Degree Project in Fibre and Polymer Technology

Second Cycle, 30 credits

Upcycling of Poly(ethylene terephthalate) to UV-Curable Resins

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Abstract

This research aimed at a sustainable strategy to upcycle PET poly(ethylene terephthalate) and waste into UV-curable, reprocessable thermosets through glycolysis, methacrylation and dynamic covalent chemistry. PET was depolymerised with ethylene glycol at 180 °C to yield bis(2-hydroxyethyl) terephthalate (BHET), and PBT was depolymerised with butane-1,4-diol at 240 °C to produce bis(2-hydroxybutyl) terephthalate (BHBT). Both intermediates were methacrylated with methacrylic anhydride to give MA-BHET and MA-BHBT. In parallel, Methacrylated VanillinJEFM (MA-VAJ) was prepared to introduce dynamic imine bonds. Blending MA-BHET and MA-BHBT with MA-VAJ in a 1:1 ratio and curing under UV light produced the final thermosets, denoted as MA-BHET and MA-VAJ and MA-BHBT and MA-VAJ. The presence of exchangeable imine linkages endowed the networks with reprocessability.

Comprehensive characterisation validated the synthetic route and highlighted differences between the two systems. FTIR and ^{1}H NMR confirmed successful glycolysis, methacrylation and Schiff-base formation. Thermogravimetric analysis (TGA) showed that all materials were stable up to ~250–300 °C, with MA-BHET and MA-VAJ displaying slightly higher thermal stability than MA-BHBT and MA-VAJ due to the more rigid ethylene spacer. Differential scanning calorimetry (DSC) revealed no melting peaks, consistent with amorphous networks, and glass-transition temperatures of ~99–113 °C for MA-BHET and MA-VAJ and ~76–78 °C for MA-BHBT and MA-VAJ, again reflecting the effect of the more flexible butylene spacer. Hot-press experiments demonstrated that both networks could be reprocessed, producing films that remained uniform after multiple cycles. Tensile testing showed that MA-BHBT and MA-VAJ was more ductile, with tensile strengths of 1.7–1.9 MPa and elongations of 8–12%, whereas MA-BHET and MA-VAJ was too brittle for reliable testing. Solvent-resistance experiments further distinguished the two systems: MA-BHET and MA-VAJ exhibited superior chemical stability with minimal weight loss across all solvents tested, while MA-BHBT and MA-VAJ lost more mass—particularly in dichloromethane and alkaline media—due to its more flexible but less densely crosslinked network.

Overall, this study demonstrates that PET and PBT waste can be transformed into high-performance, reprocessable thermosets by combining methacrylated polyester-derived monomers with a bio-based Methacrylated VanillinJEFM (MA-VAJ) resin. The approach balances thermal and solvent resistance (MA-BHET and MA-VAJ) against ductility and flexibility (MA-BHBT and MA-VAJ), offering a pathway to recyclable thermosets that advance circular-economy strategies in polymer design.

Sammanfattning

Denna studie presenterar en hållbar strategi för att uppgradera PET polyetylentereftalat och polybutylentereftalat flaskor och textilier till UV-härdande mekaniskt återbearbetsningsbara härdplaster genom glykolys, metakrylering och dynamisk kovalent kemi. PET depolymeriserades med etylenglykol vid 180 °C för att erhålla bis-2-hydroxietyltereftalat (BHET) och PBT depolymeriserades med butan-1,4-diol vid 240 °C för att producera bis-2-hydroxibutyltereftalat (BHBT). Båda intermediaterna metakrylerades med metakrylsyraanhydrid för att ge MA-BHET respektive MA-BHBT. Parallellt framställdes metakrylerat vanillinJEFM (MA-VAJ) för att införa dynamiska iminbindningar. Genom att blanda MA-BHET och MA-BHBT med MA-VAJ i ett 1:1-förhållande och UV-härda blandningarna framställdes de slutliga härdplasterna, benämnda MA-BHET and MA-VAJ och MA-BHBT and MA-VAJ. Närvaron av reversibla iminbindningar möjliggjorde mekanisk återvinning

