxidation with platinum metals	Garcia et al (1994), Kimura (2001), Bauer et al (2005)
	Selective oxidation of glycerol with platinum- bismuth catalyst	
	Microbial fermentations in batch/semi continuous process ( <i>G. oxydans</i> )	
Polyesters	Reacting glycerol with adipic acid in presence of tin catalysts	Stumbe and Bruchmann (2004), Pramanick et al (1988), Alksnis et al (1976), Nagata et al (1996), Agach et al (2012)
	Reacting citric acid and glycerol at different molar ratios	
	Polycondensation of oxalic acid and glycerol	
	Reacting glycerol and aliphatic dicarboxylic acids	
	Polycondensation of glycerol and succinic acid	
Polyglycerols	Selective etherification of glycerol	Clacens et al (2002)
Polyhydroxy- alkanoates	Fermentation of hydrolized whey permeate and glycerol	Koller et al (2005)

## **1.6. Plastics vs. bioplastics: Characteristics, comparison and market scenarios**

Plastics are present in our everyday life in a wide range of applications, ranging from automotive parts to food packaging. The total plastic production in 2012 in the US was of nearly 106 billion lbs. (~48 million tons) with a predominant production of various form of polyethylene (PE, 35%), polypropylene (PP, 15%) and polyvinyl chloride (PVC, 14.2%) [20]. In the European Union, the amount of plastics produced in 2012 reached 57 million tons, with a predominant presence of polypropylene (18.8%), various form of polyethylene (17.5%) and polyvinyl chloride (10.7%) [21]. The major sector of applications for polymers in both American and European Market are packaging applications and the total world plastic production reached 288 million tons in 2012 [20,21].

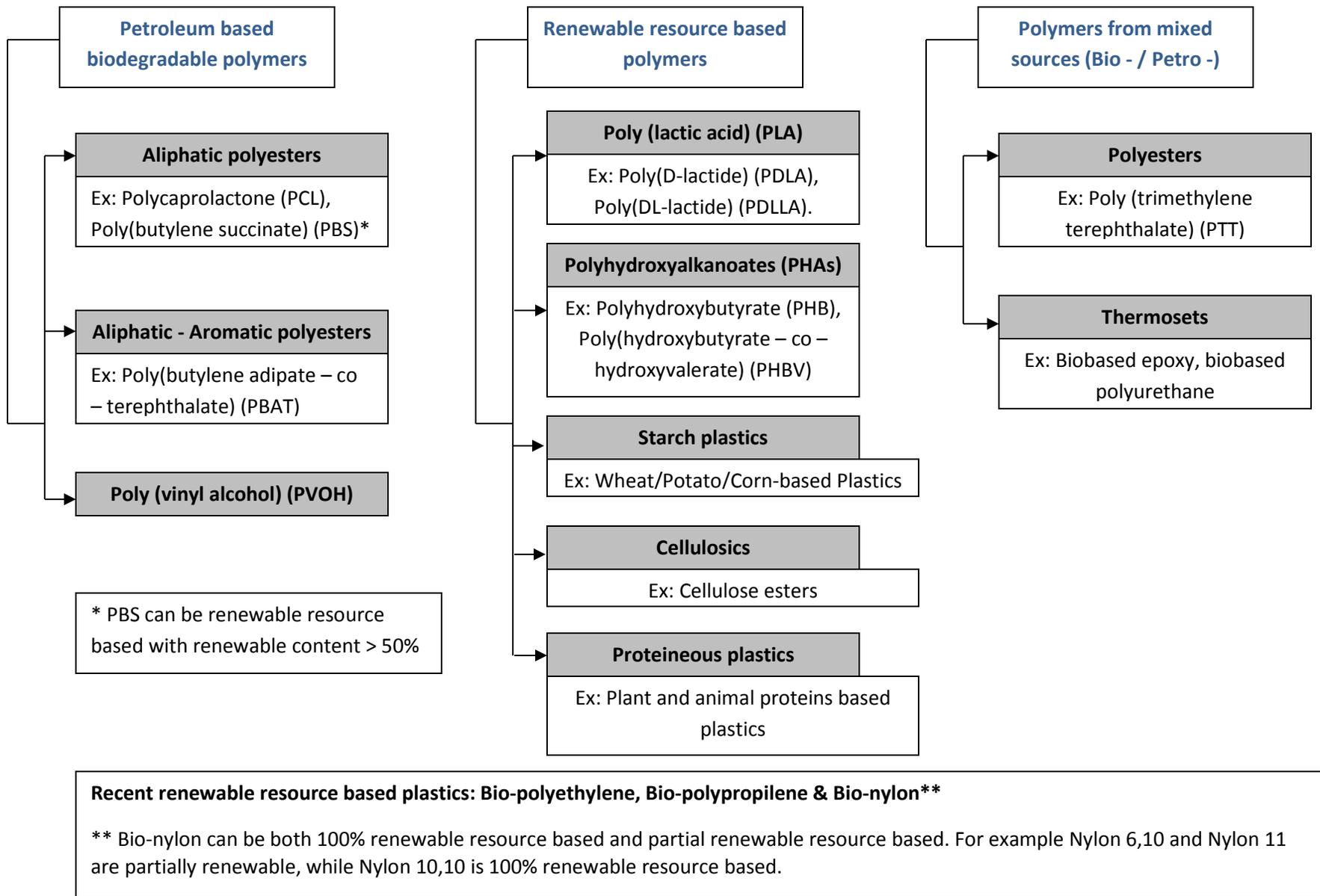
The aforementioned polymers (polyethylene, polypropylene and poly vinyl chloride) are being produced with extensive use of petroleum derived resources. Furthermore, these polymers are not biodegradable, and after the completion of its use, they can be present on the environment for many decades and even centuries. The fossil nature of the feedstock used for plastic production and its limited biodegradability which forces to dispose in landfills the plastic waste which is not recycled, remaining there for many decades without degradation, leads to concerns about economic and environmental sustainability of plastic usage. The petroleum dependence can be gradually alleviated by the introduction of bioplastics to the market, which can be synthesized partially or totally from renewable resources. Moreover, some bioplastics present the great environmental advantage of being biodegradable. Bioplastics represent a wide spectrum of thermoplastics that are obtained from biological resources and fossil resources or combination of both [22]. Market projections about bioplastics indicates that their production will reach 2.3 million tons in 2013 and 3.5 million tons in 2020, with an average annual rate of 37% from 2009

to 2013 and 6% from 2013 to 2020, which is much higher than the expected 5% annual growth of traditional plastics [4]. Undoubtedly, the adoption of bioplastics in the modern industry will contribute to increase the sustainability of our economy, without compromising the wellbeing of the society.

### **1.7. Bioplastics: classification and uses**

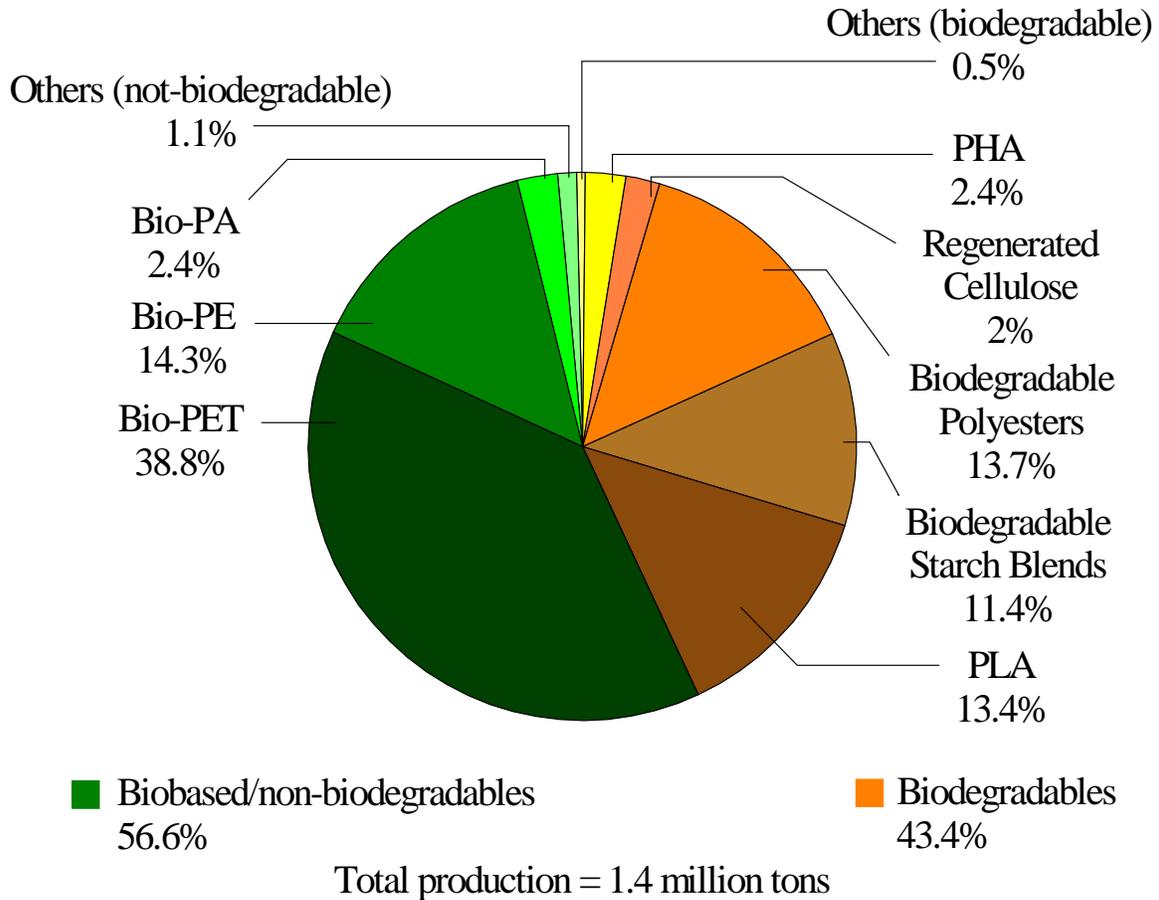
A plastic can be called bioplastic when it fulfills one or both of these requirements: being biobased, or being biodegradable [4]. Biobased means a polymer that is totally or partially synthesized using renewable resources or its derivatives. That is, polymers that can be obtained directly from nature as starch, or polymers that can be synthesized using at least a fraction of monomers obtained directly or indirectly from biomass, as bio-polyethylene that has been recently synthesized using ethanol from sugarcane. Biodegradable in the practical sense means a polymer which is compostable, meaning that it will be disintegrated into biocompatible (non ecotoxic) molecules in a 60 wt% or a 90 wt% in 180 days under composting conditions, according to different standard measurements [23, 24]. Bioplastics can be classified according to their production methods as follows (Figure 6) [22].

- (i) Renewable resource based bioplastics: The polymers in this family include those synthesized naturally in living organisms as plants and bacteria, and also those synthesized entirely using renewable resources. Examples of this family of polymers are: poly (lactic acid) (PLA), polyhydroxyalkanoates / polyhydroxybutyrates, starch, cellulose, lignin, chitosan and proteins, etc. Recently, polypropylene, polyethylene and nylon have been synthesized using renewable resources, being included in this family of bioplastics.
  
- (ii) Petroleum based bioplastics: The polymers from this family are those synthesized from petroleum derived resources being biodegradable at the same time. Examples of this family of polymers are polycaprolactone (PCL) and poly (butylene adipate-co-terephthalate) (PBAT), etc.
  
- (iii) Bioplastic from mixed sources: This family of polymers comprises those polymers synthesized using a combination of renewable and non-renewable monomers. Some examples of polymers from this family are poly (trimethylene terephthalate) (PTT), biobased thermosets and biobased blends, etc.



**Figure 6.** Classification of bioplastics based on their production routes. Redrawn after ref [22] with permission.

Bioplastic production in past few years has been dominated by the so called drop-in alternatives. This means, polymers that have been traditionally produced from petro-based resources, which now have been synthesized using biobased monomers, or a combination of biobased and petro-based monomers. These drop-in solutions have dominated the market of the bioplastics in recent years because they do not need any technological reconversion of the polymer processing facilities for its introduction as replacement of petro-based resins. Among drop-in polymers, the most remarkable examples are poly (ethylene terephthalate) (PET), polypropylene (PP) and polyethylene (PE), which are widely used petro-based polymers, but recently they have been developed using at least a fraction of biological feedstocks, and introduced into the market directly as substitution of petro – based analogues. The main advantage of using these drop – in biopolymers is that at least a fraction of them has been obtained from renewable resources, contributing to reduce the petroleum dependence of the market. Figure 7 shows the total bioplastics production capacity in 2012. Biobased PET and PE dominated more than 50% of the global bioplastics production reaching more than 500.000 tons produced, due to its direct application for replacing petro-based bottles and packaging respectively [59].



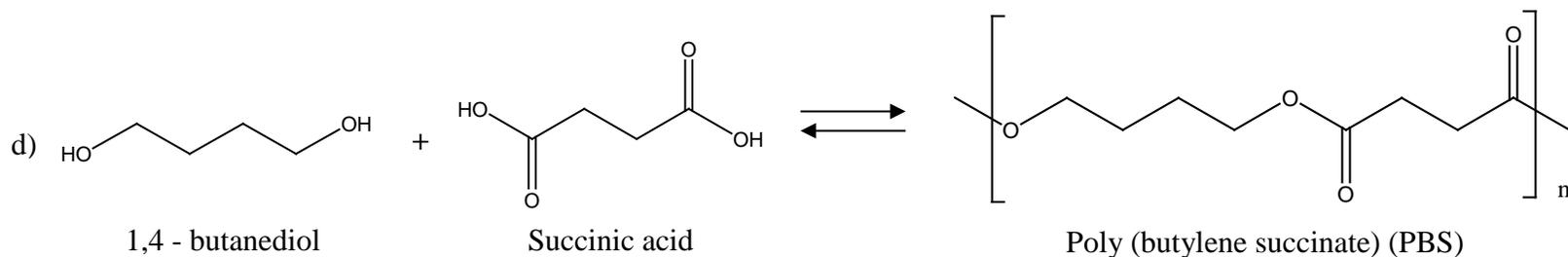
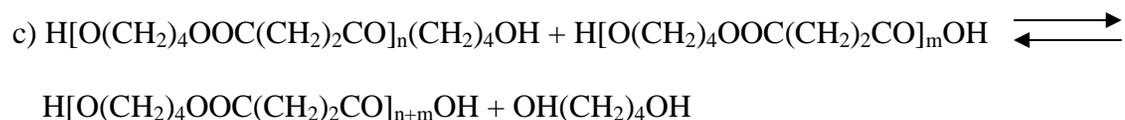
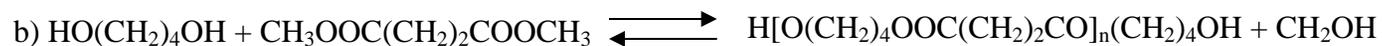
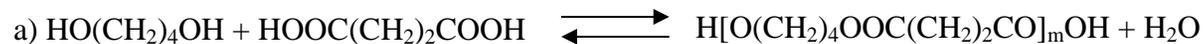
**Figure 7.** World bioplastic production in 2012. Redrawn after ref [59] with permission.

The introduction of biobased polypropylene (PP), polyethylene (PE) and poly (ethylene terephthalate) (PET) represents a great contribution towards reducing our petroleum dependence. Unfortunately, these polymers are still not biodegradable. New kind of biopolymers have been introduced in the market which exhibit biodegradability such as poly (lactic acid) (PLA) or poly (hydroxyalkanoates) (PHAs) aiming to replace non-biodegradable commodity plastics. Nevertheless, in a cost-performance basis, they are still away from overcoming traditional commodity plastics such as polypropylene, because they present many disadvantages from the processing and application point of view compared to traditional non-biodegradable polymers

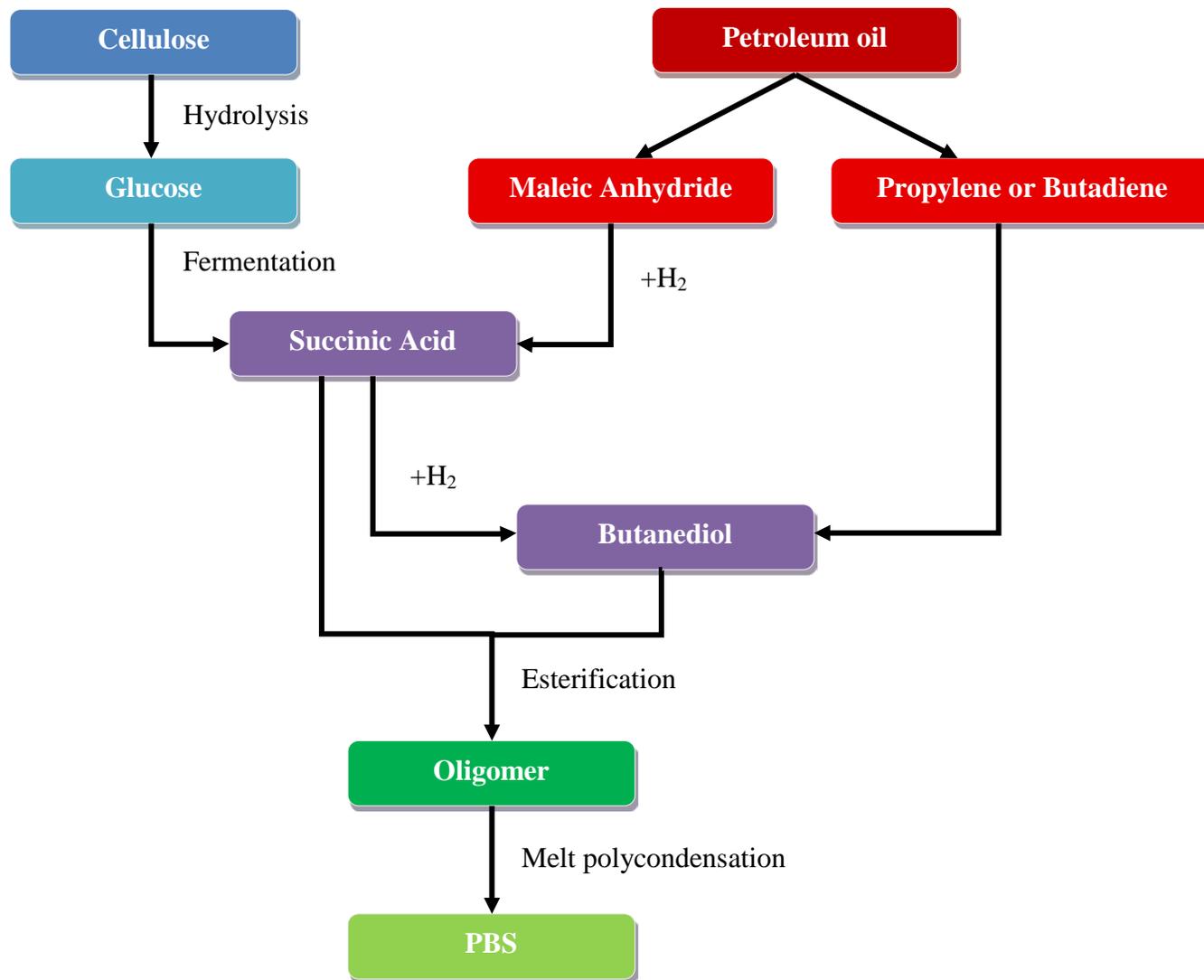
[27]. In spite of this, biodegradable plastics are receiving more and more attention from polymer processing companies and a wide range of applications for these polymers has been developed and will continue to grow. The most produced and utilized biodegradable bioplastics nowadays are poly (lactic acid) (PLA), poly (hydroxyalkanoates) (PHA), and starch plastics. A recent report showed that the capacity of production of these two biopolymers is expected to quadruple in 2020, with major investments in Asia and South America because of easier access to feedstocks and favorable political framework [61]. These bioplastics find many uses in short useful life applications, such as flexible films, injection – molded objects, and agricultural mulches. Biobased polyols, prepared from vegetable oils such as soybean or canola oil, are reaching the market for the synthesis of polyurethanes [4].

