



Non-Phthalate Plasticizer/Poly (Vinyl Chloride) Compound for Sustainably Based on Biomaterials Using Glycerol from Biodiesel Process

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ABSTRACT

The phthalate replacement trend the globe began when the European Union put a ban on Dioctyl Phthalate (DOP) and other. This trend will continue as environmental and sustainability concerns increase. These polymers, made from renewable sourced (plant based) raw material, as bio based development plasticizers to gain some functionality. At the same time, the biodiesel sector produces an excess glycerol, prompting scientists to look for new uses for this material. The main goal is to create a non-phthalate plasticizer for Poly Vinyl Chloride (PVC) utilizing crude glycol from the biodiesel process, corn Starch (S), sunflower oil, Citric acid (C) and Benzoic acid (B). Glycerol diacetomonolaurate plasticizer will be developed utilizing glycerol from the biodiesel process. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared spectroscopy (FTIR) will be used to examine the plasticizer production, universal testing equipment will be used to determine the mechanical properties of the plasticizer PVC compound, Thermal Gravimetric Analysis (TGA) and the experimental values will be compared with phthalate plasticizer PVC compound. The plasticizing performances of the sample of non-phthalate contain SCB rivaled that of (DOP) phthalate, from this study suggesting that they have the potential to replace phthalate in soft PVC materials.

Keywords: Phtahalates; Plasticizers; Non-phathalete; Eco-friendly; Sustainable; Poly Vinyl Chloride (PVC)

INTRODUCTION

Plasticizers are frequently utilized as additives in the polymer industry. The major function of these compounds as phthalates to increase polymer flexibility and processability by lowering the second order transition temperature, also known as the glass transition temperature (T_g). Phthalates are a group of chemicals that can be used as an addition in plastics

to control the material's performance. Polymers are softened with them to make them more flexible and durable. Phthalates are sometimes used to aid the molding process by decreasing polymer melting points. Plasticization is essential for most polymers to be treated particularly true for Poly Vinyl Chloride (PVC). As worries about environmental contamination, toxic effect, and consequences on human health and safety get more and more significant, polymers

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and polymer additives derived from biomaterials are gaining in interest. Bio-plasticizers have also been put to the test to see if they can perform better in terms of functionality than phthalate-based plasticizers and non-toxicity during metabolism. The advantages of bio-plasticizers contribute to over standard phthalate plasticizers, when it especially true comes to flame retardants and plasticizers. Starch is both biodegradable and inexpensive, but it is also extremely hydrophilic. It has already been intensively investigated as a major raw material for environmental and medicinal applications. Native starch is partially crystalline and occurs as separate granules with 20 percent-45 percent crystallinity. Because there are many hydrogen bonds between the starch macromolecules, which limit their motion, native starch is difficult to process. Thermo Plastic Starch (TPS) is made by destroying granules in the presence of plasticizers under controlled conditions. Much research and effort has gone into the combination of plasticizers with nanoparticles before placing them into the polymer (CaCO_3 , SiO_2). While this helps to reduce migration to some level, the amount of plasticizers that remain escape constitutes a health risk. This research focuses on the fundamentals of plasticizers, stressing the drawbacks of traditional phthalates based plasticizers, as well as the necessity for environmentally friendly bio based plasticizers it also examines numerous biomass sources in order to find the finest available biomass sources. Starch is a natural renewable polysaccharide that has been considered as a possible raw material for bio plastics manufacture. However, it must undergo extensive change in order to lose its natural structure and become thermoplastic. Thermo Plastic Starch (TPS) is a remarkable material for producing non-durable products. Citric acid could be a suitable choice for expanding the variety of properties that can be accessed. In comparison to other chemicals used for derivatization, Citric Acid (CA) is considered nutritionally safe. It's a harmless body metabolic product that's previously been approved by the Food and Drug Administration (FDA) for human usage. Citric acid and starch could form an ester bond. Esterification could occur between the carboxyl groups on citric acid and the hydroxyl groups on starch. Even if there is no ester link between citric acid and starch, citric acid has been shown to establish significant hydrogen bond interactions with starch, even stronger than glycerol. The thermoplastic starch's heat and water sensitivity was then enhanced, and retro gradation was prevented. Trans-esterification is a step in the biodiesel production process that produces glycerol as a byproduct. Because it is an unprocessed raw material that must be purified for its many uses, the utilization of this glycerol is limited. Several studies have looked into the potential applications of unprocessed glycerol. Mekonnen T, et al., studies the bio-based plastics and impact on the performance of these materials such as poly (lactic acid). Howell BA, et al., used non-phthalate plasticizers derived from well-defined glycerol/adipic acid hyper branched polyesters has been produced. Adipic acid and glycerol are two low toxicity renewable biomaterial's. These materials are thermally stable, completely compatible with a PVC matrix, provide effective plasticization at acceptable levels, have a low migratory

