Synthesis and characterization of polyesters derived from glycerol, azelaic acid, and succinic acid

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A research was conducted to synthesize new elastic polymers via polyesterification of glycerol (GE) with azelaic (AZ) and succinic acids (SU) as an added value to the surplus of GE from palm oil industry in Malaysia. This paper reports the successful, simple synthesis of unique elastic polyesters via the catalyst-free polyesterification of multifunctional monomers derived from GE, AZ, and SU. The ratio of the diacid to the alcohol used in this experiment was 1:1. The resulting polyesters, specifically, poly(GE/azelate/succinate), p(GAS), were characterized using nuclear magnetic resonance spectroscopy (NMR), Fourier-transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). The thermal stability increases with an increasing number of azelate units in the polyesters. The desired final product can be achieved by tuning the monomer ratio and the water removal efficiency.

Keywords: azelaic acid; polyesterification; glycerol; succinate

1. Introduction

The development of bio-based polymers to replace or reduce the use of polymers from petrochemicals continues to exhibit strong growth. The decline of petroleum reserves, the fluctuating price of petroleum-based products, and stringent environmental regulations have prompted the use of chemicals derived from natural, renewable resources in both the scientific and industrial communities (1–3). In addition, the environmental pollution and waste management issues from bio-resistant synthetic plastics have become increasingly concerning in recent decades. Many countries have placed great emphasis on reusing and recycling plastic waste.

In the meantime, the development of biodegradable polymers offers an alternative solution. Among these synthetic polymers, aliphatic polyesters have attracted considerable attention because they are biodegradable, biocompatible, and have physical or chemical properties comparable to many traditional, non-biodegradable polymers such as low-density polyethylene (LDPE) and polypropylene (PP) (4, 5). Bio-based polymers have been developed and applied in many fields including packaging, agriculture, and sanitation (6). These materials have also been used in biomedical applications such as resorbable surgical sutures, implants, and controlled drug delivery systems. Among these biodegradable materials, aliphatic polyesters appear to be the most promising because their hydrolytic and/or enzymatic degradation products can be naturally metabolized into nontoxic substances that are susceptible to biological attacks (7). Studies of aliphatic polyesters derived from the polycondensation reaction of dicarboxylic acids and diols is therefore increasing (8). Furthermore, because the \( \omega \)-carboxy fatty acids of medium-to-long chain length carboxylic acids are natural metabolic intermediates and because the US Food and Drug Administration (FDA) has approved glycerol (GE) for medical applications, polymers of GE and diacids have garnered considerable interest for the development of bioresorbable materials (9). The dicarboxylic acid, azelaic acid (AZ), is a good choice as it is made from renewable resources and is suitable for biomedical applications because of its antibacterial properties. AZ can be obtained by the oxidative cleavage of oleic acid, and it is commercially produced by ozonolysis of oleic acid. Oleic acid is the most common unsaturated fatty acid and is a major component of commercially available vegetable oils (10, 11). Meanwhile, succinic acid (SU; butanediolic acid) is a four-carbon dicarboxylic acid that is a solid at room temperature which is soluble in water, alcohol, acetone, and ether. According to the US...
FDA, SU is generally regarded as safe and is used as a flavor enhancer, a pH control agent in food products, and as an ingredient in toothpaste (12).

GE is a tri-functional compound that may be combined with dicarboxylic acid to produce polyesters. GE is the principal byproduct from the hydrolysis of vegetable oils and is obtained during the preparation of biodiesel (13). These vegetable oils can be obtained from palm oil or from other sources, such as canola, rapeseed, and soybean oil. However, compared with other vegetable oils, palm oil has far better advantage and potential as feedstock for biodiesel production. Palm oil is a perennial crop, unlike soybean and rapeseed. Perennial crop means the production of oil is continuous and uninterrupted, though annual production has its seasonal peak and down cycle (14). Malaysia has become one of the biggest producers and exporters of palm oil and palm oil products (15, 16). According to Malaysian Palm Oil Board (MPOB), Malaysia had been exporting 237,589 metric tons and 231,277 metric tons of GE worth MYR467.2 million and MYR432.8 million in the year 2009 and 2010, respectively (17).

The increasing use and production of biodiesel have resulted in an increase in GE production and a decline in its price, which makes GE a particularly attractive molecule for the synthesis of other chemicals (18, 19). The high demand for fatty methyl esters as an alternative diesel fuel, biodiesel, has generated a surplus of GE. The development of new markets for GE would also have a significant impact on biodiesel production because an increased credit for this coproduct could improve the economics of biodiesel, making it more commercially competitive to petroleum-derived diesel. Over the past several years, efforts to synthesize aliphatic polyesters have focused on other alcohols with little emphasis given to GE. Thus, we feel the need to explore the use of underutilised material with great potential, GE, for the synthesis of polyesters (Figure 1).