Omfattande karakterisering bekräftade den syntetiska processen och belyste skillnader mellan de två systemen. FTIR och ^{1}H-NMR bekräftade lyckad glykolys, metakrylering och bildning av Schiff-baser. Termogravimetrisk analys (TGA) visade att alla material var stabila upp till cirka 250–300 °C, där MA-BHET and MA-VAJ uppvisade något högre termisk stabilitet än MA-BHBT and MA-VAJ på grund av den styvare etylengruppen. Differentiell svepkalorimetri (DSC) visade inga smältpunkter, vilket överensstämmer med amorfa nätverk, och glasomvandlingstemperaturer på cirka 99–113 °C för MA-BHET and MA-VAJ och cirka 76–78 °C för MA-BHBT and MA-VAJ, vilket återspeglar effekten av den mer flexibla butylengruppen. Varmpressförsök visade att båda härdplaster kunde återbearbetas och de bildade filmer som förblev enhetliga efter flera cykler. Dragprovning visade att MA-BHBT and MA-VAJ var mer duktilt, med draghållfasthet på 1,7–1,9 MPa och brottöjning på 8–12%, medan MA-BHET and MA-VAJ var för sprött för att testas på ett tillförlitligt sätt. Lösningsmedelsbeständighetstester skiljde ytterligare de två systemen: MA-BHET and MA-VAJ uppvisade överlägsen kemisk stabilitet med minimal viktförlust i alla testade lösningsmedel, medan MA-BHBT and MA-VAJ förlorade mer massa – särskilt i diklormetan och alkaliska medier – på grund av sitt mer flexibla men mindre tätt tvärbunden struktur.

Sammanfattningsvis visar denna studie att PET och PBT kan omvandlas till högpresterande, ombearbetningsbara härdplaster genom att kombinera metakrylerade polyesterhärledda monomerer med ett biobaserat Metakrylerat VanillinJEFM (MA-VAJ)-harts. Metoden balanserar termisk och kemisk resistens (MA-BHET and MA-VAJ) mot duktilitet och flexibilitet (MA-BHBT and MA-VAJ) och erbjuder en väg till återvinningsbara härdplaster som främjar cirkulära ekonomistrategier inom polymerdesign.

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Contents

1. Introduction

1.1 Background

Plastic pollution is considered to be one of the most urgent environmental issues that we have nowadays. One major contributor is poly(ethylene terephthalate) (PET). PET is a thermoplastic polyester which has many advantages such as durability, clarity and ease of processing. These advantages of PET are considered of high value to be used in bottles, textiles and packaging materials (Al-Sabagh et al., 2016). Nevertheless, these same benefits are the reason that PET is an issue in our environment that creates a significant challenge when it comes to waste management.

One of the ways that is used to manage the waste that comes from plastic is mechanical recycling. It is considered to be quite useful, but at the same time it has its own limitations. For instance, utilizing mechanical recycling on PET would result in lowering the quality of PET when repeated several times (Schyns and Shaver, 2021). On the other hand, chemical recycling methods such as hydrolysis, methanolysis, and glycolysis mainly recover monomers that are repolymerized into PET (Al-Sabagh et al., 2016). To maintain a closed loop recycling strategy, chemical recycling is considered to be the most effective.

The focus of this research is to incorporate chemical recycling and introduce a higher value resin through the upcycling process. Post-consumer PET waste is used as feedstock for research which supports the principle of circular economy (Joseph, 2024). The PET (plastic pellets) will be converted into a UV-curable resin that will be used to synthesize higher value resin to divert it from landfills. These UV-curable materials can be used for coatings, adhesive, inks and 3D printing applications.

Due to their rapid curing, UV-curable resins have had a lot of interest. Due to their ability to cure rapidly under UV light at room temperature and without high thermal energy input, UV-curable resins have attracted significant interest (Guo et al., 2022). In recent studies, acrylate or urethane-acrylate structures were obtained from PET suitable for UV-curable applications (Liu et al., 2023) using a solvent free glycolysis, showed that PET can be broken down with cardanol diol, and products were then utilized further into polyurethane acrylates that cured well. Similarly, Pastore et al. (2023) made terephthalamide diol monomers from PET, which was later used in UV-curable formulations that showed good mechanical strength.

1.2 Problem Statement

Despite advances in converting PET into UV-curable resins, several challenges remain. The depolymerization process still requires optimization to improve efficiency and reduce side reactions. Furthermore, the synthesis of UV-curable resins from PET waste has yet to fully address resin formulation, performance consistency, and long-term stability. Therefore, there is a need for more efficient upcycling pathways that can reliably transform PET waste into high-value resins suitable for industrial applications.