potential. Lakeev SN, et al., provide details on new plasticizers made from terephthalic acid are being researched as a possible replacement for the hazardous dioctyl phthalate. The properties of non-phthalate plasticizers based on benzene, toluene, naphthalene, cyclohexane, and norbornene have been investigated. The utilization of plasticizers made from renewable vegetable raw materials such citrates, succinates, triglycerides, fatty acid esters. The objectives of this work is to produce glycerol as a byproduct of the biodiesel manufacturing process, and then to make plasticizers (non-phthalate plasticizers) from glycerol, citric acid, benzoic acid, sunflower oil, miscibility with polymer polyvinyl chloride at the best mixing ratio. On the other hand, we looked into how composition affects PVC plasticization. In addition to prepare films containing different plasticizer and varying amounts of plasticizer were created [1-6].

MATERIALS AND METHODS

Materials

Alpha chemical (Mumbai, India) provided citric acid (99% purity) and benzoic acid, corn starch, the acetic acid, was obtained from Merck. Dioctyl Phthalate (DOP) was obtained from Aldrich chem. The sunflower oil glycerol was obtained as a byproduct from biodiesel production. Low molecular weight poly (vinyl chloride) was purchased Alexandria based Egyptian petrochemical business.

Preparation of Glycerol from Biodiesel Process

At the same time, heat the 800 ml vegetable oil to 55°C, and then add the methanol NaOH solution to the heated oil until the methanol is immiscible with the vegetable oil, and a layer forms. This is why it's important to stir vigorously to avoid any problems forming, which would cause the reaction to fail. At 500°C, the mixture must be stirred for 30 minutes. "Liberating the fatty acid from the glycerol backbone" is the trans-esterification reaction. Stirring is stopped after 30 minutes, and the mixture is allowed to settle for at least an hour. The solution will split into two layers: The glycerol in the lower layer and the biodiesel in the upper layer.

Preparation of Plasticizer

With the addition of distilled water, the water content of corn starch was increased to 20% (wet base). Glycerol and sunflower oil were mixed first, and then corn starch was blended using the GH-100Y high speed mixer. When the citric acids and benzoic acids were melted, they were first combined with a mixture of glycerol, sunflower oil, and corn starch. The mixture was sealed and stored overnight. **Table 1** lists the many samples prepared and their components. The melt blending technique took 13 minutes in the Haake Rheomix (Thermal Electron Co., USA) at 130°C and 80 revolutions per minute [7-12].

Table 1: Samples composition proportions (Wt%).

	Starch	Glycerol	Citric acid	Benzoic acid	Sunflower oil	DOP
Sample (1) (SGCBSu)	20	20	20	20	20	
Sample (2) (SGCB)	25	25	25	25	0	
Sample (3) (SCB)	33,33	0	33,33	33,33	0	
Sample (4) (DOP)	0	0	0	0	0	100

Mixing Procedure

The following is an example of a common experimental procedure. Mixing was done with an internal mixer and a two roll mixing mill to prepare the master batch for final mixing four different plasticizers with polyvinyl chloride content were added to the mixer, as shown in **Table 1**. The compounds were then cured in a molding press (Carver, WMV50H, and USA). Plasticizer and PVC weight percent ratio (25:100). We assume the compound, combination that we made is homogeneous with the PVC because we stirred it under 160°C: PVC and NON Ph (1), PVC and NON Ph (2), PVC and NON Ph (3), PVC and Ph (DOP) (4).

Film Production

Prepare flow sheet of PVC film with different type of plasticizer (phathaleta and nonphthalte as shown in **Figure 1**.

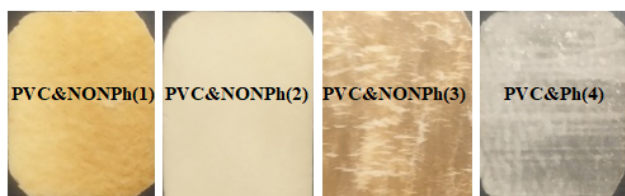


Figure 1: Flow sheet of PVC film with different type of plasticizer.