### **1.8. Poly (butylene succinate), (PBS): Advantages and drawbacks**

Poly (butylene succinate) (PBS) is a biodegradable aliphatic polyester which has been traditionally produced by polycondensation reactions involving succinic acid (or dimethyl succinate) and butanediol. Both monomers had been traditionally obtained from petroleum resources, but nowadays, biotechnological processes have been established for the production of both monomers from biobased resources. Furthermore, the synthesis of biobased poly (butylene succinate) using biobased succinic acid has already been established at industrial scale [25, 26]. Poly (butylene succinate) is usually synthesized in two steps. The first step of reaction, involves the oligomerization of the dicarboxylic acid and the diol (usually succinic acid and butanediol) and the second step consist in a melt polycondensation, where oligomers are further polymerized to render a high molecular weight polymer product (Figure 8) [62]. A schematics of poly (butylene succinate) synthesis process involving petro or bio – based monomers as feedstocks is shown in Figure 9.



**Figure 8.** Schematics of poly (butylene succinate) synthesis. Oligomerization of 1,4 – butanediol with a) succinic acid and b) dimethyl succinate followed by c) melt condensation of oligomers to render high molecular poly (butylene succinate). d) Molecular representation of poly (butylene succinate) synthesis from condensation of 1,4 – butanediol and succinic acid. Redrawn after ref. [62] with permission.



**Figure 9.** Flow chart of poly (butylene succinate) (PBS) synthesis. Redrawn after ref. [62] with permission.

The world production of poly (butylene succinate) (PBS) on 2011 was lower than 1 million tons. This production is expected to grow steadily as more and more companies join the business, reaching 2 million tons by 2020 [61]. A list of companies producing poly (butylene succinate) can be found in Table 4.

**Table 4.** Global producers of poly (butylene succinate) (PBS). Modified after refs. [27, 62]

<b>Manufacturer</b>	<b>Location</b>	<b>Product</b>	<b>Capacity (thousands of tons/year)</b>
Hexing Chemical <sup>a</sup>	China	Hexing PBS	10
Xinfu Pharmaceutical <sup>a</sup>	China	PBS, PBSA	3
Jinfa Tech <sup>a</sup>	China	PBSA	0.3
BASF <sup>a</sup>	Germany	Ecoflex	14
Eastmann <sup>a</sup>	USA	East Bio	15
Showa <sup>a</sup>	Japan	Bionolle	5
Mitsubishi Chemical <sup>a</sup>	Japan	GS Pla	3
IPC-CAS <sup>b</sup>	China	PBS, PBSA	5
IRE Chemical <sup>b</sup>	Korea	Enpol	3.5
Kingfa <sup>b</sup>	China	PBSA	1
Mitsubishi Gas Chemical <sup>b</sup>	Japan	Iupec	3
Nippon Shokubai <sup>a</sup>	Japan	Lunare	NA
Ube <sup>a</sup>	Japan	ETERNACOLL 3050	NA
SK Chemical <sup>a</sup>	Korea	Skygreen	NA
Dupont de Neumours <sup>b</sup>	USA	PBST	NA
Myriant <sup>c</sup>	USA	NA	NA
Reverdia <sup>d</sup>	Netherlands	NA	NA

NA: No information available.

<sup>a</sup> Data taken from ref. [62]

<sup>b</sup> Data taken from ref. [27]

<sup>c</sup> Data taken from ref. [25]

<sup>d</sup> Data taken from ref. [26]

PBS has been used for applications such as mulch film, packaging, and flushable hygiene products and also used as a non-migrant plasticizer for polyvinyl chloride (PVC). In addition, it is used in foaming and food packaging application [27]. Poly (butylene succinate) (PBS) is a promising bioplastic showing excellent processability and mechanical performance. This semi crystalline polymer presents a melting point similar to low density polyethylene (LDPE) and a tensile strength between polyethylene (PE) and polypropylene (PP). The mechanical properties of poly (butylene succinate) and its processing characteristics are highly influenced by its molecular weight ( $M_w$ ). It has been reported that a poly (butylene succinate) with a  $M_w$  lower than 100,000 can be extruded or injection molded, but the products obtained are of brittle nature showing an elongation at break of only 10% and notched Izod impact strength lower than 40 J/m. On the other hand, a poly (butylene succinate) with a higher  $M_w$  exceeding 180,000 is much more ductile, and can be processed via blowing, displaying an elongation at break of 270% and notched Izod impact strength of 73 J/m [62]. Up to know, the main drawback of PBS is its brittleness at room temperature due to relatively high crystalline content, traduced in a low impact resistance which restricts its application in many fields [28].

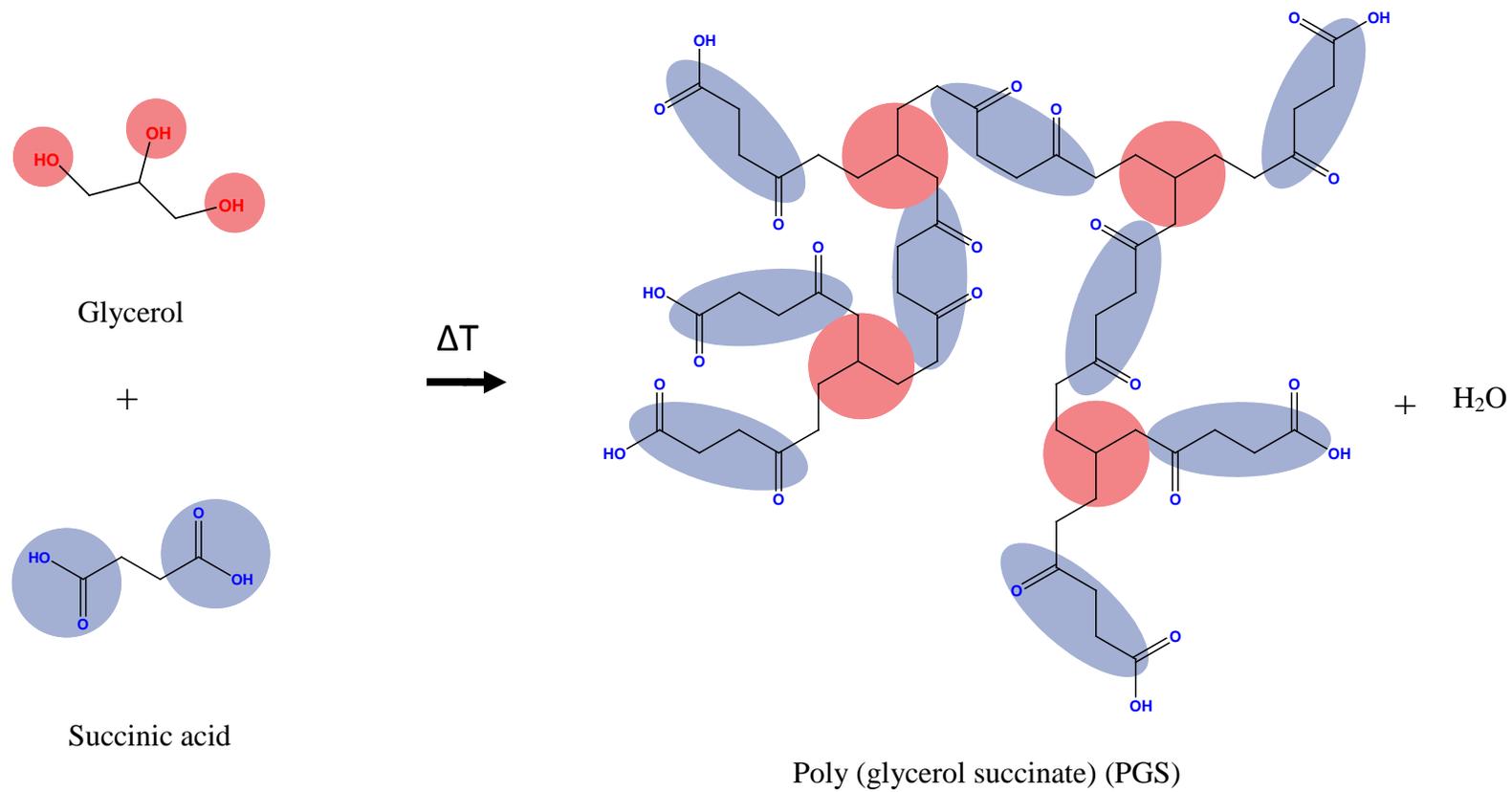
Several strategies have been reported for the modification of impact properties of poly (butylene succinate), including additive incorporation such as nanofillers and impact modifiers and blending with other tougher polymers [29]. Blending technology has proven to be satisfactory on increasing impact resistance of poly (butylene succinate) matrix, though a decrease in tensile properties is often evidenced with the inclusion of a tough blending partner for PBS. Some examples of polymers blended with poly (butylene succinate) (PBS) for impact modification are poly(hydroxybutyrate) (PHB), poly(vinylidene fluoride) (PVF), poly(ethylene oxide) (PEO), poly(butylene terephthalate) and poly (butylene carbonate) [30].

It is well known that the addition of rubber particles to plastic matrixes can enhance their impact properties, due to the amorphous nature of the additive which allows more energy to be absorbed before breaking [31]. Hyperbranched polymers synthesized from glycerol present elastomeric characteristics at room temperature, which renders them as candidates for blending with poly (butylene succinate) aiming to increase its impact properties, and also to decrease the cost of the blend by the introduction of a blending partner based on a co-product of biodiesel industry. The development of a biobased elastomeric polyester from glycerol, and its use as impact modifier for poly (butylene succinate), could greatly enhance both cost/performance balance of poly (butylene succinate) blends and sustainability of biodiesel production.

## 2. Literature review

### 2.1. Hyperbranched polyesters from glycerol: A green alternative for elastomers

Glycerol is the simplest trihydric alcohol containing two primary and one secondary hydroxyl groups on its structure. It can be produced either from petroleum derived propylene or from oleochemical and biodiesel industries co-product. Because of the exponential growth of its production from biodiesel derived crude glycerol and because of serving as a precursor for the synthesis of many organic compounds, glycerol has been pointed out as part of the top 12 value added chemicals from biomass list elaborated by U.S. Department of Energy in 2004 [60]. One particular application of glycerol is the synthesis of polymers, giving the presence of three reactive hydroxyl groups in glycerol which makes it a candidate for performing polycondensation reactions, rendering glycerol based polymers. If the glycerol used in the synthesis of polymers is coming from renewable resources, such as refined glycerol coming from biodiesel industry, the materials synthesized can be called biopolymers. When glycerol is reacted in bulk with a dicarboxylic acid such as adipic, sebacic or succinic acid, a hyperbranched structure is formed, composed of multiple ester bonds called hyperbranched polyester. Figure 10 shows schematically the reaction involved in the synthesis of glycerol and succinic acid based hyperbranched polymers.



**Figure 10.** Reaction schematics and idealized structure of poly (glycerol succinate) (PGS).  $\Delta T$ : temperature increment.

The synthesis conditions can greatly influence the physical and mechanical properties of hyperbranched polyester because of differences in cross-linking density, degree of branching and molecular weight attained in products [32 - 38]. The molar ratio of reactants, which determines the ratio of hydroxyl to carboxylic functionalities to react, is the most important parameter in the reaction, and by controlling it, liquid or solid (gelated) state polyesters can be produced [39]. The avoidance or occurrence of gelation, characterized for extensive cross-linking of dendritic molecules, is the crucial issue that determines the physical nature of the obtained hyperbranched polyester [40]. Liquid state hyperbranched polymers are mainly used as additives for flexible polyurethane foams, solvent replacement in paints, and oligomer precursors for anti-scratch curing applications [41]. Cross-linked hyperbranched polyesters have attracted attention on biomedical applications, due to its rubbery soft consistency which is close to soft tissues in human body [42].

Liquid state glycerol based hyperbranched polyesters are highly branched dendrimer like molecules, containing a large amount of hydroxyl functionalities on its structure. Stumbe and Bruchmann [35] reported the synthesis of liquid state hyperbranched polyester based on glycerol and adipic acid preventing gelation by viscosity measurements. Wyatt and coworkers [43 – 45] have studied the synthesis of hyperbranched polyesters based on glycerol and several diacids such as azelaic, iminodiazetic, glutaric, and succinic acid. They have avoided gelation by using appropriate molar ratio of reactants (stoichiometric control), and by using dilute systems, where glycerol and diacid are reacted in a solvent media preventing early cross-linking of growing branches by dispersion of the molecules in the media. The synthesis of polyesters from glycerol and succinic acid, termed poly (glycerol succinate) (PGS), has been studied by Agach and

coworkers [32, 46] who have shown the non-toxic and biodegradable nature of PGS, avoiding gelation of the product by stoichiometric control of monomer ratio.

The use of glycerol based hyperbranched polymers as solid biomaterials has been primarily proposed in the biomedical application field, due to the biocompatibility of glycerol and many diacids commonly used for hyperbranched polymers synthesis, and the elastomeric nature of these polyesters which resembles soft tissue on human body. The process for preparing solid hyperbranched polyesters comprises the prepolymerization of glycerol and the diacid for a period lower than needed for onset of gelation, and further casting and oven-curing the molded samples for increasing the cross-linking density of specimens. Using this methodology, Nagata and coworkers [37, 38] studied the polymerization of glycerol with several aliphatic diacids with chain lengths ranging from 4 to 14 methylene units and studied the effect of chain length of acid units on enzymatic degradation of these polymers. They found that enzymatic degradation is facilitated for middle chain length of the diacid (8, 9 and 10 methylene units) and hindered in short and large chain lengths of diacid units (4, 5, 6, 7, 12 and 14 methylene units). Wang et al [36] synthesized hyperbranched cross-linked polyesters based on glycerol and sebacic acid, and showed its biodegradability and biocompatibility for the first time by *in vitro* and *in vivo* studies, giving the ground for the development of biomedical applications of these polymers. Migneco and coworkers [47] studied the synthesis and biocompatibility of hyperbranched polymers based on glycerol and dodecanoic acid, obtaining an elastomeric material displaying good mechanical properties, biodegradability and biocompatibility on *in vitro* studies. Li and coworkers [33] synthesized and studied cross-linked polyesters from glycerol and sebacic acid and demonstrated that the mechanical properties of the solid polyesters can be controlled by controlling the curing conditions of the prepolymers. In fact, a higher curing time led to increased brittleness of the

materials due to increased cross-linking density of the polyester network. Halpern and coworkers [42] studied the synthesis of hyperbranched cross-linked polyesters derived from glycerol and citric acid. They showed that the temperature of reaction, the molar ratio of reactants and the reaction time can influence the cross-linking density of polyesters, and that the cross-linking density differences can be monitored by degradation temperatures of polyester networks.

Regarding crude glycerol use, polyesters synthesis has been studied by a few authors (Table 5), mainly in gelated state, and has been proved to be possible to perform. Unfortunately, the mechanical properties of these polyesters have not been reported up to now, making it impossible to develop applications for these materials. Furthermore, there is a lack of comprehensive knowledge about the possibility of using glycerol of different purity levels for biomaterial development, regarding the effect of impurities of crude glycerol on the physical, chemical and mechanical properties of polyesters synthesized from different glycerol sources. Hence, studying the mechanical properties of these novel materials developed from different glycerol sources with different purity levels in a comprehensive base could help to develop applications for them away from biomedical field, given the presence of impurities in crude glycerol sources which makes necessary to find applications where biocompatibility is not a crucial issue. In particular, exploiting the elastomeric nature of these biopolyesters from glycerol for uses in bioplastics blends could help to introduce green alternatives for traditional petroleum derived elastomers commonly used as toughening partners in plastic blends.