GE can be polymerised; however, most strategies used to make polyglycerols do not use GE as the primary propagating unit because the condensation of GE is nonselective and requires high processing temperatures (20).

This work was done for the first time and describes the preparation of easily processable thermoplastic materials that have a low environmental impact, i.e., polymers derived from renewable chemicals. Toward this goal, polyester elastomers, namely $p$(GAS), have been synthesized via a simple, catalyst-free polycondensation reaction beginning with GE, AZ, and SU, as depicted in Scheme 1. The resultant polyesters are expected to provide new surgical materials useful in orthopaedic and ophthalmic

![Figure 1. Synthesis of polyester from renewable chemicals.](image-url)

![Scheme 1. Polycondensation reaction of AZ, SU, and GE. (R = OH or hydrocarbon).](image-url)
applications, reconstructive surgery, and as drug delivery agents (21–28). These biocompatible polymers are also of interest for their potential use as cosmetics, food additives, surfactants, lubricants, and azeotropic phase separators (11).

2. Experiments

2.1. Materials
AZ (molecular weight ($M_w$) = 188.22 g/mol, melting temperature ($T_m$) = 107°C) was purchased from Thermo Fisher Scientific, Geel, Belgium. SU ($M_w$ = 118.09 g/mol, $T_m$ = 185–190°C) was purchased from Merck KGaA, Frankfurter Strasse, Darmstadt, Germany. Pure GE samples (99%; $M_w$ = 99.1 g/mol, $T_m$ = 17.8°C) were obtained from a local distiller, Natural Oleo-chemical-Sdn. Bhd., Pasir Gudang, Johor, Malaysia. All chemicals were used as received without further purification.

2.2. Synthesis of p(GAS) elastomers and sample preparation
Pre-polymer mixtures of equimolar amounts of GE and the acids [GE:(AZ/SU) = 1:1] were created for use in the polyesterification reaction. Three different monomer compositions were used to produce the pre-polymers as listed in Table 1. The pre-mixed reactants (GE, AZ, and SU) were placed in a 300-ml three-necked round-bottom flask equipped with a condenser, nitrogen inlet, and thermometer. The monomer mixture was heated and mixed at 160–165°C in a silicon oil bath for 2 hours under a constant stream of nitrogen. The resulting prepolymer p(GAS) compositions (Table 2) were used for film preparation without further purification. The pre-polymers, which are thick and viscous, were cast into Petri dishes and left in an oven at 125°C for 48 hours to produce films via further polyesterification. The final product, elastomeric p(GAS) polyester, was prepared as a 1-mm thin sheet. The synthesized and processed p(GAS) polyesters exhibit thermoplastic behavior, as confirmed by their repeated moldability. All films were produced under identical reaction conditions, and the samples were stored in a desiccator for further analysis.

2.3. Fourier-transform infrared spectroscopy
Small slabs of fully cured polyester samples were subjected to Fourier-transform infrared spectroscopy (FTIR) analysis to observe the esterification process and to estimate the extent of the reaction. Spectra were collected using a Thermo Nicolet IR 200 spectrometer with a diamond attenuated total reflection. The samples were scanned 128 times at a resolution of 4 cm$^{-1}$ over the range of 500–4000 cm$^{-1}$.

2.4. NMR spectroscopic analysis
A sample of p(GAS) pre-polymers was purified for nuclear magnetic resonance spectroscopy (NMR) analysis by precipitation in water followed by constant mixing, filtering, and freeze-drying. The reaction yield was calculated by comparing the masses of both the non-purified and purified pre-polymers and was found to be $\sim$80% for all three compositions, although a portion of the material was lost during the filtering process. Small portions of the purified pre-polymer mixtures were dissolved in CDCl$_3$. The $^1$H NMR spectra were recorded using a Bruker 600 MHz FT-NMR spectrometer with a cryoprobe (Avance 111). The chemical shifts were measured relative to the solvent peak as a secondary standard.

2.5. Gel permeation chromatography
The number average molecular weight ($M_n$), the weight average molecular weight ($M_w$), and the polydispersity index ($M_w/M_n$) of the p(GAS) pre-polymers were determined using a Perkin-Elmer gel permeation chromatography (GPC) chromatograph equipped with a refractive index detector. The flow rate was 1 ml/min, and the measurements were performed at 35°C. The equipment was calibrated with polystyrene standards of a narrow molecular weight distribution. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1 ml/min, and a solution of polystyrene in THF was used as the calibration standard. Twenty microliters of a 1% polymer solution in THF was injected for all runs.