1.3 Objectives

This thesis focuses on the development and evaluation of a method used for the upcycling of PET waste into UV-curable resin. This will be achieved by depolymerizing PET pellets through chemical recycling which is glycolysis to obtain bis(2-hydroxyethyl) terephthalate (BHET), which will be methacrylated to produce a resin that can be UV cured. The study further investigates the curing behavior and mechanical properties of the resulting resins,

1.4 Scope and Limitations

This study is limited to the upcycling of PET waste through glycolysis and methacrylation, followed by the preparation and UV curing of methacrylated BHET-based resins. The focus is on evaluating the curing performance, thermal stability, and mechanical properties of the resulting resins. Other recycling methods (e.g., hydrolysis, methanolysis) and large-scale industrial feasibility are outside the scope of this work. The study emphasizes laboratory-scale synthesis and characterization to provide a foundation for future research in PET upcycling.

2. Literature Review

2.1 PET and Its Environmental Impact

Since the demand of PET has been coming a lot from the packaging industries, especially beverage bottles, it has led PET to be one of the most widely produced and consumed plastics globally (Tamburini, 2025). Looking at the market globally, more than 500 billion plastic bottles are used annually to package products in the beverage industry (Defend Our Health, 2022). This huge amount of PET production has caused a large contribution to the global plastic waste crisis.

Since PET has a high resistance to microbial degradation with its chemical stability, the main environmental concern is that PET is persistent in the environment. This leads landfills to be accumulated with PET, with degradation taking hundreds of years (Webb et al., 2013). Mismanaging PET waste causes pollution, especially as plastic bottles would cause the waste to go into rivers and oceans, which contributes to marine pollution. The plastic in I this case would decompose into microplastics that will pose risks to aquatic organisms through ingestion and potential bioaccumulation (Jambeck et al., 2015; Sharma and Chatterjee, 2017).

To produce PET, it relies mostly on petrochemical feedstocks, specifically ethylene glycol and p-xylene, highlighting its dependence on non-renewable fossil resources (Jiménez and Toledo, 2015). A life cycle assessment (LCA) has been undertaken in Bangladesh that estimated the carbon footprint of a 500ml PET water bottle to be approximately 0.25 kg CO_2-equivalent (LCA of PET Bottles, Bangladesh, 2024). This can be reduced by recycling, but globally, the rates of recycling remain low. Only small amount of plastic bottles are collected for recycling, with a significant amount of plastic bottles ending up in landfills or the environment (U.S. EPA, 2018).

Furthermore, the additives that are used in plastic bottles can cause toxicological concerns when leaching. It has been reported that trace leaching of antimony, which is utilized as a catalyst in PET production, from bottles into bottled water under prolonged storage or high temperature conditions (Allafi, 2020). This contributes to a long-term health impact, not to mention the ecological risks it adds of additive migration when bottles enter waste streams.

PET is a recyclable material, but unfortunately, the current recycling processes face limitations. As mentioned, mechanical recycling will cause loss of PET quality, which is referred to as downcycling due to thermal degradation of the polymer chains. On the other hand, chemical recycling is energy-intensive and is still under investigation for industrial use (Al-Sabagh et al., 2016). Meanwhile, large amounts of PET bottles keep contributing to global waste burdens.

To conclude, PET bottles are very useful in daily life, providing consumer convenience, but their environmental footprint, resource use, carbon emissions, and waste persistence make them a critical focus for sustainable waste management strategies and circular economy initiatives.

2.2 Chemical Recycling of PET

Chemical recycling is a technique that is getting more interest because it can provide new virgin quality PET. It can be done through different solvolytic reactions, such as hydrolysis, methanolysis, glycolysis, and aminolysis, all of which break down PET into its monomers or oligomers, such as terephthalic acid (TPA), dimethyl terephthalate (DMT), and bis(2-hydroxyethyl) terephthalate (BHET) (Al-Sabagh et al., 2016; Ghosal et al., 2022). Within these different techniques, glycolysis is the most studied and the most relevant to the industry. In this technique, PET is reacted with glycols, commonly ethylene glycol, at a temperature between 180–240 °C to obtain BHET and lower oligomers, with the process being influenced by the catalyst used, temperature, and the ratio between PET and glycol (Xin et al., 2021; Amundarain et al., 2024).