Characterization

Fourier Transforms Infrared (FTIR): FTIR spectroscopy is a potent qualitative and semi quantitative analytical method. Organic molecules absorb electromagnetic radiation with a frequency range of around 100 cm^{-1} - 4000 cm^{-1} and transform it into molecular vibration energies: Stretching and deformation (bending). The relative masses of the atoms, the shape of the atoms in the molecule, and the force constants of the bonds between atoms determine the frequency of absorption. Characterizing film is done using incident radiation FTIR (Agilent Technologies, Cary 630). The spectra are recorded in the 400 cm^{-1} - 4000 cm^{-1} wavenumber range.

X- Ray Diffraction (XRD)

To assess the degree of crystallinity in the produced disc, X-ray diffraction scans were performed at room temperature with a (X-ray 7000 Schimadzu-Japan) in the Bragge angle (2θ) range of 10°C to 80°C . The X-ray source was a Cu target with 30 KV and 30 mA settings with a scan speed of 4 degrees per minute.

Scanning Electron Microscopy

Scanning electron microscopy was used to examine the surface morphology of the sample. The samples were made as follows: The dried film was sliced and placed on a brass. The film was then sputter coated with a tiny layer of gold using a (JSM IT200, LaB6) microscope.

Thermo Gravimetric Analysis (TGA)

The samples were examined using a TGA model (Linseis STA PT 1000). This research is required in order to identify the degradation temperature. The sample was heated in a silica crucible at a constant rate of 10 k/min from 24°C to 700°C .

Mechanical Tests

Film of PVC had their tensile strength and percent elongation at break average values evaluated at room temperature using an Instron 3382 (100 KN) universal testing machine with a crosshead speed of 10 mm/min, according to ASTM D882-028.

RESULTS AND DISCUSSION

Structure Investigation

Infrared spectroscopy was used to analyse the chemical structure of plasticizer (SGCBSu) revealed a growing transmission band of the CA starch chain. The stretching vibration of 'C-O' in 'C-O-C' is attributed to the peak at 1023 cm^{-1} (**Figure 2**). The height of the peaks at 1024 cm^{-1} dropped as the (C) content increased. The reference peak was again chosen as the stretching, vibration peak of 'C-O' in the 'C-O-H' group at 1289 cm^{-1} . The drop in the 'C-O-C' caused the peak height to fall. The reason for this could be that the greater the (C) level, the more glycosidic linkages are acid hydrolyzed. The following characteristics were also noticed:

Two broad bands separated by 3255 cm^{-1} and 3048 cm^{-1} . Between 1669 cm^{-1} and 1298 cm^{-1} , there are three distinct, powerful bands: The CO peak at 1669 cm^{-1} is most likely a coalescence peak formed by the ester bond and carboxyl CO groups in citric acid, because all of the carboxyl groups are unlikely to be esterified. The peak at 1709 cm^{-1} , which is attributable to the C=O stretching, vibration in carboxyl groups, was only identified as a reference in the FTIR spectra of pure CA. The presence of ester linkages was demonstrated by the shift in the position of the CO peak in the sample (1,2,3), and the esterification reaction between starch and CA occurred during the process of melt blending.

We despite the fact that the system contains some esterified carboxyl groups, the number of esterified carboxyl groups rose as the number of ester linkages grew. As a result, the rise in peak height at 1669 cm^{-1} can also be attributed to the increase in ester bonds. When a 'C–O–H' on the starch reacted with (C) molecule to produce a 'C–O–C,' the starch received a new 'C–O–H' from the CA, and the total quantity of 'C–O' bonds in 'C–O–H' groups were regarded to be the smartest that a broad peak of C=O stretching, vibration could not occur. Heights of the other peaks were addressed. The esterification occurred during melt mixing, according to FTIR results, and the (C) % increased. Inter and intermolecular hydrogen bonds can be disrupted by the esterified citric acids that were linked to the starch chains. The free carboxyl groups connected to esterified citric acid may also help to promote starch solubility and avoid crystallization. Although there is some carboxyl groups that have not been esterified (Figure 2).