Table 1. Initial mole ratio of the monomers used in the polyesterification reaction of p(GAS).

| Monomer ratio (GE:AZ:SU) | Abbreviation of polymer samples |
|--------------------------|-------------------------------|
| 1:1:0                    | p(G1A1S0)                     |
| 1:0.5:0.5                | p(G1A0.5S0.5)                 |
| 1:0.75:0.25              | p(G1A0.75S0.25)               |

Table 2. GPC results for p(GAS) pre-polymers of varying composition.

| Pre-polymer samples | $M_n$(Da) | $M_w$(Da) | $M_w/M_n$ |
|---------------------|-----------|-----------|-----------|
| p(G1A1S0)           | 515       | 13,883    | 26.9      |
| p(G1A0.5S0.5)       | 1612      | 18,617    | 11.5      |
| p(G1A0.75S0.25)     | 3656      | 24,626    | 6.73      |
2.6. Differential scanning calorimetry

Differential scanning calorimetry analysis (DSC1, Mettler Toledo) was performed to observe the thermal transition of the p(GAS) polymers. The samples were heated from 50°C to 300°C at 10°C/minute, maintained at 300°C for 1 minute, cooled from 300°C to −80°C at 10°C/minute, and subsequently heated for a second cycle to 300°C at 10°C/minute under a nitrogen atmosphere. The second heating cycle was performed during the DSC analysis to obtain a clear glass transition by overcoming the irreversible processes that accompany the glass transition during the first heating cycle. The DSC thermograms were analyzed using Mettler: STARe V.9.00 software to determine the p(GAS) glass transitions ($T_g$) and the melting temperatures ($T_m$).

2.7. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the p(GAS) elastomers was conducted using a Netzsch STA 449 F3 Jupiter®. TGA measurements were taken under a nitrogen flow at a scanning rate of 10°C/minute in the range of 25–500°C.

3. Results and discussion

3.1. Fourier-transform infrared spectroscopy

The FTIR spectra of the p(GAS) elastomers produced with different compositions are presented in Figure 2. The esterification reaction for all of the polyester samples is confirmed by a shift in the transmittance band from 1695.7 cm$^{-1}$ to 1739.2 cm$^{-1}$, and the band at 1740 cm$^{-1}$ is attributed to the formation of the ester linkage. The transmittance bands at 2933.6 cm$^{-1}$, 2933.3 cm$^{-1}$, and 2933.8 cm$^{-1}$ correspond to the C–H stretching of the methylene and methyl groups. Hydroxyl groups for GE should appear at 3300 cm$^{-1}$, but the disappearance of this band in FT-IR spectrum meant that the polymer was produced. Transmittance bands associated with free hydroxyls observed at 3467.8 cm$^{-1}$, 3.467.5 cm$^{-1}$, and 3460 cm$^{-1}$ correspond to the hydrogen-bonded hydroxyl groups found in the cured polymers. As reported in an earlier publication, the unreacted alcohol group exists in a mole ratio of 1:1 (acid:alcohol), which supports the idea that the secondary hydroxyl group in GE resists esterification, which is a fact that may be attributed to the steric effect arising from the primary hydroxyl esterification. The broad OH stretching of the p(G1A0.5S0.5) at 3460 cm$^{-1}$ shifts slightly to the right, suggesting that the introduction of SU may have promoted reaction with the secondary hydroxyl group of the GE, as shorter diacids tend to have better reactivity than longer diacids.

3.2. Nuclear magnetic resonance

Figure 3 shows the $^1$H NMR spectra of representative purified p(GAS) pre-polymers with varying initial AZ/SU mole ratios. The proposed structural formulas for the resulting co-polymesters in Figure 3 indicate the correlation between the various structural components and the observed NMR peaks. Peaks “A”, “B,” and “C” were assigned to the C–H aliphatic protons of AZ. Peak “D” corresponds to the –CH$_2$ group of GE. The terminal GE segments appeared toward the higher chemical shifts at 5.0–5.3 ppm, as indicated by peak “E”. The SU segments in the pre-polymer chain are indicated by peak “F”, and the difference in the signal intensities for both types of protons in Figure 3(b) and 3(c) agreed with the initial feed monomer ratio (Table 1). The NMR results indicated the existence of both terminal and fully esterified acid groups in the p(GAS) pre-polymers.