The catalyst that was found to be most effective for glycolysis is zinc acetate, which helps in transesterification reaction. Other catalysts that have been used in research include sodium methoxide and carbonate bases that have been found to promote sustainability and avoid heavy metal residues (Javed et al., 2023). Additionally, organocatalysis for glycolysis, mainly organobases such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), which can help with glycolysis under milder conditions has been studied. Heterogenized organocatalysts improve catalyst recovery and recyclability (Fukushima et al., 2011; Fehér et al., 2022).

The integration of ionic liquids (ILs) and deep eutectic solvents (DESs) has shown promise in enhancing glycolysis efficiency and selectivity. These solvents can be used as the reaction media and as a catalyst. This enables a faster depolymerization and potentially a higher BHET yield. For example, it was reported by Li et al. (2024) that PET-derived polyurethane elastomers was obtained through glycolysis using DESs. Also, Ha et al. (2024) showed microwave-assisted DES glycolysis to be effective in achieving a rapid and high yield

depolymerization. Attallah et al. (2021) similarly showed that dual-function DESs can deliver high monomer recovery under relatively mild conditions.

Regardless of these findings, large-scale applications remain limited due to feedstock heterogeneity, energy demand, and other challenges such as purification. However, glycolysis has shown great potential for the chemical recycling of PET into industrial practices when integrated with more environmentally friendly catalysts and more energy-efficient technologies (Al-Sabagh et al., 2016; Ghosal et al., 2022).

2.3 Glycolysis of PET

As has been mentioned in section 2.2, glycolysis is the most interesting chemical recycling technique that can be used in large scale applications. Glycolysis from post-consumer plastic bottles is one of the most studied chemical recycling routes that helps in obtaining the monomer bis(2-hydroxyethyl) terephthalate (BHET) which can be utilized in polymer production. This process involves reacting the PET plastic bottles with excess ethylene glycol (EG) in the presence of zinc acetate as a catalyst at temperatures around 180 °C. Under these conditions, high conversion and selectivity toward BHET are typically achieved (Mohammadi, 2023).

It has been demonstrated by Mohammadi (2023) that zinc acetate can effectively promote the depolymerization of PET with ethylene glycol at approximately 180 °C, producing BHET with high yield and purity. This has also been proven in another study by Al-Sabagh et al., (2014), showing that zinc acetate outperforms other metal acetate catalysts such as manganese, cobalt, or lead acetates, providing higher BHET yields and cleaner product recovery.

2.4 UV Curable Resins: Applications and Benefits

To formulate a UV curable resin, methacrylates are considered to be among the most important monomers for these kinds of systems mainly due to their high reactivity under rapid radical photopolymerization and their suitability for additive manufacturing applications (Ligon et al., 2017). These are intermediates that are further utilized in the crosslinking when exposed to UV in the presence of photoinitiator. This crosslinked structure is a thermoset network that has the desired properties of mechanical and chemical resistance.

One of the advantages of UV-curing of methacrylated resins as mentioned is the fast polymerization at ambient temperature, with minimal volatile organic compound (VOC) emissions. Coatings are one product that is produced from UV curing with solvent free processing that has good durability, hardness and chemical resistance (Huang et al., 2020). To compare both UV and thermal curing, UV has shown much less energy than thermal curing which makes it highly attractive for sustainable material design (Golden, 2012).

There are many applications for methacrylated UV-curable resins such as the formulations that are based on urethane acrylate oligomers. These materials have demonstrated excellent abrasion resistance, strong substrate adhesion, and durability. This high performance of the resins adds to its value (Hu et al., 2022). For 3D printing applications, methacrylated resins

are commonly used in stereolithography (SLA) and digital light processing (DLP) due to their tunable viscosity, fast curing, and the ability to create high-resolution structures (Ligon et al., 2017; Bagheri and Jin, 2019). In other applications such as biomedical applications, methacrylated polymers derived from renewable sources have also been explored for UV-cured hydrogels. For example, high gel content and strong swelling performance can be produced from bio-based methacrylated BPHUs that have favorable biocompatibility, benefiting from controllable crosslinking (Hennig et al., 2025).

Circular economy can be promoted by polymer upcycling utilizing recycled PET monomers. This can be achieved by reacting BHET with methacrylates to produce methacrylated BHET that can be further used to produce UV-curable materials effectively merging chemical recycling with the performance benefits of methacrylated resins (Pastore et al., 2023).

2.5 Previous Work in PET Upcycling

Upcycling involves the traditional recycling of PET into higher value-added materials instead of just re-producing the same material or a lower quality material. PET can be used as a precursor to produce advanced resins, coatings, vitrimers and specialty polymers that have much greater performance and commercial value (Ghosal et al., 2022; Hou et al., 2021; Carniel et al., 2024).