**Table 5.** Examples of polyesters synthesized from crude glycerol

<b>Feedstocks</b>	<b>Objective</b>	<b>Key issue</b>	<b>Reference</b>
Crude glycerol + phtalic acid	Investigate the feasibility of synthesize polyesters using crude glycerol and aromatic dicarboxylic acids	Polyesters from crude glycerol and aromatic dicarboxylic acids was proven to be possible to synthesize	[48]
Crude glycerol + citric acid	Investigate the feasibility of synthesize polyesters using crude glycerol and citric acid	Polyesters from crude glycerol and citric acid was proven to be possible to synthesize	[49]
Crude glycerol + adipic acid	Investigate the effect of varying molar ratio of glycerol to adipic acid in thermal and chemical properties of polyesters synthesized	Properties of polyesters synthesized were different for different formulations of glycerol to adipic acid used for the synthesis	[50]

## **2.2. Hyperbranched polymer use as bioplastics additive**

The use of hyperbranched polymers as additive for bioplastics has been reported by a few authors, mainly as a strategy for increasing toughness of brittle biopolymer matrixes such as poly (lactic acid) and poly (butylene succinate) through melt blending processing. Bhardwaj and Mohanty [51] reported a ~570% enhancement of toughness of poly (lactid acid) with the addition of 5.4% by weight of polyalcohol hyperbranched polyester. Lin and coworkers [52] were able to improve the elongation at break of poly (lactic acid) up to 10 times without sacrificing tensile strength with the addition of 20% by weight of poly (ester amide) hyperbranched polymer. Recently, the use of hyperbranched polymers as impact modifiers for poly (butylene succinate) has been reported. Run and co-workers [28] used poly (amide ester) hyperbranched polymers in melt blending with poly (butylene succinate) (PBS) showing an increased storage modulus of the blend compared to neat PBS using 10% by weight of hyperbranched polymer. However, they did not report any significant improvement in impact strength of PBS blends after hyperbranched polymer addition.

Solid state polyesters from glycerol present elastomeric characteristics which make them attractive for biomaterials development due to its tough behavior, because their elastomeric nature allows them to resist high impact so they could be used as impact modifiers for biobased polymers, rendering a biobased blend with enhanced impact properties. In particular, synthesizing polyesters using crude glycerol, or refined glycerol derived from biodiesel industry, and succinic acid, both molecules being recently produced from renewable resources, could represent a green alternative to petroleum derived elastomers and rubbers. Furthermore, the use of these elastomers for impact modification of bioplastic matrixes could represent an alternative

for solving some drawbacks of bioplastic application, together with providing value added applications for biodiesel crude glycerol co – product.

In our approach, due to the impossibility of molding test bars from the glycerol and succinic acid based poly (glycerol succinate) polyesters (PGS), we have blended them with poly (butylene succinate) (PBS), a commercial biodegradable bioplastic from the aliphatic polyester family presenting great technological advantages but still being expensive when compared with conventional petroleum derived plastics. In this way, we expect to observe the effect caused by addition of hyperbranched polyesters from glycerol (PGS) to the PBS matrix, and to relate this effect to the chemical and physical characteristics of PGS in order to address its mechanical properties and its possible use as filler in bioplastic matrixes for improving impact properties.

### **3. Objectives**

#### **3.1. General Objective**

The goal of this research is to study and determine the influence of chemical composition of glycerol source used for the synthesis of poly (glycerol succinate) (PGS) on the physical and chemical properties of poly (glycerol succinate) (PGS) and its blends with poly (butylene succinate) (PBS).

#### **3.2. Specific objectives**

- To conduct a complete chemical characterization of crude glycerol derived from biodiesel production in pilot or commercial scale factories.
- To study the differences in the physical and chemical properties of polyesters synthesized from different glycerol sources and succinic acid.
- Study and compare the mechanical properties of blends of poly (butylene succinate) and polyesters synthesized from different glycerol sources and succinic acid.

#### **4. Hypothesis**

Biobased polyesters can be synthesized from any grade of glycerol, without the need of refining glycerol to highest purity level (purity > 99.9% wt%). The partial refination of crude glycerol to a semi refined or technical level (98% wt% glycerol content) could be enough for developing biomaterials with acceptable mechanical properties that allow their use as blending partners for bioplastic matrixes improving the mechanical performance of the matrix after blending.

## **5. Methodology**

### **5.1. Crude glycerol characterization**

Crude glycerol samples were collected directly from biodiesel producers and characterized in order to determine their content of free glycerol, fatty acid methyl esters (FAMES), free fatty acids (FFAs), soaps, glycerides, water, ash and methanol. Free glycerol, FAMES and glycerides were determined through gas chromatography of samples (GC), according to ASTM standard method D6584 – 10a. Free fatty acids were determined by titration according to ASTM standard method D4662-08. Soaps were determined by titration following the procedure described by Li et al [11]. Water content was determined by volumetric Karl Fischer titration. Ash content was determined by gravimetric analysis of solid residue after burning a crude glycerol sample at 750 °C for 3 h.

### **5.2. Crude glycerol refining**

Crude glycerol refining was performed by chemical methods, according to Manosak et al [53]. Briefly, crude glycerol was acidified using concentrated phosphoric acid until pH 2. At this point, two phases were in samples, corresponding to separated non - polar (oil rich) top phase and polar (glycerol rich) bottom phase. The bottom phase was collected and neutralized using 5 M KOH solution until pH 6. The excess of water was removed by means of vacuum distillation and the product was filtered to eliminate excess precipitated salt. The refined glycerol was analyzed through gas chromatography to determine its glycerol content and stored in a plastic capped bottle until further use.

### **5.3. Poly (glycerol succinate) (PGS) synthesis**

#### **5.3.1. Pure glycerol, refined glycerol and technical glycerol based synthesis**

The starting materials for the polycondensation reaction were succinic acid (99+ wt%, KIC Chemicals, UK) and glycerol (100 wt%, Fischer Scientific, Canada) and were used with no further purification. Alternatively, refined glycerol containing 75 wt% glycerol or technical glycerol containing 95 wt% glycerol was employed. The materials were mixed together without catalyst or solvent to a total mass of 120 g in a glass reactor equipped with temperature control and stirring. The mixture was heated to 180 °C and was stirred constantly at 350 rpm under atmospheric pressure. Water was evaporated from the open vessel allowing the equilibrium of the reaction to shift to product formation. When the solution reached 180 °C this was recorded as time zero of the reaction. The reaction was continued until viscosity became too high for stirring to continue or visible gelation occurred. Solid state, gelated PGS was collected, cooled down in a Teflon plate and stored at room temperature until further use.

#### **5.3.2. Crude glycerol based synthesis**

When crude glycerol was used as starting material, the synthesis procedure was analogous, but due to high amount of not reactive FAMEs present in crude glycerol, a liquid and a solid phase was recovered after reaction was completed. The end product of the reaction, composed of a liquid and a solid phase, was cooled by quenching the vessel in cold water and allowing the two phases to separate by gravity. Once the mixture was cooled, the liquid phase, mainly comprised of FAMEs and fatty acids was discarded, and the solid PGS phase was recovered and stored at room temperature until further use. Table 6 presents the formulations used for synthesis of different glycerol grade based PGS.

**Table 6.** Formulations employed for PGS synthesis from crude, refined and technical glycerol and succinic acid

Glycerol source	Mass ratio of reactants (g glycerol / g succinic acid)	OH groups (mol) <sup>a</sup>	COOH groups (mol) <sup>b</sup>	FFA + Soap COOH (mol %) <sup>c</sup>	OH/COOH molar ratio
Pure glycerol	0.5	1.95	2.03	0.0	0.9
Technical glycerol	0.59	1.86	1.73	0.0	1.1
Refined glycerol	0.8	2.61	1.78	4.7	1.5
Crude glycerol 1	1.29	0.89	1.27	6.9	0.7
Crude glycerol 2	1.91	0.53	1.11	8.4	0.5

<sup>a</sup> considers glycerol –OH groups only. Methanol and water –OH are not considered due to reaction is carried at 180 °C.

<sup>b</sup> total initial mol of –COOH mol in initial mixture. considers succinic acid, free fatty acid and soap –COOH groups.

<sup>c</sup> mol % of total –COOH coming from free fatty acid and soap –COOH groups.

#### 5.4. PGS characterizations

Fourier transform infrared (FTIR) spectroscopy was obtained in a Thermo Scientific Nicolet 6700 FTIR to investigate functional groups composition of polyester. Also the presence of unreacted glycerol or succinic acid could be detected by this technique.

Thermal properties were studied using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Using TGA the samples were heated to 600 °C from room temperature under N<sub>2</sub> at a rate of 20 °C/min in a TGA Q500, TA instruments. For DSC all samples were heated to 180 °C and then cooled to -20 °C at a rate of 10 °C/min in a DSC Q200, TA instruments. The complete cycle was repeated twice and the data from the second cooling and heating cycle was considered for further analysis.

#### 5.5. Blending of poly (butylene succinate) PBS and PGS

PGS (derived from pure, crude, refined or technical glycerol) and PBS were dried at 80 °C overnight and then blended at a ratio of 70% PBS to 30% PGS by weight to a total mass of 10

g per cycle, using a twin screw micro-compounder at 150 °C and 100 rpm (DSM Xplore). The polymers were fed in a 1 minute interval, followed by 1.5 minutes of mixing, and molded at 30 °C in a micro-injector into impact, flexural and tensile test bars and rheometry discs.

### **5.6. Mechanical testing of PBS/PGS blends**

The samples were tested according to ASTM standard D256 for impact, ASTM D638 for tensile and ASTM D790 for flexural properties using Instron 3382 Universal testing machine equipped with a 100 kN load cell using a rate of 50 mm/min and 14 mm/min for tensile and flexural tests respectively. Notched Izod impact tests were performed in an Izod impact tester equipped with a 0-5X0.05 ft. lbs hammer. Impact test bars were notched 48 h before testing. All samples were kept undisturbed in closed plastic bags for 48 h at room temperature before mechanical testing to minimize mechanical effects induced by manipulations of samples. All measurements were performed at least 5 times and average and standard deviation of the properties was calculated and reported.

### **5.7. SEM imaging of blends**

The blend structure was examined with a scanning electron microscope (SEM) in order to observe dispersion and morphology of PGS in PBS matrix. Tested samples from impact analysis were directly observed at the fracture site. Alternatively, a set of impact tested samples was kept in a 3 M KOH solution at 55 °C for 2 h in order to etch PGS phase from PBS matrix, washed with distilled water and dried overnight at 80 °C. The samples were coated in gold before being placed in an Inspect S50 SEM with a spot of 4.0 and high voltage of 20.000 kV for enhancing charge dissipation and preventing heat accumulation on the surface.

## **5.8. Melt Rheology**

Rheological properties were measured in an Anton Paar 302 MCR rheometer using a parallel plate measurement device with a gap of 1 mm between plates. All tests were performed under atmospheric pressure at 150 °C. A strain sweep test was performed initially to determine the viscoelastic range, and strain amplitude was set to 1%. Frequency sweeps were carried in the 0.625 – 625 rad/s interval and data was acquired through Rheoplus software.

## **5.9. DMA analysis**

The storage modulus and tan delta of PBS and PBS/PGS blends were measured as a function of temperature by a DMA Q800 from TA Instruments. The analysis was performed between -60 °C to 80 °C at a heating rate of 3 °C/min. The experiment was carried out in a dual cantilever clamp with 1 Hz frequency and 15 µm oscillating amplitude.

## 6. Results

### 6.1. Glycerol characterization

The composition of glycerol source employed in poly (glycerol succinate) (PGS) synthesis was investigated in order to establish the influence of the chemical composition of glycerol source on the properties of PGS, and ultimately, in mechanical properties of blends with poly (butylene succinate) (PBS). Two different crude glycerol samples collected from industrial facilities (CG1 coming from multi feedstock alkaline transesterification, and CG2 coming from waste frying oil two steps acid – alkaline esterification), refined glycerol produced through chemical refinement of one crude glycerol sample and technical grade glycerol produced industrially from purification of crude glycerol were characterized and the results are shown in Table 7.

**Table 7.** Characterization of different glycerol samples employed for PGS synthesis

	Pure glycerol (PG)	Technical glycerol (TG)	Refined glycerol (RG)	Crude glycerol 1 (CG1)	Crude glycerol 2 (CG2)
Free glycerol (wt%)	100.3 ± 2.6	95.1 ± 2.0	75.1 ± 1.2	30.2 ± 1.2	15.4 ± 1.5
Soap (as sodium oleate) (wt%)	-	-	31.9 ± 1.7 <sup>1</sup>	29.1 ± 1.4	22.4 ± 1.6
FFA (as oleic acid) (wt%)	-	-	-	0.5 ± 0.1	2.1 ± 0.1
FAMEs (wt%)	-	-	-	22.4 ± 2.6	30.9 ± 4.5
Others* (wt%)	-	4.9 ± 2.0	-	17.8 ± 3.2	29.2 ± 5.0

\* Calculated by mass balance. Water, methanol and ash presence was detected in crude glycerol samples by Karl Fischer titration, distillation at 80 °C and gravimetric determination respectively (Data not shown).

<sup>1</sup> Soap determination by titrimetric method considers sodium oleate molecular weight (MW) for conversion of acid number to soap content as an average. The presence of larger MW soap residues in crude glycerol makes the soap content to be slightly overestimated making total wt% of refined glycerol exceed 100%. (107.0 ± 2.1).

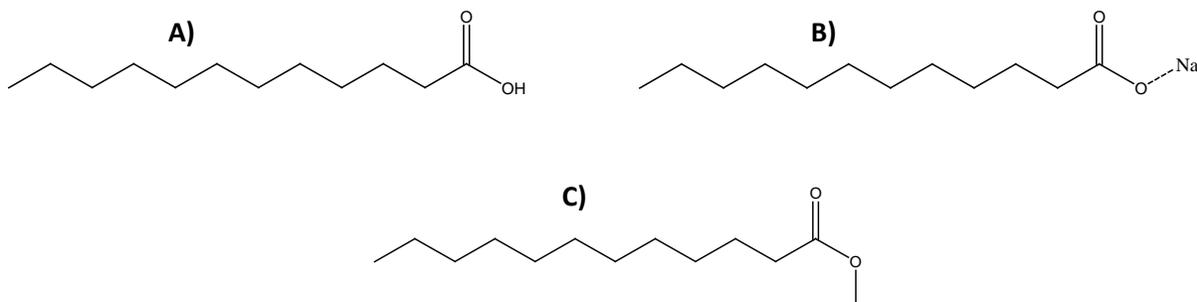
As reported in early literature, crude glycerol samples contained free glycerol, free fatty acids (FFA), soaps, fatty acid methyl esters (FAMES), methanol, water and ash in different proportions. This variability in glycerol samples is due to the heterogeneous nature of the feedstock and process employed in each biodiesel factory [11, 18]. Free glycerol fractions in crude glycerol samples are low, corresponding only to 30.2 wt% and 15.4 wt% of crude glycerol samples 1 (CG1) and 2 (CG2) respectively, showing how biodiesel production steps and feedstock can dramatically affect the quality of crude glycerol obtained as a co-product. A major fraction of both crude glycerol samples corresponds to fatty acid methyl esters (FAMES a.k.a biodiesel) and soaps, which remain in the crude glycerol phase after its separation from FAMES phase by decantation. Free fatty acids, methanol, water and ash were also found in both crude glycerol samples, corresponding to residual fatty acids from oil, solvent and catalyst remaining from transesterification reaction. Regarding functional monomers that could participate in a polycondensation reaction carried at 180 °C the components of interest are glycerol (hydroxyl trifunctional monomer), fatty acids (carboxylic monofunctional monomer) and soaps (carboxylic monofunctional monomer). Fatty acid methyl esters (FAMES) and ashes, presenting no chemical functionality will be present in the reaction mixture as an inert. Water and ethanol will be evaporated from the system at 180 °C. The presence of carboxylic monofunctional monomers such as free fatty acids and soaps in crude glycerol, which can also react with hydroxyl functionalities from glycerol rendering an ester group, implies that the properties of synthesized PGSs from crude glycerol and pure glycerol will be different, as has been shown in theoretical polymerization studies [54]. Moreover, the properties of the blends of different glycerol grades will be depending in the variability among glycerol grades. In an effort to better understand the effect of different impurities of crude glycerol on PGS synthesis, we produced a chemically

refined glycerol from a crude glycerol sample (CG2), partially following the procedure described in early literature [53]. The purification consisted in an acidification step to phase separate non polar components from polar components, followed by neutralization and evaporation of water from refined glycerol sample. It can be seen in Table 7 (column 3) that this treatment dramatically reduced the impurities of glycerol sample, rendering a refined glycerol sample comprised mainly of free glycerol and soaps. The FAMES and FFA fractions were eliminated, as well as the ash content; the color of the sample was clearer, and the glycerol content was raised from 15.4 wt% to 75.1 wt%, producing thus a semi purified glycerol. Finally, technical glycerol (TG), refined industrially from crude glycerol was employed. This highly refined glycerol showed an average glycerol content of 95.1 wt%, indicating that most of the impurities from biodiesel production have been already reduced. These five grades of glycerol and also pure glycerol were employed in PGS synthesis in order to establish how the impurities are affecting the properties and quality of PGS as filler for PBS matrixes.