3.3. Gel permeation chromatography

The number average molecular weight ($M_n$), weight average molecular weight ($M_w$), and polydispersity ($M_w/M_n$) for each p(GAS) pre-polymer, as determined by GPC are listed in Table 2. The $M_w$ and $M_n$ values of a p(GAS) pre-polymer increase in the following order: p(G1A0.75S0.25) > p(G1A0.5S0.5) > p(G1A1S0). The molecular weights of the pre-polymer samples were found to depend on the polyesterification method used. The molecular weight of the p(GAS) pre-polymers was increased and the molecular weight distribution was narrowed with the addition of SU into the polyesterification reaction. This
result may be attributed to the incorporation of shorter diacids to increase the conversion of the total acid end groups for the p(G1A0.75S0.25) because SU can act as its own catalyst in the esterification reaction (2). Moreover, the increase in the molecular weight of the p(G1A0.75S0.25) pre-polymer is probably due to the chain extension promoted by SU, although the molecular weight decreases with an increase in
the quantity of SU. A high molecular weight is essential to achieve polymeric materials with sufficient mechanical properties. However, the synthesis of high molar mass aliphatic polyesters through the conventional polycondensation method is difficult, due to the competitive reactions of condensation and degradation, which take place simultaneously (30). Various synthetic strategies can be used to optimize the reaction and to control further polymerisation (31). Elastomers are generally defined as lightly cross-linked polymers that easily undergo large, reversible deformations with a complete recovery (32). The molecular weights of these synthesized pre-polymers are acceptably high for further studies and applications.

3.4. Differential scanning calorimetry

The thermal behavior of the p(GAS) polyesters was studied using DSC analysis. The first heating scan of the p(GAS) films indicates endothermic melting ($T_m$) peaks, as illustrated in Figure 4(a). However, the endothermic melting peaks were absent in the second heating curve, this shows that the endothermic peaks which appear in the first heating is caused by the evaporation of water of crystallization. Figure 4(b) shows the apparent glass transition ($T_g$) for all of the p(GAS) polyesters from the second heating scans within the range of $-24$ to $-7°C$. The glass-transition temperatures ($T_g$), which are considered an important characteristic, were determined for all samples and revealed the molecular dynamics of the polymer chains within a given temperature range. p(G1A0.5S0.5) recorded the highest $T_g$ ($-8.26°C$), while p(G1A1S0) recorded the lowest $T_g$ ($-23.36°C$). As shown in Figure 4(b), all synthesized p(GAS) polyesters exhibit a $T_g$ below room temperature, which is a characteristic feature that determines their elastomer-like behavior (33). Elasticity is caused by a high mobility in the macromolecules at temperatures above their $T_g$ (34). The addition of a short-chain dicarboxylic acid—SU in this experiment—shifted the glass transition temperature to a higher value. $T_g$ is linked to the chain mobility of a polymer and increases with the enhanced restriction of a polymer chain’s mobility. The relatively high $T_g$ for p(G1A0.5S0.5) is attributed to the stronger intermolecular hydrogen bonding. Thus, increasing the cross-link density resulted in a decrease in the chain mobility, which, in turn, increased the $T_g$ of the polymer.

3.5. Thermogravimetric analysis

The thermal stability of the synthesized p(GAS) films was evaluated using TGA. The polyester must have adequate thermal stability or practical applications will be limited. Figure 5(a) and 5(b) shows the weight loss curve and the derivative curve of the weight loss for the p(GAS) films, respectively. The typical shape of the TGA curves reveals a two-step degradation process for all examined samples, indicating high stability and a high degree of polymerization. The initial weight loss corresponds to the elimination of residual (or adsorbed) water molecules. From the temperature at which 90% weight loss occurs, one can observe that p(G1A1S0) is the most stable of the synthesized polyesters. This investigation indicated that the thermal stability depends on the composition of the polymer. The thermal stability of p(GAS) increases with an increase in the AZ concentration in the polymer. Similar behavior also has been reported by Soccio et al. (2). The primary degradation of the polymeric backbone took place at temperatures higher than 400°C, indicating that all of the synthesized p(GAS) polyesters exhibit high thermal stability.
4. Conclusions

Types of polyesters have been successfully synthesized using a simple, catalyst-free polyesterification process with GE, AZ, and SU as monomers. The new synthesized polyesters were characterized by using spectroscopical techniques. The reaction of these monomers in a 1:1 mole ratio yields an elastomer that is soft and pliable after removal from the oven and hardens upon cooling at room temperature. The synthesis process involves a simple procedure without any catalyst (for the first time) or extreme operating conditions. The addition of SU in the formulation improved the molecular weight of the final product. The thermal stability increases as the concentration of AZ units increases. The chemical, physical and physico-chemical properties of these polyesters can be tuned to suit the final application by changing the mole ratio of the monomers. The efficiency with which water is removed is crucial for desirable properties in the final product. These materials can be further exploited by imparting biofunctionality to the polymers, for example, by attaching biomolecules, such as proteins. We believe that this new material will significantly improve the ease of fabrication and the performance of biocompatible elastomers for future biomedical applications.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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