Glycolysis the most common chemical recycling techniques that is used to upcycle PET where PET is broken down into bis(2-hydroxyethyl) terephthalate (BHET) at about 180–240 °C and ethylene glycol. Then, as mentioned previously the BHET is used as the raw material for another reaction with methacrylic anhydride to produce the needed resin that can be cured under UV light. In a study done by Karayannidis et al. (2006), PET waste was glycolyzed and methacrylated to dimethylacrylated oligomers which where cured and polymerised. This confirms that PET can be used in the case of UV curing. Bio-based cardanol diol was used to depolymerize PET and then prepared UV-curable polyurethane acrylates (PUAs) (Liu et al., 2023). In another scenario, terephthalamide diol monomers was produced from PET and used in UV-curable PUAs (Pastore et al., 2023). Microwave-assisted glycolysis of PET has also been reported as an efficient route to obtain oligoesters, which were subsequently used to produce flexible polyurethane and polyisocyanurate foams (de Dios Caputto et al., 2022).

PET can be also upcycled into vitrimes which are dynamic crosslinked polymers that can be reprocessed, reheated and reshaped. This feature combines the durability of thermosets (Hou et al., 2021). Broader reviews show that PET upcycling can also produce epoxy resins, alkyds, coatings, and other high-value chemicals, making it an attractive pathway in the transition toward a circular economy (Ghosal et al., 2022).

There are still challenges to overcome such as separating catalysts, purifying BHET and handling mixed waste. The upcycling route is seen to be practical and valuable compared to conventional recycling because it reduces waste and creates new materials that have strong performance and higher economic value.

3. Materials and Methods

3.1 Materials

Polyethylene terephthalate (PET) pellets, ethylene glycol (EG, ≥99%), zinc acetate ($Zn(OAc)_2$, ≥98%), methacrylic anhydride (MAA, ≥94%), 4-dimethylaminopyridine (DMAP, ≥99%), dichloromethane (DCM, ≥99.8%), chloroform ($CHCl_3$, ≥99.8%), vanillin (VL, 99%), JEFamine® (polyetheramine, molecular weight ~400 $g \cdot mol^{-1}$), ethanol (EtOH, ≥99.5%), and bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (BAPO, ≥97%) were used in this study. All reagents were used as received without further purification.

3.2 Glycolysis of PET Pellets

Polyethylene terephthalate (PET) pellets were employed as the feedstock for the glycolysis reaction. Ethylene glycol (EG, ≥99%) served as the depolymerizing agent, while zinc acetate ($Zn(OAc)_2$, ≥98%) was utilized as the catalyst to promote the transesterification process. The reaction was carried out under controlled temperature and stirring conditions to obtain bis(2-hydroxyethyl) terephthalate (BHET) as the primary product. The resulting glycolyzed product was purified and subsequently dried prior to use in the methacrylation step.

3.3 Methacrylation of BHET

The methacrylation of BHET, obtained from the PET glycolysis step, was performed using methacrylic anhydride (MAA, ≥94%) as the functionalizing reagent. 4-Dimethylaminopyridine (DMAP, ≥99%) acted as the catalyst, and dichloromethane (DCM, ≥99.8%) was used as the reaction solvent. The reaction mixture was maintained under inert atmosphere and continuous stirring to facilitate esterification of hydroxyl groups with methacrylate functionality. The obtained methacrylated BHET (MA-BHET) was washed and purified to remove residual catalyst and unreacted reagents.

3.4 Methacrylation of BHBT

For the methacrylation of bis(4-hydroxybutyl) terephthalate (BHBT), derived from the glycolysis of polyester fabric, a similar procedure was followed. DMAP (≥99%) was employed as the catalyst and DCM (≥99.8%) as the solvent. The reaction was conducted under the same molar ratio conditions as for MA-BHET to ensure consistent degree of methacrylation. The final methacrylated BHBT (MA-BHBT) product was purified and dried under vacuum prior to characterization.

3.5 Methacrylation of Vanillin

Vanillin (VL, 99%) was used as the starting material for methacrylation. The reaction was carried out in the presence of methacrylic anhydride (MAA, ≥94%) as the functionalizing agent, with DMAP (≥99%) serving as the catalyst. Chloroform ($CHCl_3$, ≥99.8%) was used as the solvent. The reaction proceeded under mild conditions with continuous stirring to yield methacrylated vanillin (MA-VA). The resulting product was washed with distilled water and dried to remove residual reactants and by-products.