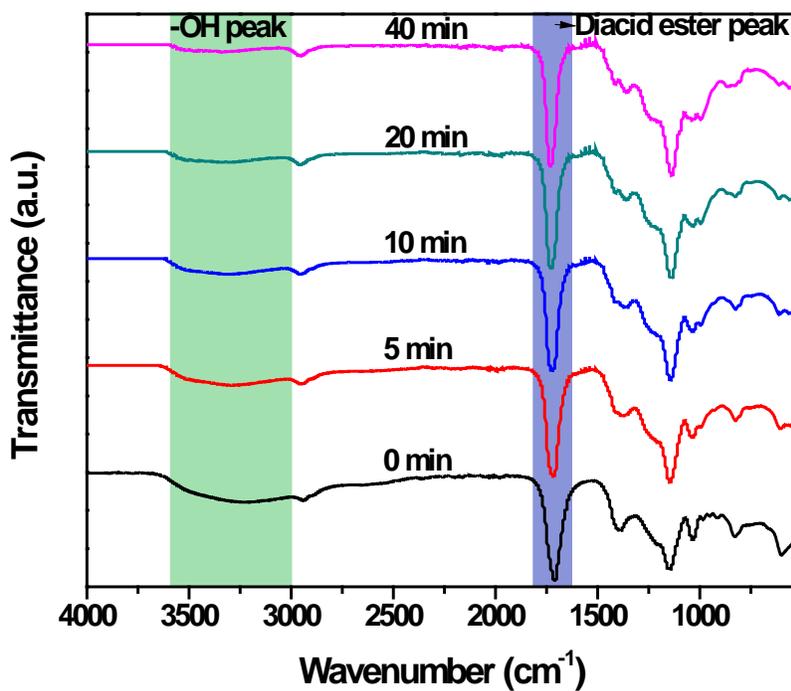
## **6.2. Poly glycerol succinate (PGS) synthesis**

PGS was synthesized using two different crude glycerol samples, refined glycerol and technical glycerol, all of these samples obtained as a co-product of biodiesel production. The molar ratio of reactants functionalities (OH/COOH molar ratio) was set in the range 0.5 – 1.5 (mol hydroxyl/mol carboxyl), in an attempt for synthesizing PGS as close as possible to stoichiometric balance of functionalities (OH/COOH = 1), which according to previous literature renders the highest molecular weight hyperbranched polymer [40]. As pointed out previously, crude glycerol and refined glycerol samples differ from technical and pure glycerol samples on the FAMES, free fatty acid and soap content. Crude glycerol samples present high content of

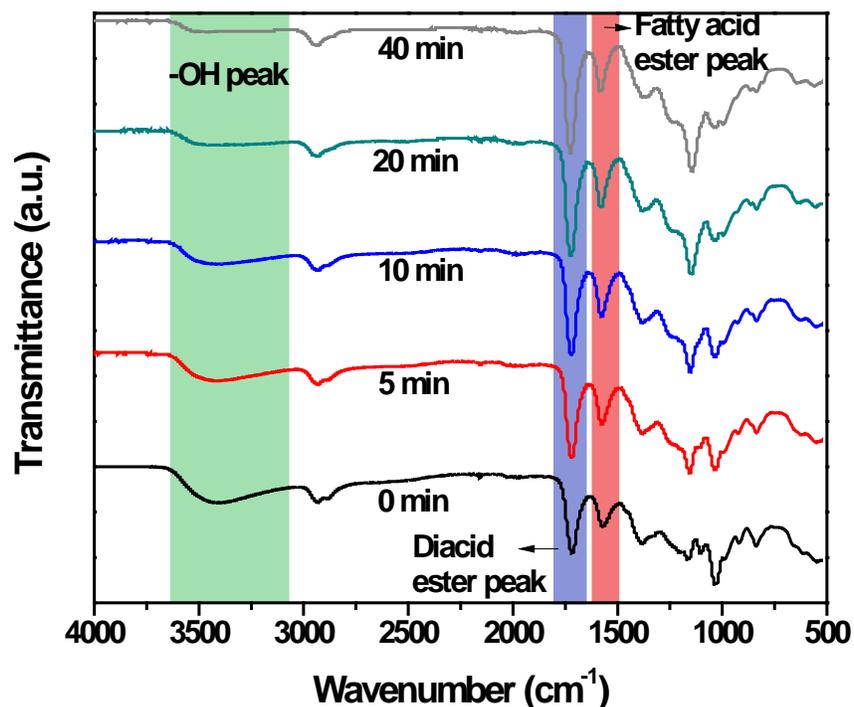
FAMEs (fatty acid methyl esters), which doesn't present neither carboxyl nor hydroxyl functionalities because the carboxyl functionality of the fatty acid (Fig. 11a) has already been



**Figure 11.** Chemical structure of A) Lauric acid, a free fatty acid (FFA), B) Sodium laureate, a soap and C) Methyl laureate, a fatty acid methyl ester (FAME).



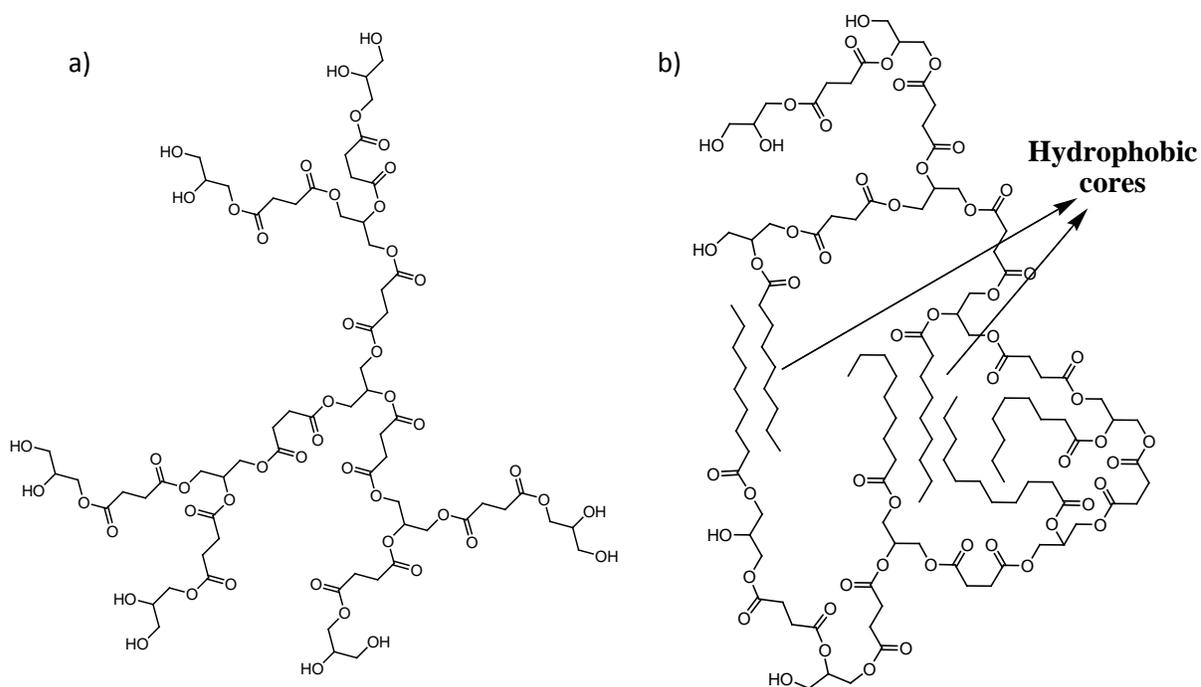
**Figure 12.** Pure glycerol based PGS synthesis FTIR spectra during the course of reaction.



**Figure 13.** Crude glycerol based PGS synthesis FTIR spectra during the course of reaction.

capped by the methyl group (Fig. 11c) during transesterification reaction and thus act as an inert solvent on PGS synthesis. Soaps, and fatty acids on the other hand, present reactive carboxylic ends (Fig. 11b and 11c), which enable them to react with glycerol and form part of the structure of PGS. This different incorporation of monomers in crude and pure glycerol based PGS synthesis was analyzed through real time FTIR spectroscopy at 180 °C, which allows to visualize the conversion of functional groups during the course of the reaction (Figures 12 and 13). Figure 12 shows the sharpening of diacid ester peak at  $1723\text{ cm}^{-1}$  and the consequent reduction of hydroxyl peak at  $3450\text{ cm}^{-1}$ , indicating the reaction of these functionalities giving raise to ester bonds in the backbone of PGS. Figure 13 show the same trend, but an additional peak appearing at  $1550\text{ cm}^{-1}$  shows the same sharpening with the concurring hydroxyl disappearing noticed at

3450  $\text{cm}^{-1}$ . This new peak at 1550  $\text{cm}^{-1}$  corresponds to fatty acid ester bond, and denotes the incorporation of fatty acids and soaps to the backbone of PGS. This structural difference is causing the crude glycerol based, and refined glycerol based PGS to hard and brittle after cooling down to room temperature, whereas technical and pure glycerol based PGS presents soft rubbery nature. This difference can be explained looking into the structure of pure glycerol and crude glycerol based PGS (Fig. 14). The presence of aliphatic residues pending from the PGS network in crude and refined glycerol based PGS causes the degree of mobility of the PGS network to decrease, due to packing of these chains promoted by their hydrophobicity. This tightly packed hydrophobic core, composed of fatty acid esterified residues, causes PGS to be a hard, brittle polymer at room temperature, and to soften as a rubber when the temperature is increased above

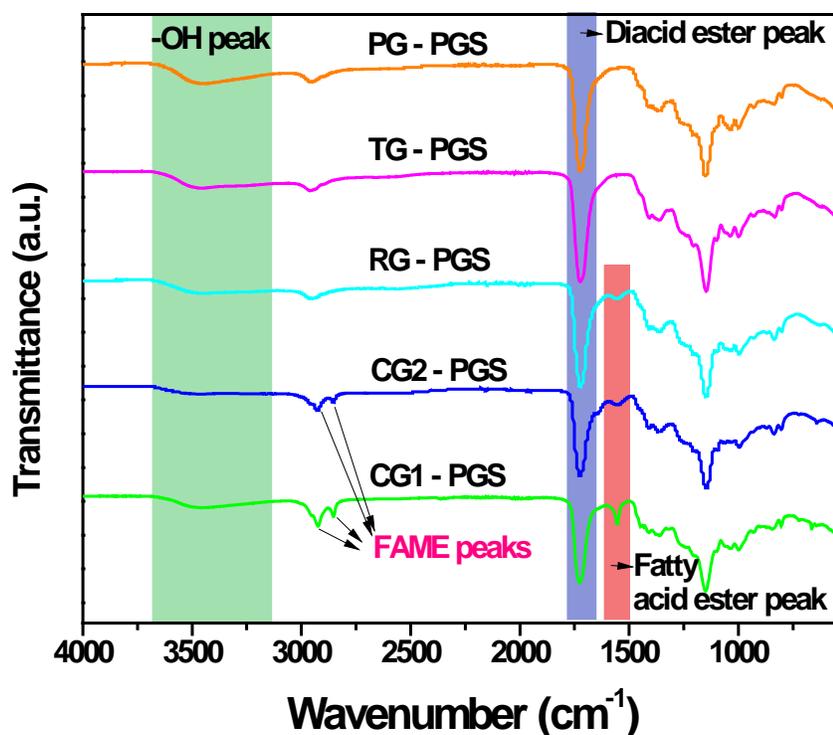


**Figure 14.** Idealized structure of a) Pure glycerol based PGS and b) Crude glycerol based PGS.

room temperature (30 °C). Pure and technical glycerol based PGS on the other hand, doesn't present these hydrophobic residues on its structure, so its network is free to move by stretching and reorienting the branches in response to loads.

Another remarkable difference between pure glycerol based and crude glycerol based PGS is the mass yield of the reaction. Pure glycerol based PGS yield is in the range of 0.7 to 0.83 g PGS/ g initial mixture of reactants. Crude glycerol based PGS on the other hand, presents mass yield as low as 0.5 g PGS/ g initial mixture of reactants. The remaining mass is recovered as a liquid product, mainly composed of FFA and FAMES, and corresponds to about 0.3 g liquid/ g initial mixture. This liquid co-product represents the unreacted fraction of crude glycerol mainly comprised of FAMES, which lacks of hydroxyl or carboxyl functionality and are present as an inert throughout the reaction, being recovered by phase separation once the synthesis reaction is completed. A fraction of this liquid product however remains entrapped in the synthesized PGS from crude glycerol samples, posing a challenge in the reproducibility and homogeneity of synthesized PGS from crude glycerol, due to the heterogeneous nature of crude glycerol samples coming from different biodiesel producing facilities. Figure 15 shows FTIR spectra of crude, refined, technical and pure glycerol based PGS. It can be seen that for crude and refined glycerol based PGS (CG1 PGS, CG2 PGS, RG PGS) a peak appears at  $1550\text{ cm}^{-1}$ , indicating the presence of esterified free fatty acids in the backbone of PGS as it was mentioned, whereas for pure and technical glycerol based PGS this peak is not detected. Also, for crude glycerol based PGS (CG1 PGS, CG2 PGS) sharp peaks can be seen at  $2852\text{ cm}^{-1}$  and  $2923\text{ cm}^{-1}$ , corresponding to increased presence of methylene groups in PGS. The increased presence of methylene groups can be attributed to the presence of unreacted FAME molecules remaining entrapped in PGS network after synthesis, which can act as a lubricant for these formulations. In refined glycerol sample on

the other hand, due to the elimination of FAME impurities from crude glycerol before the synthesis is carried, these FAME peaks are not present, indicating that the assignment of these extra methylene groups in PGS to FAME molecules is correct.



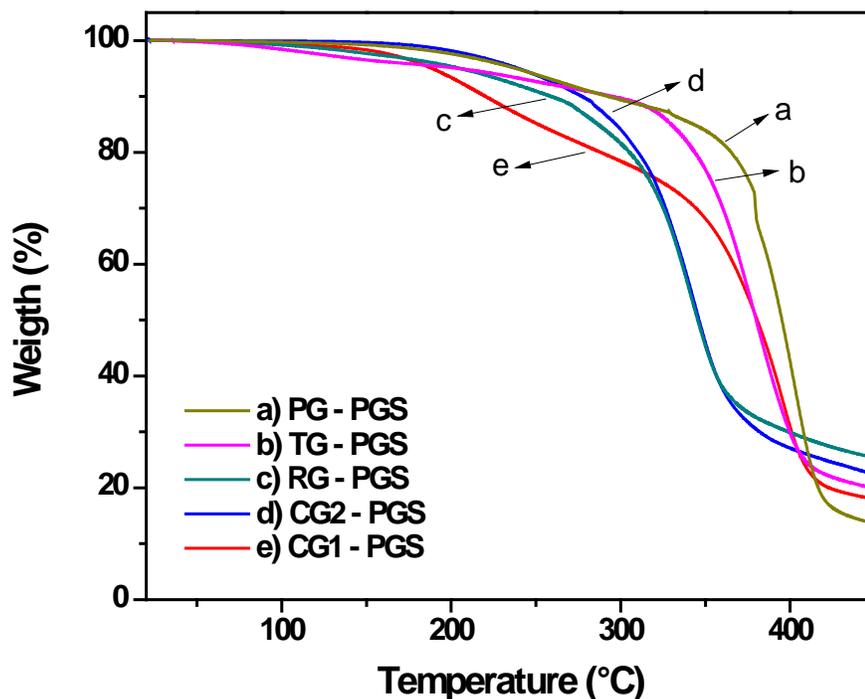
**Figure 15.** FTIR spectra of synthesized PGSs from crude glycerol and succinic acid. CG1 – PGS: Crude glycerol 1 based PGS, CG2 – PGS: Crude glycerol 2 based PGS, RG – PGS: Refined glycerol based PGS, TG – PGS: Technical glycerol based PGS, PG – PGS: Pure glycerol based PGS.

These results highlight the role of the purity of glycerol employed in the synthesis of PGS. Technical and pure glycerol samples, with a glycerol content of at least 95 wt% are producing consistent soft PGS products with high mass yields (0.8 g PGS/g initial mixture of monomers) in short reactions times (0.7 – 0.8 h) and elastomeric characteristics at room

temperature. Crude glycerol samples with low glycerol content (<30 wt%) and refined glycerol sample with high glycerol content (75 wt%) both having in common high soap content (>20 wt%) are producing hard PGS polymers which present brittleness at room temperature, probably caused by esterified fatty acid residues. Moreover, crude glycerol samples present low product yield (as low as 0.5 g PGS/ g initial mixture for crude glycerol 2), being a co – product of the reaction an oily solution comprised mainly of FAMES and FFA. A fraction of these oily co product remain entrapped in PGS matrix, rendering a product soaked in oily impurities, which poses a challenge for the direct utilization of these products as additives for bioplastic matrixes, due to the difficulties for reproducing a consistent PGS product from an heterogeneous raw material as crude glycerol.

### **6.3. Thermogravimetric analysis**

Figure 16 shows thermogravimetric analysis of PGS synthesized using different glycerol sources. It can be seen that glycerol source is affecting greatly the degradation characteristics of PGS at high temperatures. Pure glycerol and technical glycerol based PGS have the highest thermal stability, evidenced as a 10% loss weight occurring at 292 °C, whereas crude glycerol 1, crude glycerol 2 and refined glycerol present 10% degradation at 220 °C, 277 °C and 256 °C respectively. Moreover, the main degradation step for pure glycerol and technical glycerol based PGS is occurring at 390 °C and 370 °C respectively, whereas crude glycerol 2 and refined glycerol based PGS main degradation steps are occurring at 337 °C. Crude glycerol 1 based PGS shows a two-step degradation mechanism, with the first degradation step occurring at 150 – 350 °C range, with a 20% weight loss, and the second degradation step occurring at 370 °C. These differences in degradation temperatures can be ligated to the cross-linking density obtained in every PGS formulation, which in turn is related to the monomer content of glycerol source and to



**Figure 16.** Thermogravimetric analysis of PGS synthesized from different glycerol sources. CG1 – PGS: Crude glycerol 1 based PGS, CG2 – PGS: Crude glycerol 2 based PGS, RG – PGS: Refined glycerol based PGS, TG – PGS: Technical glycerol based PGS, PG – PGS: Pure glycerol based PGS.

molar ratio of reactants used in PGS synthesis. It has been shown [42] that for glycerol based hyperbranched polymers a lower degradation temperature is linked to a lower cross-linking density. Pure and technical glycerol based PGS are showing the highest degradation temperature, suggesting that the highest cross-linking density is obtained for these PGS formulations, whereas crude glycerol 2 and refined glycerol is showing a lower cross-linking density, evidenced as a lower degradation temperature. This can be explained looking into the molecular structure of PGS. Crude and refined glycerol based PGS, because of the presence of fatty acid residues on

their glycerol sources, are incorporating these fatty acid residues on PGS network, preventing further cross-linking to occur on that branch. This means that fatty acid residues are acting as a branching terminal unit, preventing the branching and cross-linking to reach further extent. In the pure or technical glycerol case every residue present in the PGS branches is susceptible of being further polymerized extending the cross-linking degree of PGS at gel state. Thus, using crude or refined glycerol for synthesizing PGS is affecting PGS thermal stability because of the presence of fatty acid or soap residues which act as end capping monomer on PGS branches. This leads to lower cross-linking of PGS to occur compared to pure or technical glycerol based PGS, which doesn't contain these end capping monomers (free fatty acids).