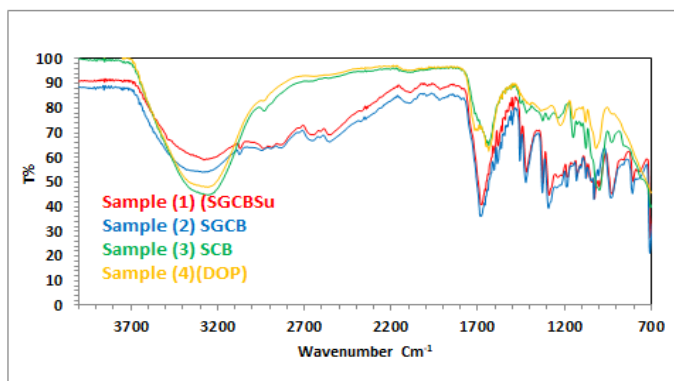


Figure 2: FTIR spectra of different plasticizer.

The FTIR spectra of PVC are shown in Figure 2. The CH group stretching is responsible for the band at 2898 cm^{-1} , while the CH aliphatic carbon stretch is responsible for the band at 1405 cm^{-1} . In addition, the absorbed water's H-C-H bending group occurred at 1266 cm^{-1} . The C-H bending peak was at $1,380\text{ cm}^{-1}$, and the C-C stretching bands were at 1066 cm^{-1} , while the bands at 710 cm^{-1} corresponded to the stretching modes of the CL-C single bond vinyl group. In addition, the FTIR spectrum of PVC and (SGCBSu) as a plasticizer (Figure 3).

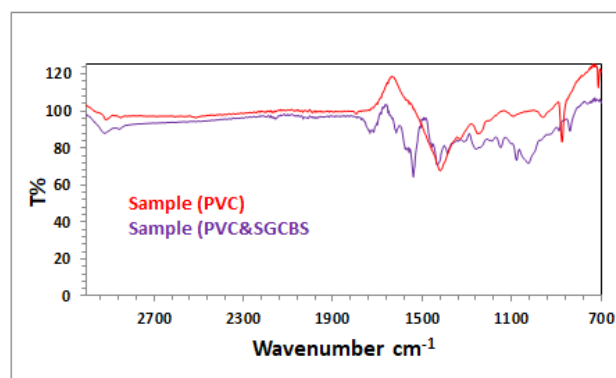


Figure 3: FTIR spectra of PVC with plasticizer (SGCBSu).

Morphological Properties of Mixture PVC and Plasticizer

The inner and exterior aggregation morphology of the PVC grains was examined using a Scanning Electron Microscope (SEM). After being axed in conductive glue, a reasonable number of sample grains were coated with a thin layer of gold using a gold sputter coater under vacuum. A scanning electron microscope was used to analyze the aggregation morphology of the PVC grains. SEM is a useful instrument for testing the compatibility of various components of polymeric materials. This method can detect the various interfaces and separation phases inside the polymeric matrix, which reflect mechanical and thermal stability as well as ionic conductivity. SEM images also reveal the shape and size of particles. According to SEM images, the non-irradiated PVC (blank) and PVC/additive mixes had clean and neat surfaces with a high degree of uniformity. SEM images of the irradiated PVC are shown in Figure 4.

The granular microstructures of PVC and SGCBS (1) may be seen in the SEM image. This could be due to the fact that it acts as a neutral scavenger *via* H-bonding and a host guest interaction controlled by the size effect and plasticizer dispersion. Figure 4 shows SEM images of the interior of a standard PVC grain and the interior of those grains formed in the presence of PVC and SGCB (2). While PVC resin, totally fused primary particle agglomerates produced by conventional suspension polymerization, PVC grains formed in the presence of PVC and SGCB (2) are made up of a large number of distinct, fine primary particles. They eventually clumped together to form primary particles on the droplet's surface and became a part of the skin. PVC and SCB showed an increase in cell population density and a reduction in the size of the miracles. Due to the addition of a vibration force field, the sample of formulation number showed a stronger orientation. Figure 4 shows how the plasticizer (DOP) affects the cell shape and density of PVC microcellular plastic. PVC and DOP and PVC and SCB morphological produced the smolset microstructure, with the lowest cell population density and homogeneous and compatible. Figure 4 shows that PVC and SGCB and PVC and SGCBSu are more the biggest cells and partial miscibility with PVC [13-18].