#### **6.4. PGS – PBS blends**

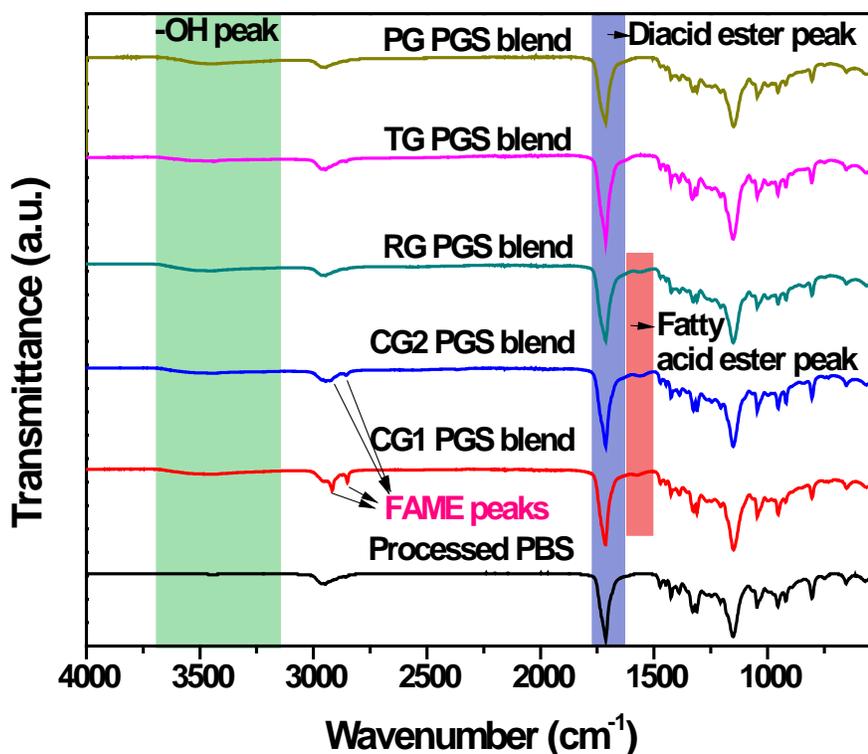
Crude glycerol based PGS and poly (butylene succinate) was blended at 70/30 wt% ratio using a twin screw extruder, and shaped into different standard test bars. Four different formulations of PGS, regarding the grade or purity of glycerol used for its synthesis, were employed for the blending experiments (Crude glycerol 1 based PGS, Crude glycerol 2 based PGS, Refined glycerol based PGS and Technical glycerol based PGS). Also, pure glycerol based PGS was used for blending with PBS, as a control for establish the effect of crude glycerol impurities in PGS physical properties reflected as mechanical properties of blends. The torque of the blending process was recorded and the average is presented in Table 8. It can be seen that refined glycerol based PGS blend (RG-PGS blend) presented the highest torque value of the set, followed by pure glycerol based PGS blend (PG-PGS blend) and technical glycerol based PGS blend (TG-PGS). This suggests that for these three glycerol grades, polymerization of PGS reached the furthest extent conferring higher gel content of the PGS products, than in the crude glycerol case, which is traduced in a bigger force required for extruding them. The lower

polymerization extent in PGS matrix in crude based formulations is obtained as a result of performing the reaction in a dilute solution, being FAMES naturally occurring in crude glycerol samples, the molecules acting as solvent for the reaction. The reaction in dilute solution system, which is naturally occurring when using crude glycerol samples for synthesizing PGS, due to the high presence of FAMES in these glycerol sources, has proven to be an strategy for obtaining less cross-linked polymers when performing  $A_3 + B_2$  polycondensations, such as glycerol and succinic acid polycondensation [44, 45]. The notoriously lower torque value for crude glycerol formulations suggests that the gel content of PGS in these samples was greatly reduced, comparing to pure or refined glycerol samples, and thus these glycerol sources are rendering PGS products with low polymerization extents and high unreacted monomer content because of the presence of residual FAMES from transesterification reaction which act as solvent in PGS synthesis.

**Table 8.** Final torque value reached in mixing process of PBS/PGS blends (70/30 wt%)

Blend	Force (N)
neat PBS	2467 ± 51
Pure glycerol based PGS blend (PG – PGS blend)	2445 ± 112
Technical glycerol based PGS blend (TG – PGS)	2031 ± 85
Refined glycerol based PGS blend (RG – PGS blend)	2582 ± 161
Crude glycerol 2 based PGS blend (CG2 – PGS blend)	575 ± 9
Crude glycerol 1 based PGS blend (CG1 – PGS blend)	864 ± 19

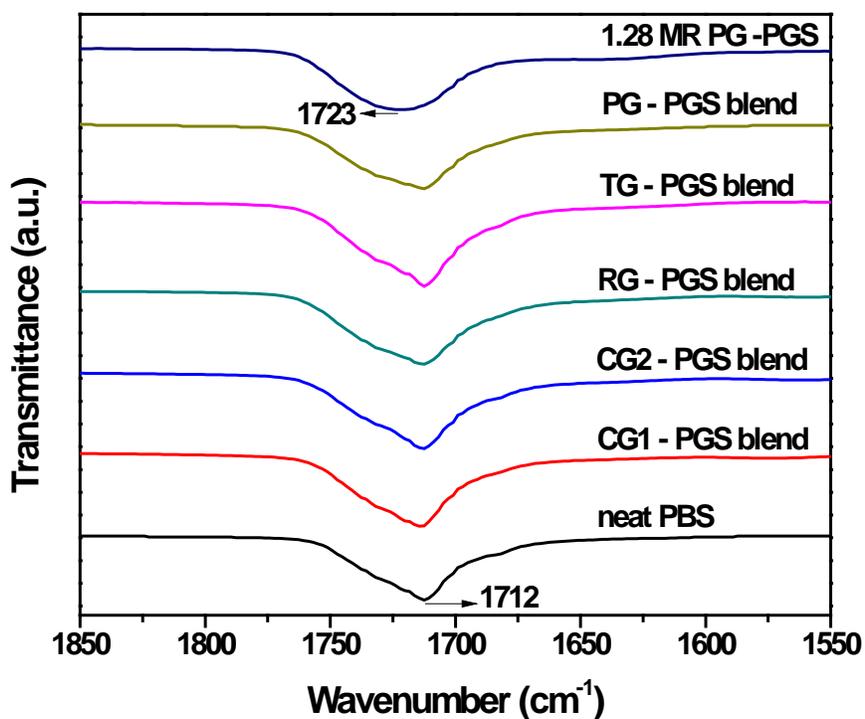
### 6.4.1. Infrared spectroscopy



**Figure 17.** FTIR spectra of PGS – PBS blends (70/30 wt%). PGS was synthesized using different glycerol grades; CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS, PG: Pure glycerol based PGS.

FTIR spectra of different glycerol source based PGS and PBS blends was obtained and is presented in Figure 17. It can be seen that –OH functionalities ( $3450\text{ cm}^{-1}$ ) and diacid ester peaks ( $1723\text{ cm}^{-1}$ ) formed from succinic acid and glycerol esterification are present in all formulations of PGS/PBS blends. For crude and refined glycerol blends, fatty acid ester peaks appear at  $1550\text{ cm}^{-1}$ , coming from esterified fatty acid or soap residues present in these glycerol sources. Moreover, for crude glycerol 1 and 2 samples, sharp peaks appear at  $2852\text{ cm}^{-1}$  and  $2923\text{ cm}^{-1}$ ,

corresponding to  $-\text{CH}_2$  groups. These methylene groups can be attributed to FAMEs which are present in crude glycerol samples in high amount ( $>20\%$  wt%) and remain entrapped in PGS after its synthesis. The presence of  $-\text{OH}$  groups from PGS and  $-\text{COOH}$  groups from PBS suggests the formation of hydrogen bonding between the two components of the blend. This could be evidenced by FTIR in the  $1600 - 1800 \text{ cm}^{-1}$  range, where ester peak slightly shifts toward higher wavenumber when the  $\text{C}=\text{O}$  group is H-bonded with  $-\text{OH}$  groups from PGS as shown in early literature [29]. Figure 18 shows FTIR of crude glycerol based PGS blends in the  $1600 - 1800 \text{ cm}^{-1}$  range together with pure glycerol based PGS 1.28, which is likely to present a



**Figure 18.** FTIR spectra of PGS – PBS blends (70/30 wt%) in  $1600 - 1800 \text{ cm}^{-1}$  range. PGS was synthesized using different glycerol grades; CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS, PG: Pure glycerol based PGS.

high amount of H-bonded C=O groups due to the high presence of –OH groups on its structure as a consequence of being synthesized in excess glycerol. It can be seen that as stated, neat PBS presents a C=O peak at 1712 cm<sup>-1</sup> whereas neat 1.28 MR PGS presents a C=O peak at 1723 cm<sup>-1</sup>, confirming the shifting to higher wavenumber of H-bonded C=O groups. Moreover, PBS/PGS blends present both peaks for C=O functionalities overlapped in a broad peak, indicating that a portion of the C=O groups of PBS presents H-bonding with –OH functionalities from PGS. The fraction of bonded C=O ( $f_b$ ) was quantified, after fitting the two C=O peaks with Lorentzian functions, using the following equation [52]:

$$f_b^{C=O} = \frac{A_b/1.5}{A_b/1.5 + A_f}$$

where  $A_b$  and  $A_f$  correspond to the H-bonded and free C=O peak area in the FTIR spectra. The result of the peak fitting and the quantification of hydrogen bonded fraction of PBS to PGS are shown in Table 9. These results show that both pure glycerol based PGS and crude glycerol based PGS in blends with PBS present interfacial interaction of blend components in the form of hydrogen bonds due to the presence of –OH groups from PGS and C=O groups from PBS. The fraction of H-bonded C=O groups in Crude glycerol 1 (CG1), Refined glycerol (RG) and Technical glycerol (TG) based PGS blends (average 9.3%) is comparable to the value obtained for pure glycerol based blend (11.9%), whereas crude glycerol 2 based PGS blend presents a lower fraction of H-bonded C=O groups, which can be attributed to the lower amount of hydroxyl groups evidenced in this PGS sample through FTIR. This lower amount of hydroxyl groups results from the low glycerol content of crude glycerol 2 sample (15% wt%) which causes the PGS synthesis reaction to be imbalanced toward –COOH functionalities of succinic acid even at high mass ratios of crude glycerol to succinic acid (as reference, mass ratio of

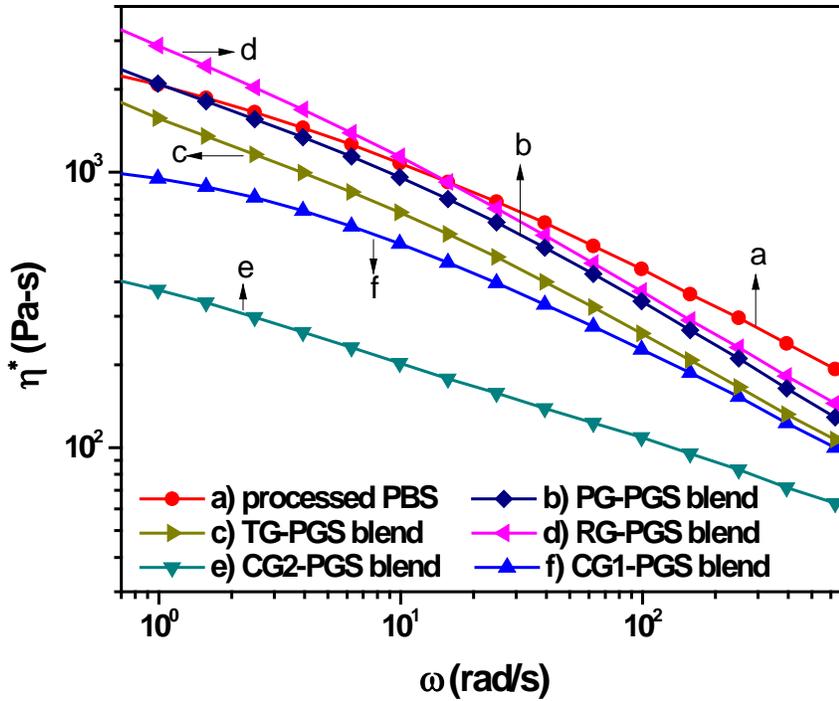
glycerol to succinic acid of CG2-PGS synthesis was 1.9 whereas for pure glycerol PGS synthesis mass ratio was 0.5). It is also important to highlight that beyond the glycerol content of the crude glycerol samples, the presence of impurities such as FAMES, FFAs, and soaps is affecting the composition of PGS and its blends. Soap and FFAs from crude or refined glycerol are being esterified with glycerol forming part of the PGS network, which can influence the compatibility of PGS/PBS blends. FAMES are acting as a solvent in PGS synthesis and some of them remain entrapped in PGS after synthesis, thus being incorporated on the PBS/PGS blends as lubricants. This means that for crude glycerol samples presenting FAME residues, the PGS synthesized from it and its blends will contain FAME molecules entrapped on its network structure as a not controlled additive which is not present on pure glycerol samples and can influence the mechanical properties of the blends.

**Table 9.** Fraction of H-bonded carbonyl groups for PBS blended with PGS synthesized using different glycerol grades (70/30 wt% PBS/PGS blends). CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS, PG: Pure glycerol based PGS

PBS/PGS blends	free C=O		H - bonded C=O		f <sub>b</sub> (%)
	$\nu$ (cm <sup>-1</sup> )	A <sub>f</sub> (%)	$\nu$ (cm <sup>-1</sup> )	A <sub>b</sub> (%)	
PG PGS blend	1713,8	83,2	1736,5	16,8	11,9
TG PGS blend	1712,9	86,9	1736,2	13,1	9,1
RG PGS blend	1712,9	86,7	1735,9	13,3	9,3
CG2 PGS blend	1713,2	90,3	1736,7	9,7	6,7
CG1 PGS blend	1714,8	86,4	1735,8	13,6	9,5

### 6.4.2. Melt rheology

PGS/PBS blends were studied through melt rheology due to its sensibility to differences in molecular weight and in structure of polymers, reflected in complex viscosity. Figure 19



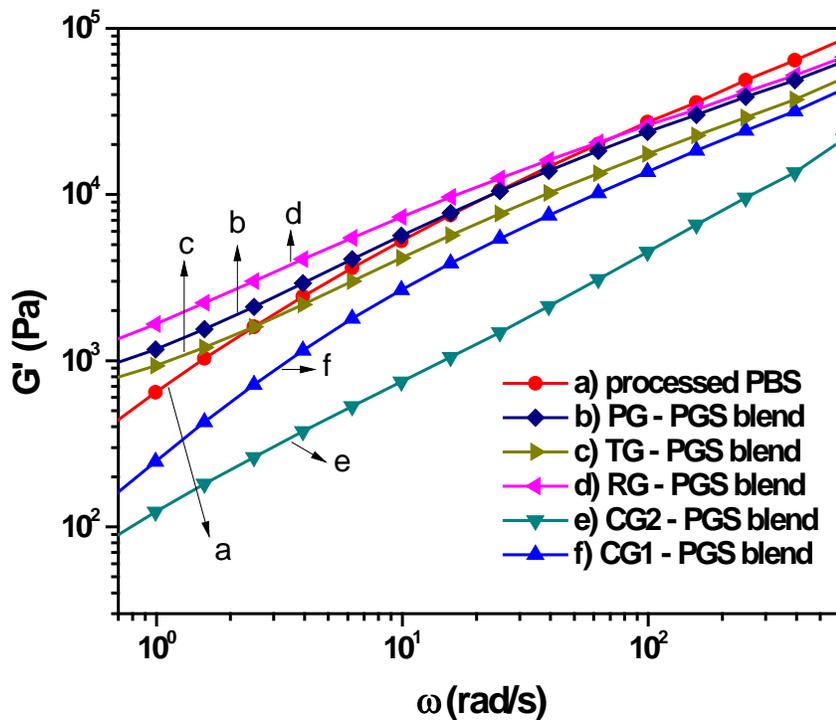
**Figure 19.** Complex viscosity of PBS/PGS blends (70/30 wt%). PGS was synthesized using different glycerol grades. CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS.

shows complex viscosity for the blends of PBS and PGS synthesized using different glycerol grades. The complex viscosity of refined glycerol, pure glycerol and technical glycerol based PGS/PBS blends are the highest from the set, indicating again that these PGS formulations reached the highest gel content from all glycerol grades. This can be explained because of the absence of solvent (FAMES) in PGS polymerization using refined, technical and pure glycerol as

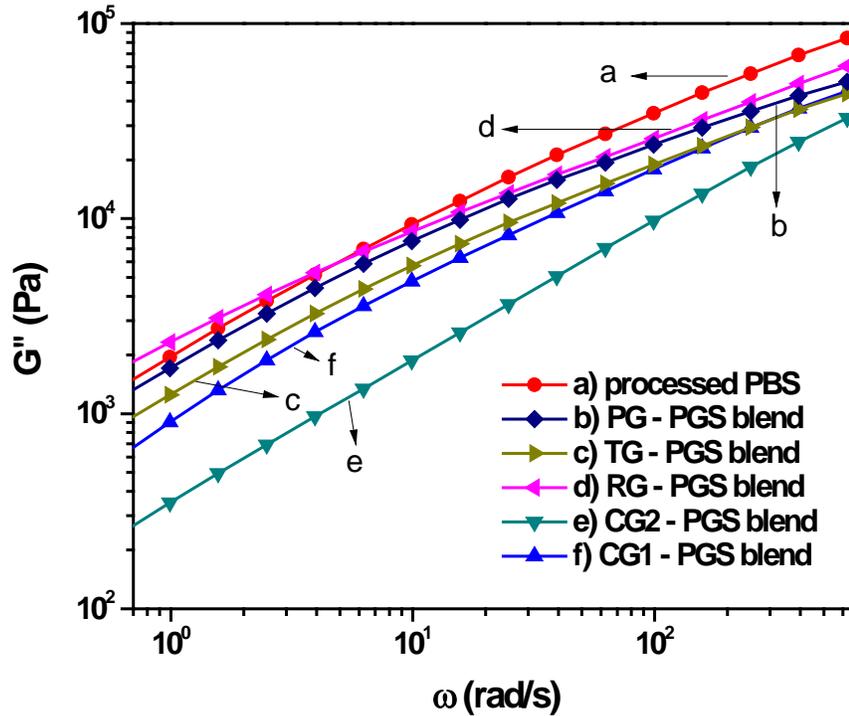
glycerol source. When crude glycerol is used, the presence of FAMEs acting as a solvent and thus diluting the polymerization, leads to a lower polymerization of PGS, rendering a product with a lower gel content and an increased amount of unreacted monomers. The increased gel content of refined, pure and technical glycerol based PGS causes the PBS/PGS blend to have an heterogeneous nature with insoluble PGS gel particles at molten state, which prevent the PBS chains to slip easily when shear is applied, which is reflected as an increased complex viscosity of these blends, being comparable to neat PBS. The crude glycerol based PGS formulations, having lower gel content, presents lower resistance to PBS chain motion after shear, and thus a lower complex viscosity.

Interestingly, at low frequencies ( $\omega < 10$  rad/s), refined glycerol based PGS blend is showing higher complex viscosity than pure glycerol based PGS blend. This can be attributed to the presence of uncross-linked branches of refined glycerol based PGS, due to the presence of end capping esterified fatty acid residues which prevented the cross-linking of these branches during PGS synthesis. These loose branches in refined glycerol based PGS, which are not likely to be present in pure or technical glycerol based PGS, can interact with PBS linear chains, forming entanglements that cannot be destroyed at low frequencies during rheology measurements. Pure and technical glycerol based PGS, probably presents higher cross-linking extent as suggested in TGA analysis, and thus presents a denser network making it difficult to entangle with PBS chains. When the frequency is increased ( $\omega > 10$  rad/s), these entanglement interaction between refined glycerol based PGS uncross-linked branches and PBS chains disappear, and thus refined glycerol and pure glycerol based PGS blends present identical behavior at high frequency range.

Complex viscosity can be decomposed in terms of storage and loss modulus. Storage modulus ( $G'$ ) express the amount of recoverable energy stored as elastic deformation and loss modulus ( $G''$ ) represents the amount of non-recoverable energy dissipated as heat. Figures 20 and 21 show the storage ( $G'$ ) and loss ( $G''$ ) modulus of the PBS – PGS blends. As can be seen, refined glycerol based PGS blend shows the highest storage modulus at low frequencies, followed by pure glycerol based PGS and technical based PGS blends. Only these three blends show higher storage modulus than neat PBS, confirming the highest gel particle content of these PGS formulations, which gives higher stiffness to the blend because of the cross-linking of PGS



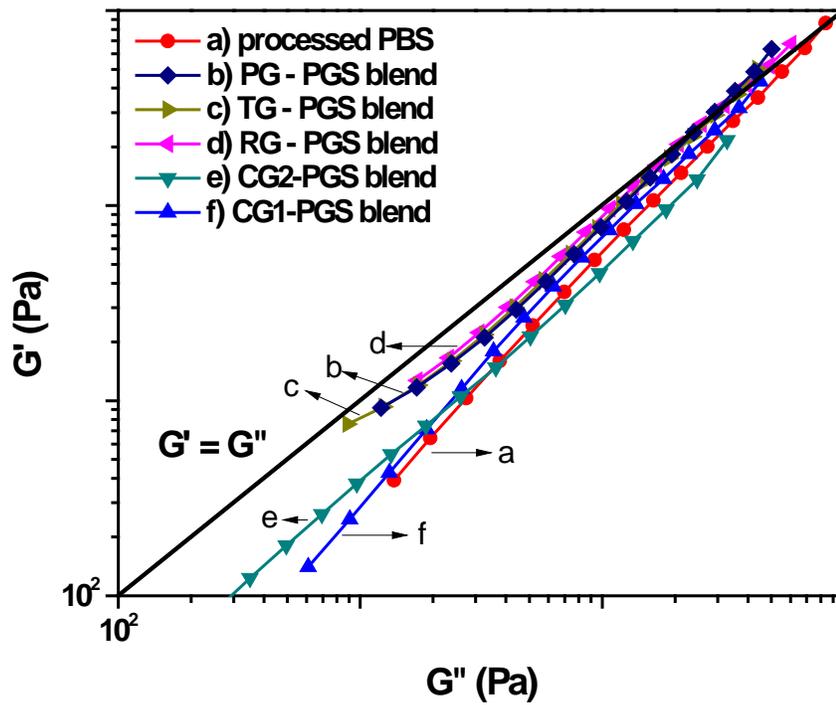
**Figure 20.** Storage modulus ( $G'$ ) of PBS/PGS blends (70/30 wt%). PGS was synthesized using different glycerol grades. CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS.



**Figure 21.** Loss modulus ( $G''$ ) of PBS/PGS blends (70/30 wt%). PGS was synthesized using different glycerol grades. CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS.

gel particles. Refined glycerol based blend presents the higher storage and loss modulus at low frequencies, which can be explained by the entanglements that this less cross-linked PGS matrix can produce with PBS chains at low frequencies, which are not possible to occur in pure or technical glycerol based PGS blend because of the higher cross-linking degree evidenced by TGA analysis. Crude glycerol based PGS/PBS blends (CG1 and CG2 blends) show the lowest storage modulus from the set, being lower than neat PBS at all frequencies. This indicates again that the gel content of these PGS formulations is lower than for other glycerol sources, which can be explained due to the high amount of FAMES and FFAs impurities in crude glycerol sources

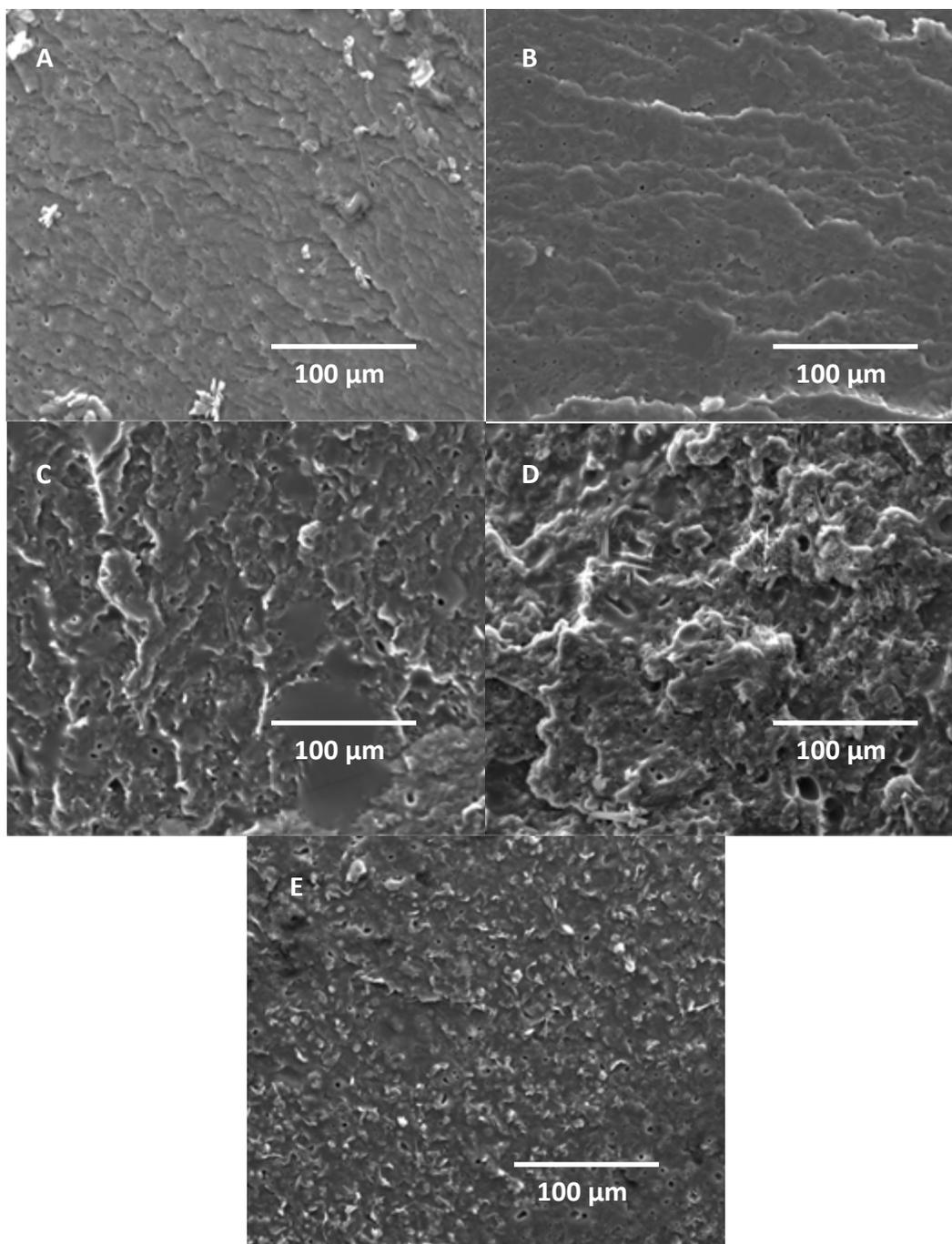
leading to low cross-linking and high FAMEs impurities entrapped on PGS matrix acting as a lubricant on blends, making easier for PBS chains to slip and dissipate energy. Loss modulus ( $G''$ ) of PBS/PGS blends (Figure 21) follows the same trend that storage modulus. A plot of  $G'$  vs  $G''$ , termed a Cole-Cole plot, shows the predominant character of the sample regarding its viscoelasticity. At  $G' = G''$  the material is perfectly viscoelastic; for samples presenting  $G' > G''$  an elastic character is predominant, whereas for samples presenting  $G'' > G'$  a viscous character is predominant. Figure 22 shows the Cole – Cole plot for crude glycerol based PGS and PBS blends. These results show that all blends present a predominantly viscous behavior, but the addition of PGS synthesized using crude glycerol 1, refined glycerol, or technical glycerol is shifting the nature of the material to more elastic region ( $G' > G''$ ), which was expected to happen due to the hyperbranched network structure of these PGS materials, its high gel content and the high fraction of H-bonding detected between PGS and PBS which suggest a good interaction between both blend components. On the other hand, when adding crude glycerol based PGS to the PBS matrix, the nature of the blend is shifting to more viscous material ( $G'' > G'$ ) or remaining unchanged in viscoelastic nature compared to neat PBS. This can be explained because of the lower polymerization extent reached when using these glycerol sources, due to the high presence of FAMEs remaining from transesterification process which acts as a solvent during PGS polymerization, preventing cross-linking to occur at high extent as in the pure and technical glycerol case. Also FAMEs remaining entrapped on PGS network can act as lubricant in the blend, which allows more energy to be dissipated at molten state, due to the lower interaction forces between PGS and PBS at the interface.



**Figure 22.** Cole – Cole plot of PBS and PBS/PGS blends (70/30 wt%). PGS was synthesized using different glycerol grades. CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS.

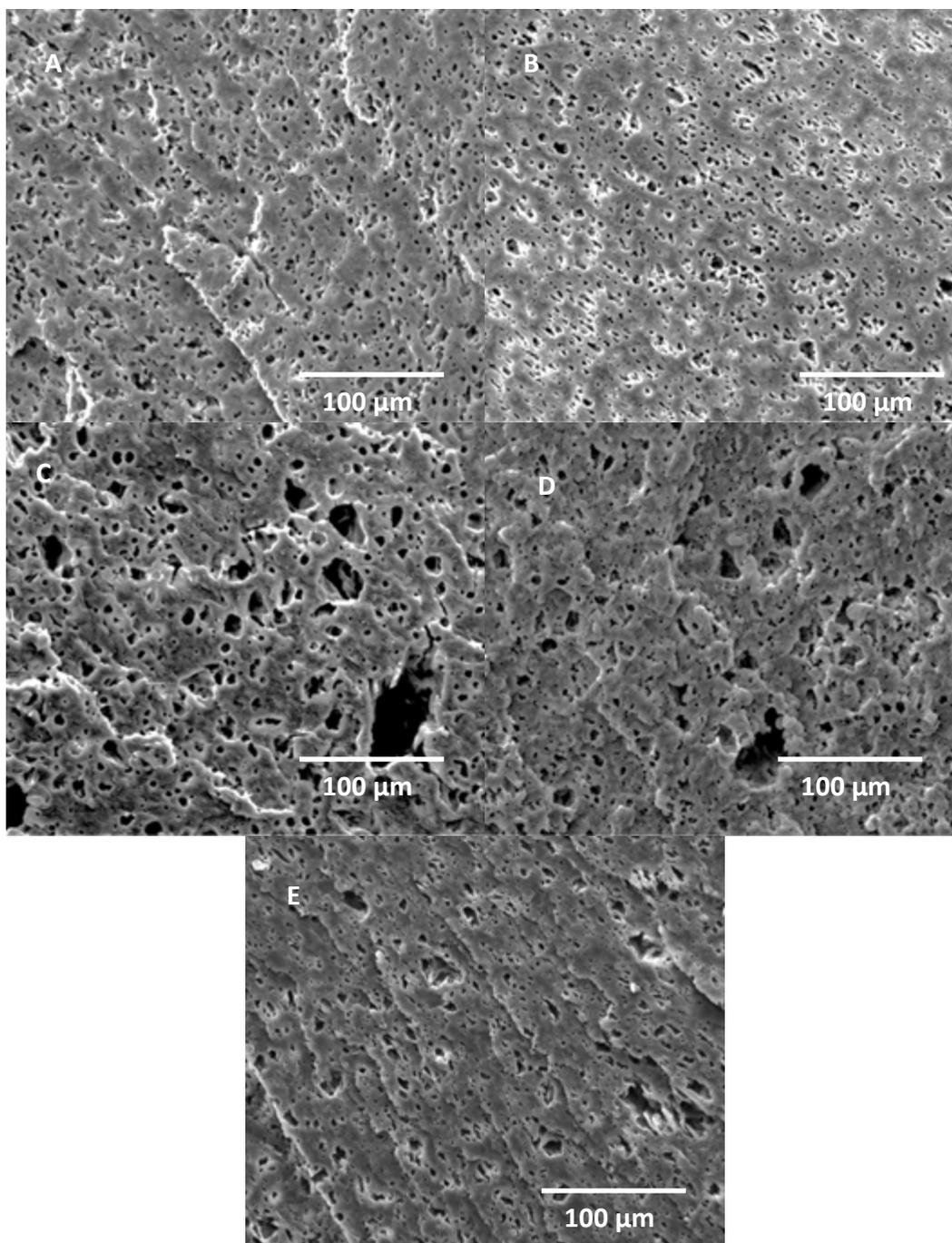
### 6.4.3. SEM morphology

Figure 23 shows SEM imaging of PGS/PBS blends (70/30 wt%) performed on fracture site of impact test bars to observe the distribution of PGS on PBS matrix and the nature of the fracture (brittle or tough). It shows that for all PGS synthesized from crude glycerol sources, there is no agglomeration of PGS phase, which is distributed as small particles embedded throughout the PBS phase. The good distribution of PGS on PBS matrix can be attributed to the H-bonding formed between –OH groups of PGS and C=O groups from PBS, which allows the PGS particles to be dispersed uniformly and to interact with PBS matrix preventing its agglomeration ( $f_b^{C=O} = 9.3\%$  average). The morphology of the fracture surface on the other hand is heavily influenced by glycerol source. Crude and refined glycerol based PGS blends show a much rougher fracture than technical glycerol based PGS blend, suggesting that technical glycerol based PGS displays the best compatibility with PBS phase. This difference in compatibility can be explained in terms of the architectural changes induced in PGS particles due to crude and refined glycerol impurities. The presence of fatty acid residues on its glycerol sources, which end cap branches –OH functionalities preventing its cross-linking with PGS network, creates more randomly sized branches with irregular architectures of PGS networks. Pure and technical glycerol based PGS, being synthesized only from glycerol and succinic acid, with no end capping molecules on the reaction system, are more likely to growth branches evenly and to cross-link them to a further extent rendering more uniform structures with less loose branches. These structural features of PGS are in agreement with a higher degradation temperature of pure and technical based PGS in comparison with crude and refined glycerol based PGS evidenced in TGA measurements, suggesting a more cross-linked structure of pure and technical glycerol based PGS.



**Figure 23.** SEM images of fracture site of impacted test bars at 800X magnification for PBS/PGS blends (70/30 wt%). PGS was synthesized using different glycerol sources. A) PG: Pure glycerol based PGS, B) TG: Technical glycerol based PGS, C) RG: Refined glycerol based PGS, D) CG2: Crude glycerol 2 based PGS, E) CG1: Crude glycerol 1 based PGS.

The more regular structure of PGS from pure and technical glycerol can lead to better dispersion in PBS phase, through even distribution of secondary interaction forces such as H-bonding at the PBS/PGS interface. In fact, after etching PGS phase from blends, it can be seen (Figure 24) that pure and technical glycerol based PGS show a better distribution on PBS matrix. The occurrence of some agglomeration of PGS is evidenced as larger cavities shown in PBS phase after etching PGS. These results show that impurities present in crude glycerol sources are also affecting the compatibility of PBS/PGS blends. All glycerol sourced PGS blends displayed good dispersion of PGS in the PBS matrix, mainly due to the ability of PGS to form H-bonds with C=O groups from PGS, which creates a good interaction between both blend components, preventing phase separation and agglomeration of PGS particles. Nevertheless, the smoothest fractures were obtained for technical glycerol based PGS blend, together with the more even size distribution of PGS in PBS matrix, suggesting the best interaction of the blend components. This is believed to be caused by the more regular architecture of pure and technical glycerol PGS formulations, caused by the absence of free fatty acid impurities on glycerol source, which act as end capping monomers creating lower cross-linked PGS with uneven loose branches that create weak interaction zones with the PBS phase.