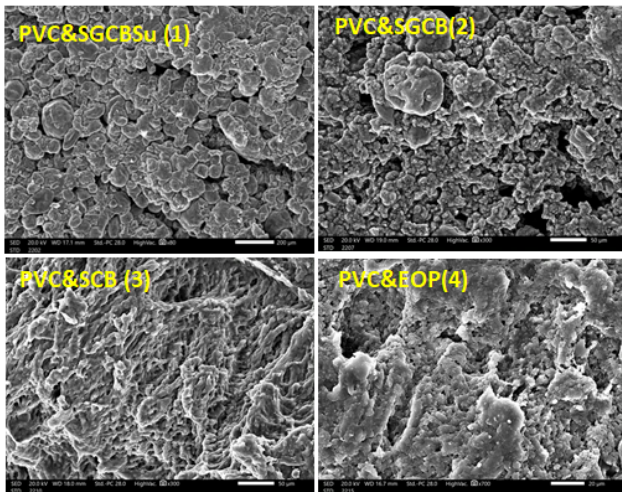


Figure 4: SEM images of surface for PVC and SGCBSu (1), PVC and SGCB (2), PVC and SCB (3), PVC and DOP (4).

X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) is a useful technique for determining the interior structural organization of solids. It can be used to distinguish between solids that are crystalline, amorphous, or semi crystalline. **Figure 5** shows the XRD pattern, which used to determine whether a crystalline phase present in the structure. The XRD curves of PVC and SGCBSu with a small amount of CA changed insignificantly as the hydrogen bonds decreased, indicating that the motional freedom of starch chains in amorphous regions increased. The internal plasticizer is the CA that has reacted with starch, while the residual CA in the mixes acts as an exterior plasticizer. Additionally, esterification can alter the groups on starch chains. On the starch molecules, additional groups (carboxyl and ester groups) were created, which can provide potential reactive locations for cross linking modification. The role of the mixture PVC and SGCBS can be studied using full range analysis of the filled samples, which exhibits a diffraction peak at roughly $2\theta=18^\circ$. The homogeneous distribution of the polymeric matrix is revealed by examining the XRD diffraction patterns of PVC films containing various types of plasticizer while PVC has an amorphous phase in general. At the location depicted in Figure 5 (1-4) ascribed to CA, benzoic acid, many peaks with lower intensities emerge. It was also discovered that the amorphous halos around $2\theta=26^\circ$ are less intense in the filled PVC films than in the pristine PVC films, indicating that the addition of plasticizer reduces the crystalline phase in PVC filled samples, in agreement with Rajendran, et al., and pointing to the formation of multiple phases in the new material composed of combined semi crystalline and amorphous phases. The XRD pattern of a polymeric for all samples shows the formation of a sharp band at about 38° and the persistence of distinctive amorphous halos around 18° and 25° .

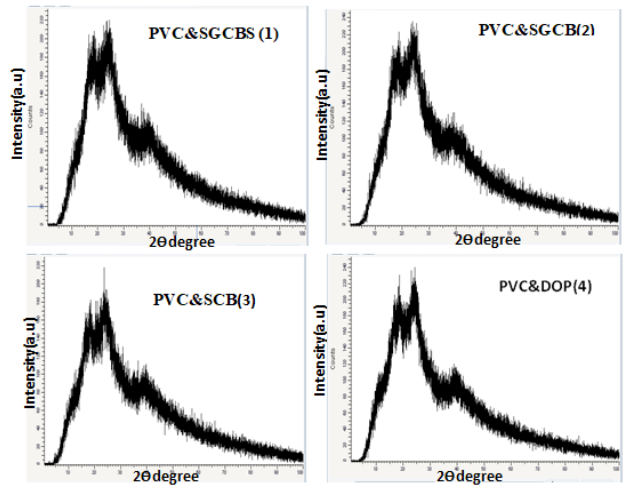


Figure 5: X-Ray diffraction scans of PVC and different plasticizer.

Mechanical Properties

The influence of several types of plasticizer on PVC sheet was investigated using the mechanical properties of the manufactured flow sheet. The mechanical testing system was used to determine the tensile strength. **Figure 6** shows stress vs strain curves for (PVC and SGCBS (1), PVC and SGCB (2), PVC and SCB (3), and PVC and DOP (4), respectively, indicating that mechanical strength increases in the order specified. The effective load transfer from PVC and SGCBSu (1) to the PVC and DOP (4) under tensile stress is responsible for the rise in modulus, tensile strength, and elongation. The following obtained data and their assignment can be summarized in **Table 2**.