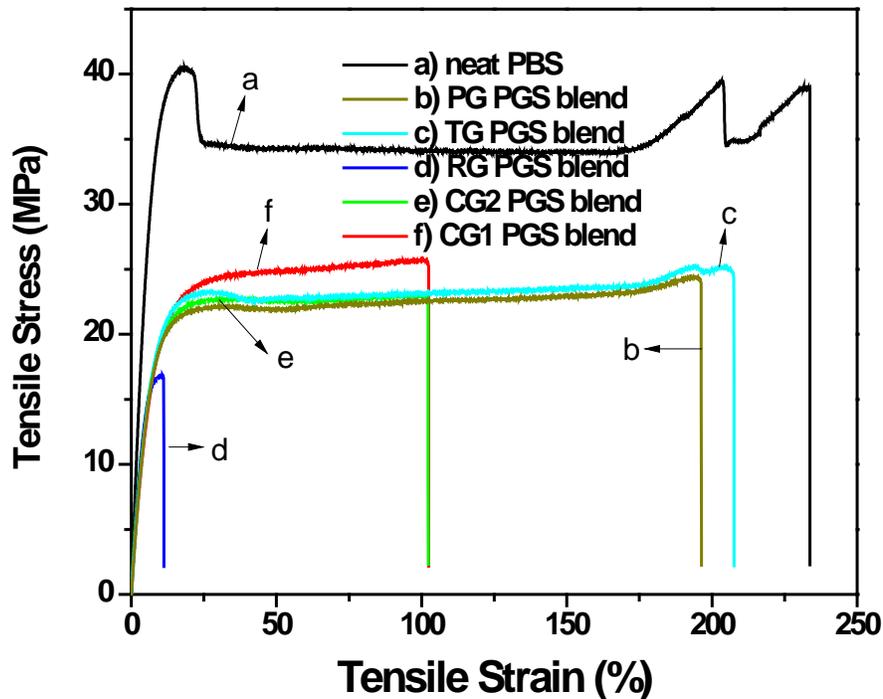


**Figure 24.** SEM images of fracture site of impacted test bars at 800X magnification for PBS/PGS blends (70/30 wt%) after PGS etching. PGS was synthesized using different glycerol sources. A) Pure glycerol based PGS, B) Technical glycerol based PGS, C) Refined glycerol based PGS, D) Crude glycerol 2 based PGS, E) Crude glycerol 1 based PGS.

#### 6.4.4. Mechanical properties

Stress – strain curves for PBS/PGS blends were recorded and are presented in Figure 25.

It shows that the addition of PGS is reducing the strength of the material to half of the original value, due to the amorphous nature of PGS which is caused by its branched structure that impedes it to crystallize. The glycerol source employed has big effect on the elongation at break, which can be analyzed from the compatibility point of view. Pure and technical based PGS blends, maintain a high elongation at break, comparable to neat PBS (>200%), indicating that the stress is uniformly distributed in the elongating sample before breaking, probably by H-bonding



**Figure 25.** Stress – strain curves for PBS/PGS blends (70/30 wt%). PGS was synthesized using different glycerol sources. CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS, PG: Pure glycerol based.

of PGS –OH functionalities with PBS C=O functionalities as shown by FTIR. Crude glycerol based PGS blend show a lower elongation at break, and refined glycerol based PGS blend shows the lowest elongation at break from the set. This can be related to differences on PGS structure induced by monomer contain in glycerol source. Crude and refined glycerol sources contain a mixture of free fatty acid residues, presenting different lengths and chemical structures, which according to FTIR evidence are incorporated as part of the PGS backbone. PGS derived from pure and technical glycerol only contain hydroxyl or succinate pendant groups on its surface. This difference in monomer content affects the regularity of the PGS morphology. Pure and technical glycerol based PGS, composed only of fix length glycerol and succinic acid residues, is more likely to present regular branched structures and regular cross-linking density. Refined and crude glycerol based glycerol PGS on the other hand, present fatty acid residues of different lengths and structures on its surface together with hydroxyl and succinate groups. Also, the free fatty acid residues were shown to act as end capping monomers, reducing the cross-linking density of PGS. These irregularities in PGS synthesized using refined or crude glycerol can lead to an uneven distribution of loads on the blends and stress concentration, which results in premature fracture of the blends. It is noteworthy mentioning that crude glycerol based PGS blends presented much higher elongation at break than refined glycerol based PGS blends, even when both glycerol sources showed fatty acid residues presence and incorporation in PGS structure. The higher elongation at break in crude glycerol based PGS is believed to be caused by the presence of FAME residues, which are not present in refined glycerol, and that remain entrapped on PGS matrix after synthesis, acting as lubricants in the blend. The presence of these lubricant molecules on crude glycerol based PGS blends, causes the PGS network to be able to move and to stretch hydrophobic cores composed of esterified fatty acid residues before

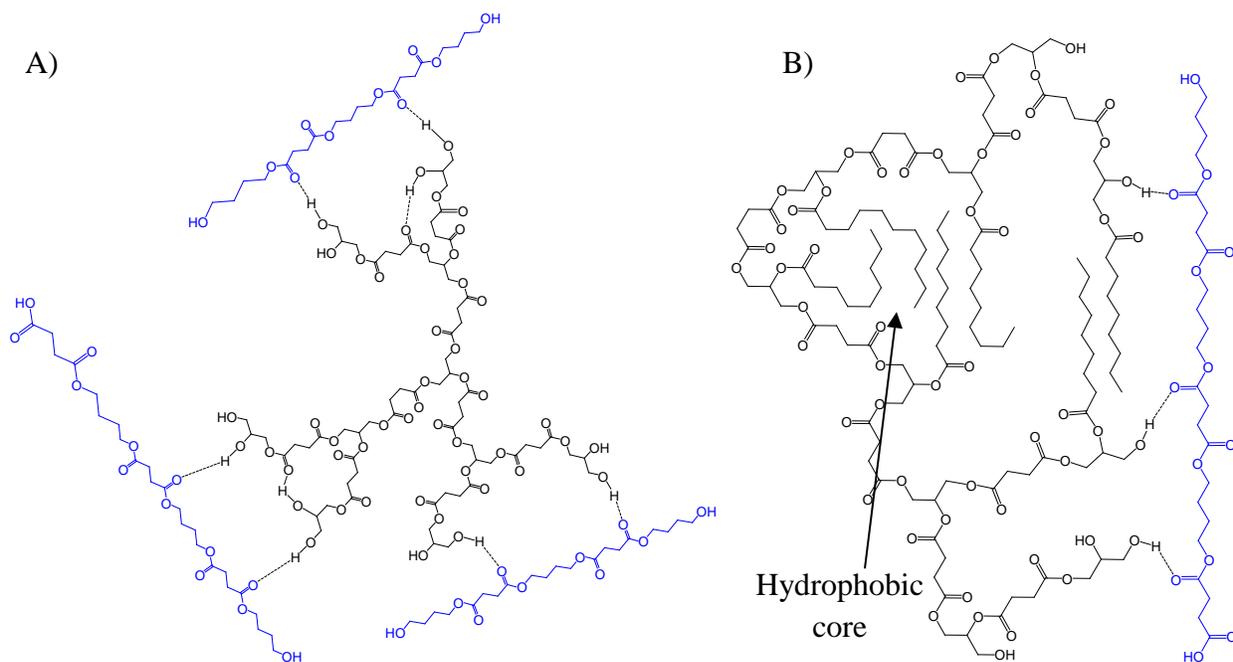
breaking. In refined glycerol case, the absence of these lubricant causes the PGS/PBS blend to fail prematurely at the interface, due to the inability of PGS to disentangle the hydrophobic cores composed of esterified fatty acid residues which reduces its flexibility and molecular movement (Figure 26).

**Table 10.** Mechanical properties of PBS/PGS blends (70/30 wt%). PGS was synthesized using different glycerol sources. CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS, PG: Pure glycerol based

Blend	Tensile Strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact Strength (J/m)
neat PBS	40.4 ± 0.3	603 ± 9.3	238 ± 5.3	36 ± 0.7	824.3 ± 30.7	31.9 ± 1.4
PG - PGS	26.8 ± 0.7	325 ± 10.8	248.3 ± 5.7	17.9 ± 0.5	378 ± 10	121.3 ± 24
TG - PGS	25.6 ± 0.5	330.8 ± 4.6	219.5 ± 11.2	16.8 ± 0.4	370.5 ± 14.6	110.9 ± 23.7
RG - PGS	17.1 ± 0.6	377 ± 5.3	11.7 ± 0.9	18.3 ± 0.7	404.3 ± 13.5	23.5 ± 1.1
CG2 - PGS	23.6 ± 0.4	406 ± 4.7	99.3 ± 23.2	16.8 ± 0.5	400 ± 10	35.2 ± 4.1
CG1 - PGS	26.5 ± 0.9	358 ± 25.2	102 ± 22.1	17.7 ± 0.8	413.7 ± 12	32.5 ± 3.7

Flexural and impact properties shown in Table 10 also confirm the high influence of glycerol source on mechanical properties of PBS/PGS blends. Flexural modulus of the blends showed to be higher for crude and refined glycerol sourced PGS/PBS blends, indicating again that at room temperature, the free fatty acid residues incorporated on PGS structure reduces its flexibility due to the formation of hydrophobic cores with restricted mobility inside PGS matrix. Pure and technical glycerol based PGS, not containing free fatty acids, are composed only of succinate and glycerol units, behaving as a flexible network at room temperature, which gives a lower flexural modulus of their blends. In the same way, impact properties of pure and technical glycerol based PGS blends showed a remarkably increment compared to neat PBS. This can be attributed to the rubbery nature of PGS at room temperature, which is caused by its cross-linked

structure that prevents it from crystallize. Crude and refined glycerol based PGS blends on the other hand, showed no improvement of impact properties, and even refined glycerol based PGS blend showed a decrease on impact strength. This can be attributed to hydrophobic cores formed on crude and refined glycerol based PGS, due to esterified fatty acid residues on the PGS network which can pack tightly inside PGS reducing its mobility and conferring a glassy state at room temperature, which makes it fail at lower energy than flexible chains in pure and technical glycerol based PGS blends. The presence of FAME residues on crude glycerol based PGSs can explain the slightly increased impact energy compared to refined glycerol based PGS. These

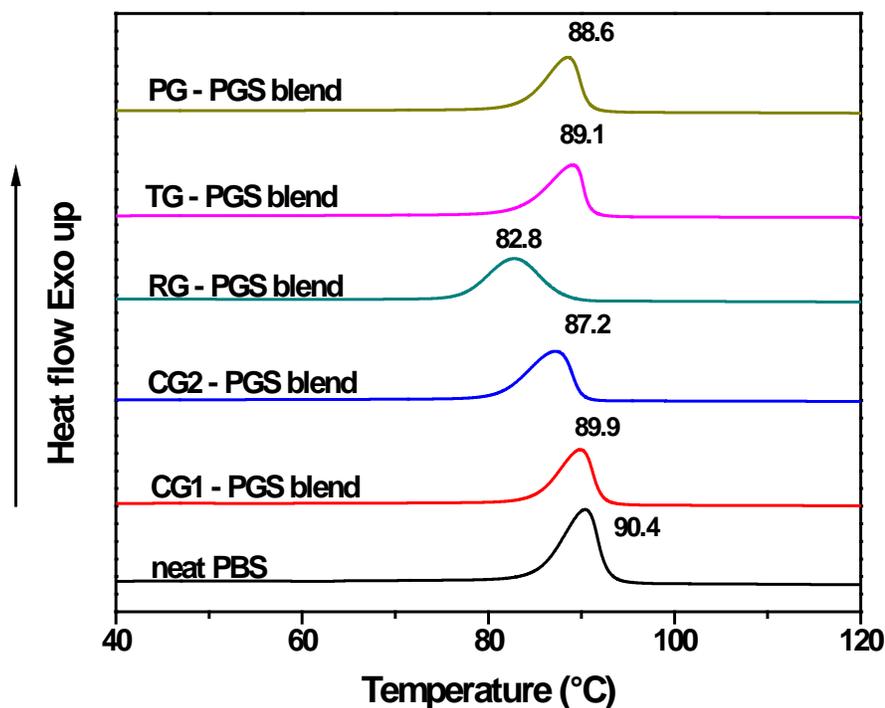


**Figure 26.** Schematic illustration of intermolecular H-bonding between branched PGS (black) and linear PBS chains (blue). A) Pure glycerol based PGS, B) Refined glycerol based PGS.

FAME molecules are acting as a lubricant on the blends, and thus help the free fatty acid hydrophobic cores on PGS to slide to some extent before breaking, which explains the extra amount of energy needed for breaking them at room temperature impact testing. (32.5 and 35.2 J/m for CG1 and CG2 PGS blend respectively vs 23.5 J/m for RG PGS blend).

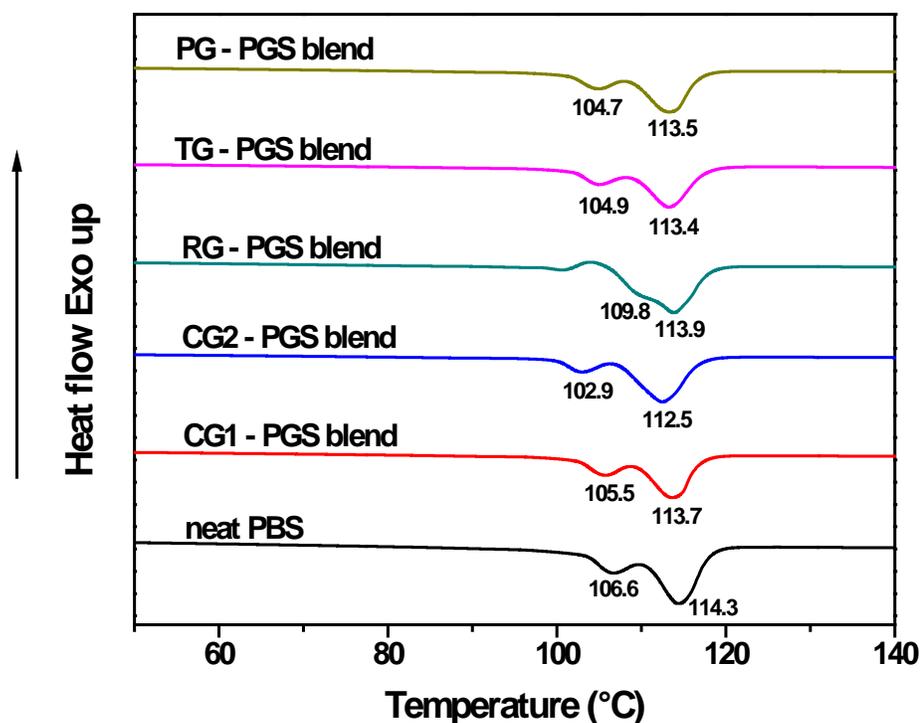
#### 6.4.5. Differential scanning calorimetry

DSC thermograms are presented in Figures 27 and 28, corresponding to crystallization and melting processes respectively. It can be seen that the addition of PGS to PBS matrix is



**Figure 27.** DSC traces of crystallization process in PBS/PGS blends (70/30 wt%). PGS was synthesized using different glycerol sources. CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS, PG: Pure glycerol based.

affecting the thermal properties of the blends. Crystallization temperature ( $T_c$ ) (Figure 27) shows a decrease after PGS addition, for all glycerol grades, indicating that the incorporation of gel type PGS particles to the blend restricts the crystal formation in PBS phase, by decreasing the possibility for PBS chains to move freely and accommodate in crystalline structures through H-bonding interactions. Remarkably, refined glycerol based PGS blend showed the highest decrease in crystallization temperature as a broad peak at 82.8 °C. Refined glycerol PGS showed



**Figure 28.** DSC traces of melting process in PBS/PGS blends (70/30 wt%). PGS was synthesized using different glycerol sources. CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS, PG: Pure glycerol based.

the highest storage modulus at low frequencies in melt rheology which indicates that for this blend there are greater interactions between PGS particles and PBS chains, probably due to higher entanglements of free (uncross-linked) branches of PGS particles and PBS chains. These loose branches in refined glycerol PGS occur as a consequence of the free fatty acid content on this glycerol source, which end caps some branches in the matrix preventing these branches to be linked to the PGS network through further polymerization. PGS branches in refined glycerol based PGS gel particles interact with PBS chains making more difficult for the PBS molecules to find proper orientation for the crystallization to occur, thus reducing the crystallization temperature. Melting process thermogram (Figure 28) on the other hand, shows that for refined glycerol some cold crystallization phenomena is occurring. This cold crystallization phenomenon occurs because of the imperfect crystal formation on refined glycerol case, due to higher interactions between phases, created by entanglements of PBS chains on PGS free branches. This indicates again that for refined glycerol based PGS the occurrence of free fatty acid residues which allows the formation of loose branches as part of PGS network creates a difficulty for PBS to crystallize, leading to imperfect crystal formation. For all other glycerol sources, melting temperature shifts down towards similar values, which matches the trend observed in crystallization process. Table 11 presents thermal data collected in DSC analysis of all glycerol sourced PGS and PBS blends.

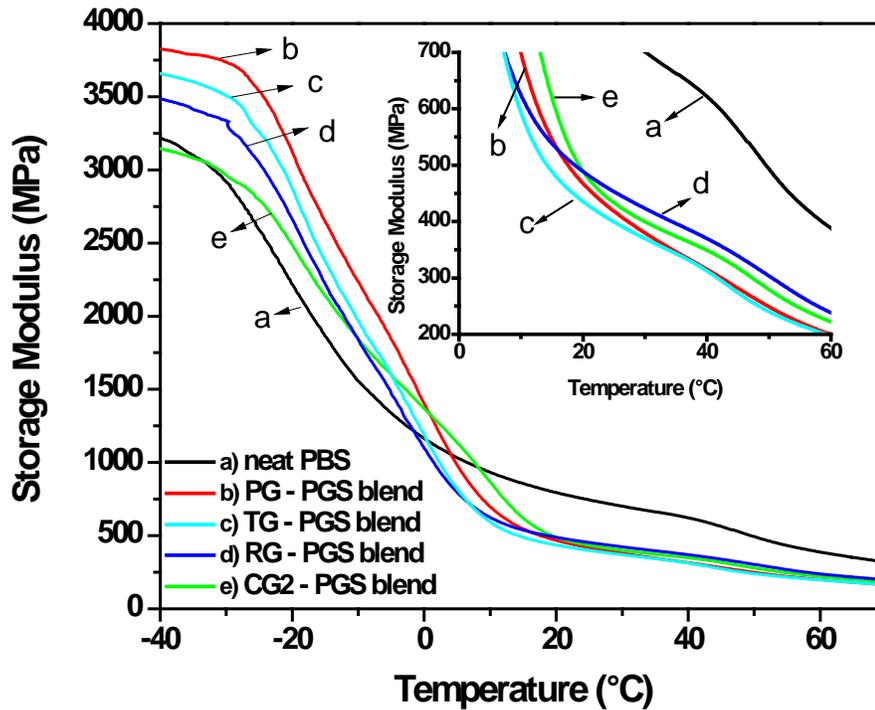
**Table 11.** Thermal transition temperatures and transition enthalpies for PBS/PGS blends (70/30 wt%). PGS was synthesized using different glycerol sources. CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS, PG: Pure glycerol based

<b>Blend</b>	<b>T<sub>c</sub> (°C)</b>	<b>T<sub>m1</sub> (°C)</b>	<b>T<sub>m2</sub> (°C)</b>	<b>ΔH<sub>c</sub> (J/g)</b>	<b>ΔH<sub>m</sub> (J/g)</b>	<b>X<sub>c</sub><sup>a</sup> (%)</b>
Neat PBS	90.4	106.6	114.3	62.4	55.9	50.6
PG - PGS blend	88.6	104.7	113.5	44.7	40.2	52.0
TG - PGS blend	89.1	104.9	113.4	44.5	38.5	49.8
RG - PGS blend	82.8	109.8	113.9	48.9	41.6	53.8
CG2 - PGS blend	87.2	102.9	112.5	48.0	43.2	55.9
CG1 - PGS blend	89.9	105.5	113.7	44.5	39.4	51.0

<sup>a</sup> % of crystallinity on PBS phase. Calculated as melting enthalpy ratio with 100% crystalline PBS value (110 J/g) [62]

#### 6.4.6. Dynamical mechanical analysis

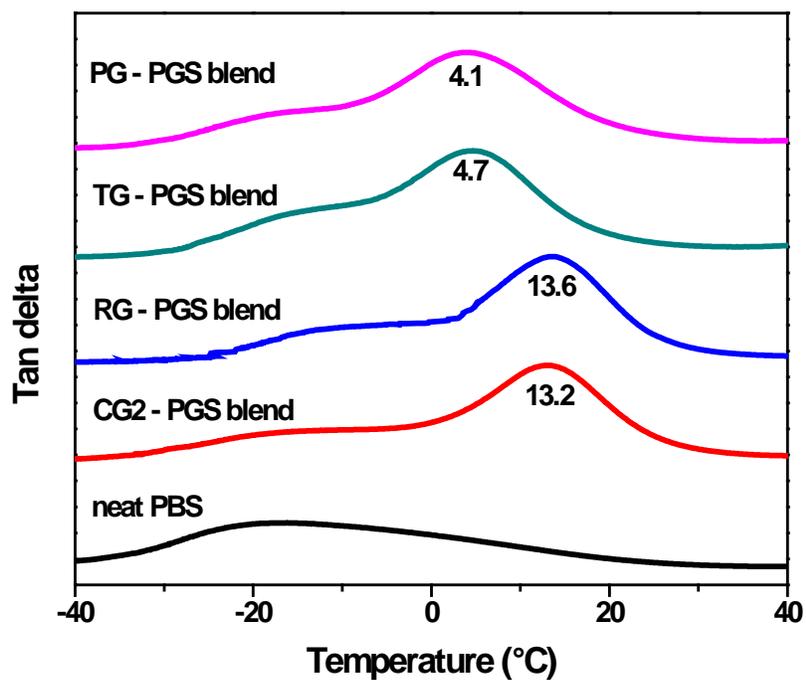
DMA analysis was performed for analyzing storage modulus of the PBS/PGS blends at a wide temperature range. Figure 29 presents storage modulus (E') of PBS/PGS blends, for PGS synthesized using different glycerol sources. It can be seen that at low temperatures (T < -20 °C), the storage modulus of the pure and technical glycerol based PGS blends are higher than for crude and refined glycerol based PGS blends. This is in agreement with the cross-linking density



**Figure 29.** Storage modulus of PBS/PGS blends (70/30 wt%). PGS was synthesized using different glycerol sources. CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS, PG: Pure glycerol based.

differences evidenced by TGA. Pure and technical glycerol based PGS are showing the highest cross-linking density, according to TGA results, which implies that they present the most regular architecture on their structure, due to the regularity of the monomers on PGS synthesis (only glycerol and succinic acid). Crude and refined glycerol based PGS on the other hand, present loose branches, which have been prevented to further cross-link through end capping of functional – OH units with fatty acid residues. These impurities cause the structure of crude and refined glycerol sourced PGS to become irregular, and to present some imperfections on the network structure, leading to lower energy storage capacity evidenced as a decreased storage

modulus at glassy state. At room temperature on the other hand (Figure 29 insert), refined glycerol and crude glycerol based PGS blends present higher storage modulus than pure and technical glycerol based PGS blend. This can be explained because as already noticed in impact and flexural properties of PBS/PGS blends, at room temperature, refined and crude glycerol based PGS present higher stiffness than pure and technical glycerol based PGS, due to the formation of hydrophobic cores composed of free fatty acid residues incorporated on PGS matrix, which restrict the movement of PGS network. In fact, Figure 30 shows tan delta peaks of PGS/PBS blends, which reveals glass transition temperatures of both blend components. PBS is showing a broad glass transition temperature at around  $-20\text{ }^{\circ}\text{C}$ , which is also present in all PBS/PGS blends with no significant changes. Hence, the second glass transition temperature observed is for PGS. The glass transition temperature of crude and refined glycerol based PGS ( $T_g \sim 13\text{ }^{\circ}\text{C}$ ) is shown to be significantly higher than for pure and technical glycerol based PGS ( $T_g \sim 4\text{ }^{\circ}\text{C}$ ). This observation matches all mechanical evidence which indicates that at room temperature, a higher stiffness of crude and refined glycerol based PGS is observed, given its more glassy state. Pure and technical glycerol based PGS on the other hand, having a much lower glass transition temperature, present rubbery nature at room temperature. This explains the higher toughening effect of pure and technical glycerol based PGS on PBS matrix, evidenced as a high increase on impact strength for these blends (4-fold increase), which is possible because of the good interaction of PGS additive with PBS matrix through hydrogen bonding as evidenced by FTIR leading to an efficient dissipation of the stress on rubbery state PGS. When adding crude or refined glycerol based PGS to PBS matrix on the other hand, at room temperature the stress is transferred from PBS matrix to glassy state PGS, which cannot dissipate the stress effectively because of its reduced mobility, and causes the failure of the material.



**Figure 30.** Tan delta of PBS/PGs blends (70/30 wt%). PGS was synthesized using different glycerol sources. CG1: Crude glycerol 1 based PGS, CG2: Crude glycerol 2 based PGS, RG: Refined glycerol based PGS, TG: Technical glycerol based PGS, PG: Pure glycerol based.

## 7. Conclusions

The synthesis and application of glycerol based hyperbranched polymers as additives for biobased blends was studied in the present research. Four different glycerol sources, coming from biodiesel production process were characterized according to its chemical composition. It was found that crude glycerol samples, taken directly after transesterification process present the lowest glycerol content ( $< 30$  wt%), along with the highest presence of other impurities, mainly fatty acid methyl esters (FAMES), free fatty acids (FFAs) and soaps. The synthesis of poly (glycerol succinate) (PGS), a hyperbranched polymer, was carried using four different sources of crude glycerol or pure glycerol and succinic acid. The presence of impurities in glycerol source is playing an important role on PGS properties, and ultimately on PGS blends with poly (butylene succinate) (PBS). Free fatty acids and soaps were found to participate of the esterification reaction of glycerol, being incorporated as part of PGS structure as evidenced by FTIR, causing dramatic changes on PGS properties. When using pure or technical glycerol for synthesizing PGS, which present glycerol content above 95 wt% and no FFA nor FAME residues, because of the presence of glycerol and succinic acid only, the PGS products obtained present low glass transition temperature ( $T_g \sim 4$  °C) evidenced by DMA and high cross-linking density evidenced by TGA, rendering increased toughness of the material at room temperature. When using crude glycerol or refined glycerol as glycerol source for PGS synthesis, the incorporation of fatty acid residues to PGS network, evidenced through FTIR, promotes the formation of hydrophobic cores with restricted mobility, which increases the glass transition temperature of these PGS ( $T_g \sim 13$  °C) turning it into a more brittle material at room temperature. In addition, when using crude glycerol directly as it comes after biodiesel production as the glycerol source for PGS synthesis, a high amount of residual FAMES is introduced to the

reaction, which acts as a solvent, preventing high polymerization to be achieved. The PGS products obtained when using crude glycerol directly for its synthesis present a high amount of FAME impurities entrapped on it which are impossible to remove, and therefore are added to blends in an uncontrolled way. This presents a challenge for the reproducibility of the PGS synthesis using crude glycerol as the glycerol source. In an attempt to overcome this situation, chemical refinement of crude glycerol was performed eliminating the FAME content and producing a refined glycerol sample with high glycerol content (> 70 wt%) and also high soap content (~30 wt%). These soap residues still present in refined glycerol can also be esterified as shown by FTIR, causing PGS to have an increased glass transition temperature, and thus increased glassy behavior at room temperature.

The physical changes introduced on PGS because of the introduction of fatty acid residues on its structure are also affecting the mechanical properties of PBS/PGS blends (70/30 wt%). All PGS formulations shown to have a similar level of H-bonding with PBS phase evidenced by FTIR, which indicates that the blends display a good compatibility. Furthermore SEM imaging showed a good dispersion of PGS filler in PBS matrix in a spherical-like morphology, with no signs of agglomeration of PGS phase. DMA data showed that there are two distinct glass transition temperatures on PBS/PGS blends, indicating the immiscibility of its components. Also it showed that refined and crude glycerol based PGS blends have higher storage modulus at room temperature, which is created by the enhanced glassy behavior of these PGS materials due to the occurrence of fatty acid hydrophobic cores on them. Mechanical properties of PBS/PGS blends is also in agreement with other experimental observations, showing that for pure and technical based PGS blends a high toughening effect is obtained, evidenced as a higher impact strength (~100 J/m) than neat PBS with a high elongation at break

which indicates a good interaction between both blend components likely through hydrogen bonding. When adding crude or refined glycerol based PGS on the other hand, a stiffening effect is observed in the blends, evidenced as low impact energy ( $\sim 30$  J/m) and low elongation at break of these samples, together with an increase of flexural modulus compared to pure or technical glycerol based PGS blends. This comes as a result of the incorporation of free fatty acid residues on PGS structure, which can pack in hydrophobic cores with reduced mobility turning PGS into a glassy state at room temperature, causing the blend to present higher flexural properties, but reduced impact resistance and elongation capacity.

To the best of our knowledge, this is the first report of the effect of glycerol purity on material properties of glycerol based hyperbranched polymers. These results highlight the role of impurities of glycerol source on its use as a reactive for biomaterial synthesis. The chemical composition of glycerol source proved to have a major effect on the mechanical properties of the synthesized hyperbranched polyesters indicating the importance of using highly refined glycerol (glycerol content  $> 95$  wt%) for producing a tough elastomeric product, which can effectively increase impact properties of PBS without compromising the tensile and flexural properties.

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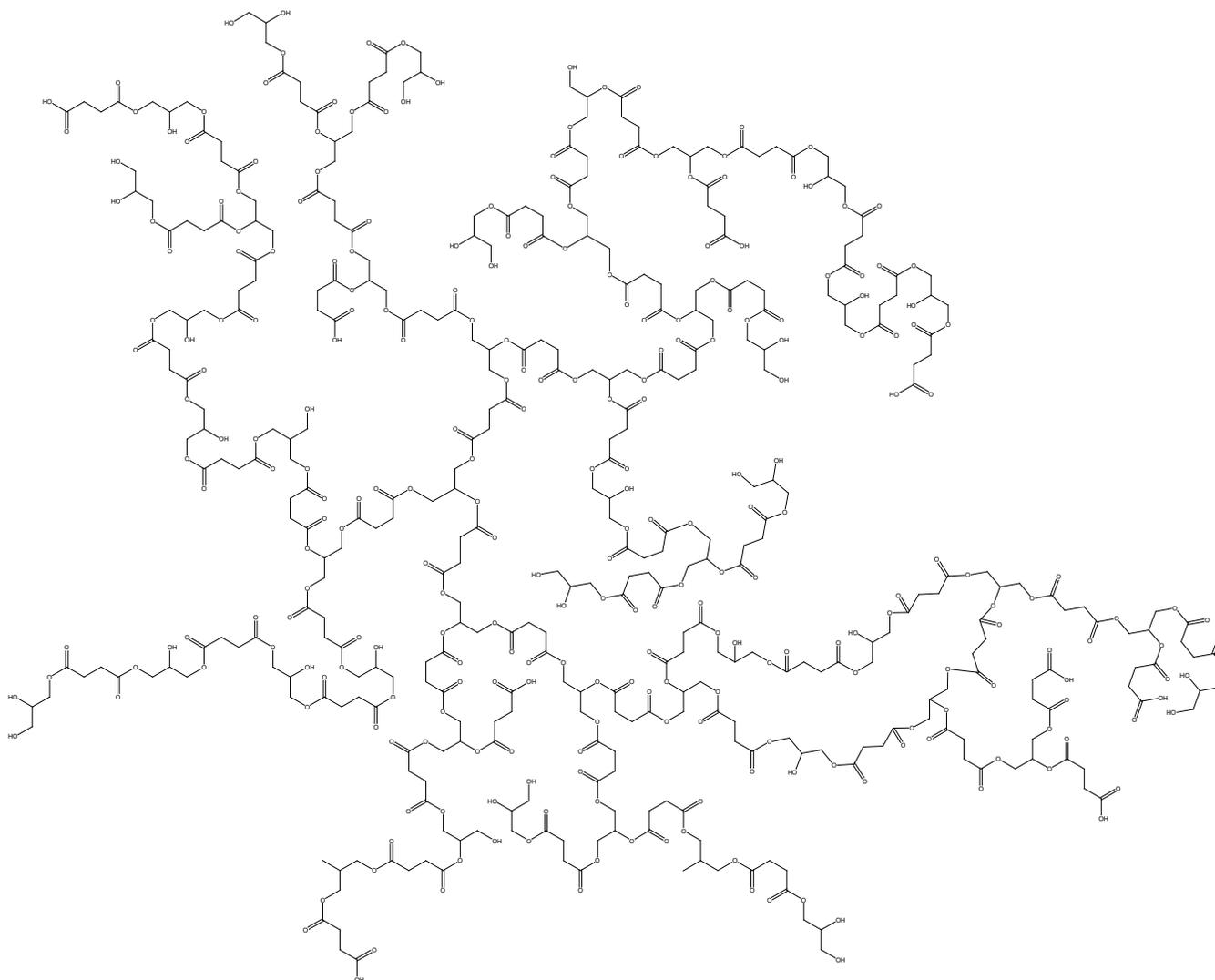
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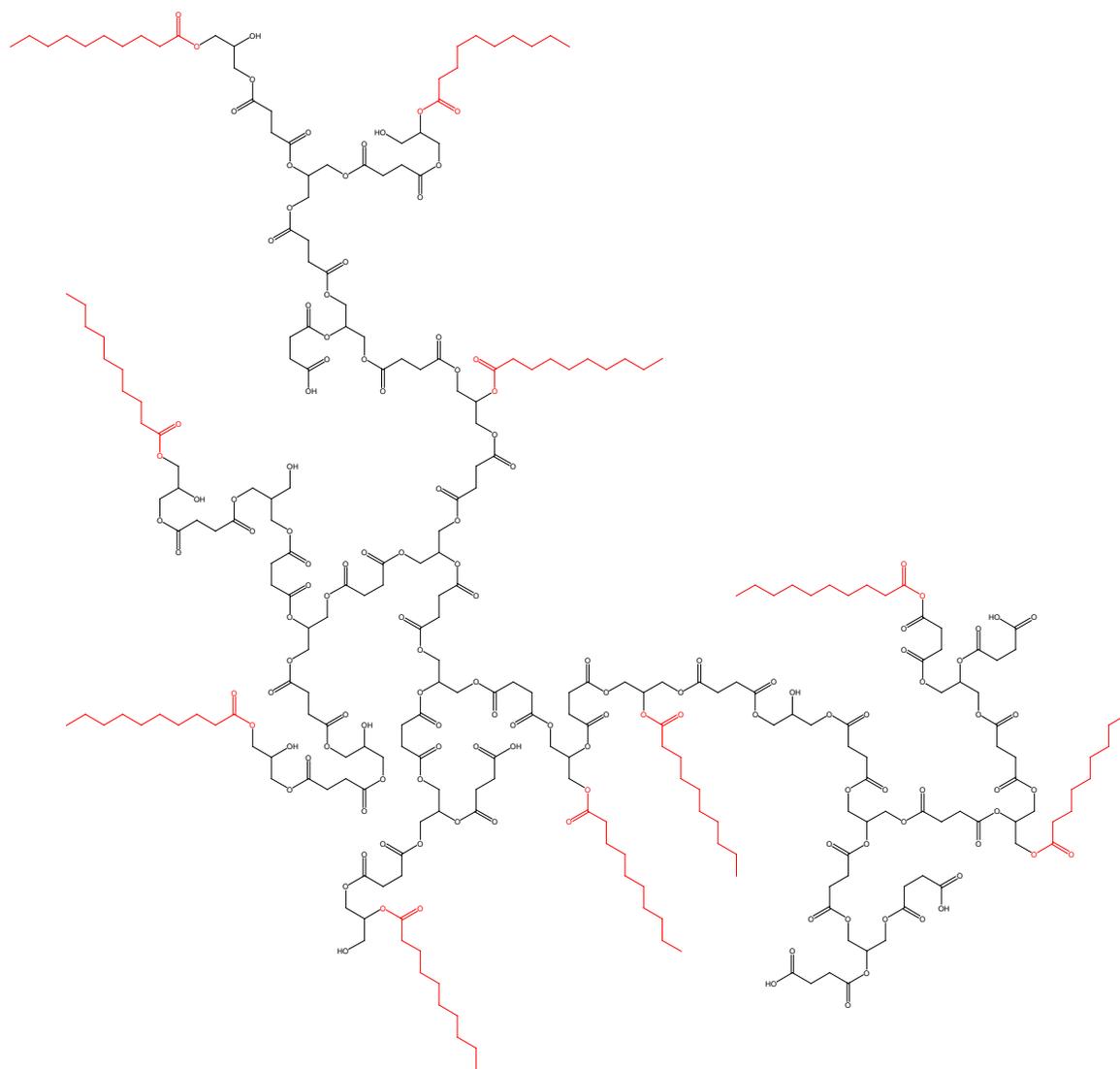
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**Appendix I.** Idealized structures of glycerol based poly (glycerol succinate) PGS.



**Figure 31.** Idealized structure of pure or technical glycerol based PGS.



**Figure 32.** Idealized structure of crude or refined glycerol based PGS. Fatty acid residues acting as branch terminal units are shown on red