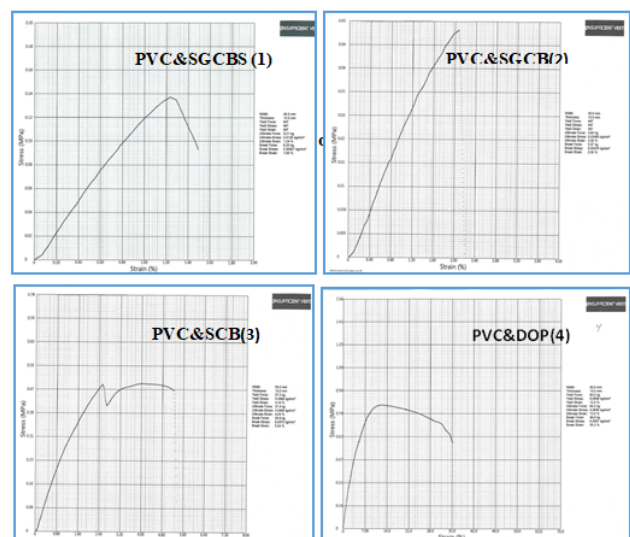


Figure 6: Stress versus strain curves of PVC and plasticizer DOP.

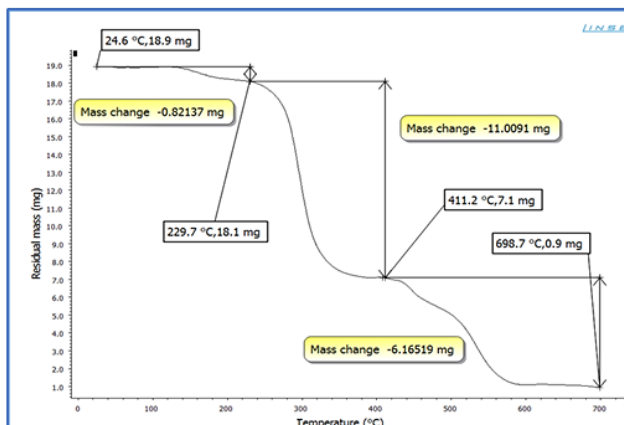
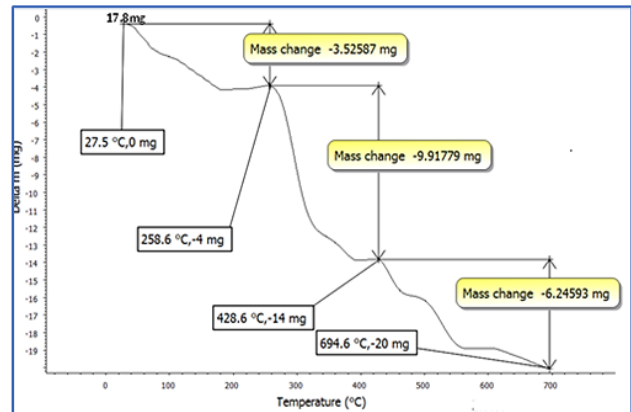
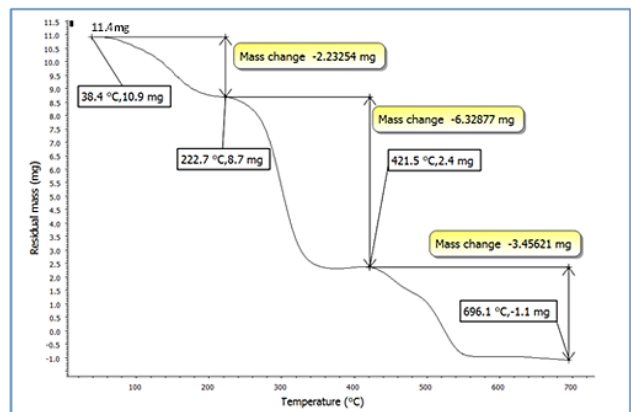
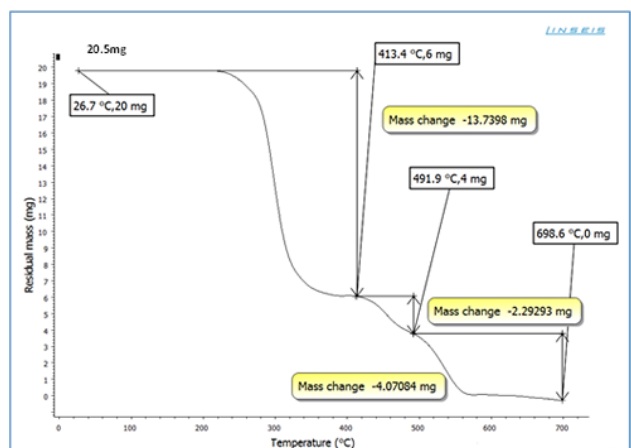
Table 2: Mechanical properties data for samples.

No	Width (mm)	Thickness (mm)	Ultimate force (Kg)	Ultimate stress (Kg/mm ²)	Ultimate strain (%)	Break force (Kg)	Break stress (Kg/mm ²)	Break strain (%)
1	45	15	9.21	0.0136	1.24	6.25	0.00927	1.5
2	50	15	3.6	0.0048	2.08	3.57	0.00476	2.08
3	50	15	37.4	0.0498	4.64	35.5	0.0475	5.24
4	50	15	64.2	0.0856	12	44.8	0.0597	35.3

Thermo-Gravimetry Analysis

The TGA curves of plasticized PVC by several plasticizer blends are shown in **Figures 7-10**. For all formulas, the curves are similar in shape, and each one shows three unique stages.

The 0.82137 mg weight percent loss (T), which is the initial weight loss temperature, the maximum degradation temperature (T_1 max and T_2 max) (229.7°C), which is the highest thermal degradation rate, temperature obtained from the peak of weight loss, the maximum speed of degradation (S_1 max and S_2 max), and the 4.6 percent weight loss residue were chosen as the characteristically thermal parameters. At around 229°C, a significant amount of HCl was eliminated. It could be due to the first stage of heat deterioration. As the process of heat degradation of polymers involves cyclization and breaking of chains, the 58.55 weight percent loss residue is attributed to crosslinking of chains containing C=C bonds. The results reveal that at a greater temperature, the PVC mixed with SGCBS begins to lose weight than the PVC step at temperatures above 411°C the third stage of deterioration begins by intermolecular cyclization of the conjugated sequences during this stage, thermal breakdown of the plan sequences yields volatile aromatic and aliphatic chemicals, leaving a 32.7 weight percent loss residue. The results of initial weight loss temperature to maximum degradation temperature (T_1 max and T_3 max) for all samples for (**Figures 7-10**) of PVC mixed with plasticizers SGCBSu, SGCB, SCB and DOP as the following 62.59%, 76.4%, 75% and 67% respectively [19-21].

**Figure 7:** TGA curves for PVC with plasticizer SGCBSu.**Figure 8:** TGA curves for PVC with plasticizer SGCB.**Figure 9:** TGA curves for PVC with plasticizer SCB.**Figure 10:** TGA curves for PVC with plasticizer DOP.

CONCLUSION

In this work were successfully prepared glycerol for the biodiesel production process as byproduct and preparation of plasticizers (non-phthalate plasticizer) from prepared glycerol, citric acid, benzoic acid, sun lower oil, miscibility with polymer polyvinyl chloride achieving the best mixing ratio. On the other hand, we studied the influence of composition on the plasticization of PVC. Consequently, various PVC films containing different plasticizer and different amounts of plasticizer were produced by the different type technique. The morphology of prepared plasticizers (non-phthalate plasticizer) and structure were confirmed by SEM, X-Ray diffraction patterns. The morphology, properties of PVC and SCB film were enhanced than the other samples, which improved the compatibility due to the presence of the carboxylic groups, ester group in the CA and basic acid. In addition the mechanical (elongation, modulus of the film), thermal stability properties of PVC and SCB showed very good behavior than the samples. Therefore, the SCB (non-phthalate plasticizer) are thought to be useful for PVC polymer. In the present work, two parameters characterize the efficiency of a plasticizer were controlled by varying amounts of a plasticizer and adding polymers of different compositions as plasticizer.

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HUMAN AND ANIMAL PARTICIPANTS

This article does not contain any studies involving animals' studies or human participants performed by any of the authors.

DATA AVAILABILITY STATEMENT

All data will be available at reasonable request from corresponding author.

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