3.6 Formation of Schiff Base

The Schiff base reaction was performed using methacrylated vanillin (MA-VA) and JEFamine® (polyetheramine, molecular weight ~400 $g \cdot mol^{-1}$) as the amine source. Ethanol (EtOH, ≥99%) was used as the solvent. The reaction mixture was stirred at room temperature, allowing the aldehyde groups of methacrylated vanillin to condense with the primary amine groups of JEFamine, forming imine (C=N) linkages. The obtained product, methacrylated vanillin imine (MA-VAJ), was isolated and dried prior to UV-curing experiments.

3.7 UV Curing of Resin Formulations

For the UV-curing experiments, resin formulations were prepared by combining methacrylated BHET (MA-BHET), methacrylated BHBT (MA-BHBT), and the Schiff base (MA-VAJ) in predetermined ratios. The photoinitiator bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (BAPO, ≥97%) was added to the formulations at a concentration of 1 wt% relative to the total resin weight. The mixtures were homogenized and cast into molds, followed by UV irradiation to initiate polymerization and crosslinking, forming the corresponding cured thermoset networks.

4. Experimental

4.1 Glycolysis of PET

To first evaluate whether the glycolysis reaction would work effectively, a small-scale test was carried out. In this trial, 5 grams of pure PET pellets were used. Zinc acetate was added as a catalyst at 0.5% of the PET weight, and ethylene glycol was added in a 1:5 ratio with respect to the PET, which corresponded to 25 mL.

All components were combined in a 250 mL round-bottom flask. The flask was placed in a heating block situated on a magnetic stirring hot plate. To maintain consistent conditions, a reflux condenser was attached to the setup, and the reaction was conducted under a nitrogen atmosphere. This was done to prevent the evaporation of ethylene glycol, especially since the temperature was kept at 180 °C.

The reaction mixture was left overnight to ensure that the PET pellets fully reacted and were depolymerized. After the overnight reaction, the resulting mixture was clear, indicating that all the PET pellets had dissolved and the reaction had reached completion (Figure 1).

Figure 1: Clear mixture after overnight glycolysis reaction

4.2 Purification and Isolation of BHET

For the purification of BHET, deionized water was used to wash away residual ethylene glycol and any remaining impurities. Initially, a small amount of the reaction product was slowly added to deionized water under stirring. Small crystals began to form, indicating the successful precipitation of BHET (Figure 2). After washing the crystals with deionized water, the mixture was filtered under vacuum, and the BHET crystals were collected (Figure 3).

The BHET crystals were further dried using tissue paper to remove excess surface water, then transferred to a beaker and placed in a vacuum oven overnight to ensure complete removal of any remaining moisture. The identity and purity of the obtained BHET crystals were confirmed using Nuclear Magnetic Resonance (NMR) spectroscopy.

After confirming that the glycolysis reaction was successful using 5 g of PET pellets, the procedure was scaled up to 40 g of PET to obtain a larger quantity of BHET for further processing.

Figure 2: Crystals forming in the deionized water indicating the precipitation of BHET crystals.

Figure 3: BHET Crystals after filtering under vacuum and dried with tissues.

It was observed that if the clear mixture obtained after the glycolysis reaction was left to cool for an extended period, it would eventually solidify, as shown in Figures 4, 5 and 6 below.

Figure 4: Directly after Glycolysis reaction.

Figure 5:BHET starts to crystallize during cooling.

Figure 6: Fully crystallized BHET after complete cooling.

4.3 Glycolysis of Coca-Cola PET and Purification of Coca-Cola BHET

Following the successful glycolysis of pure PET pellets, PET derived from Coca-Cola bottles was used as a feedstock to investigate the recycling potential through depolymerization. In this experiment, 40 g of PET (Figure 7) was reacted with 120 mL of ethylene glycol (PET:EG molar ratio of 1:3) in the presence of 0.2 g zinc acetate catalyst at 180 °C (Figure 8), and the reaction was allowed to proceed overnight. After completion, all PET fragments were fully dissolved (Figure 9), and bis(2-hydroxyethyl) terephthalate (BHET) was successfully recovered, yielding 30 g of product with a calculated yield of 56.69% (Figure 10).

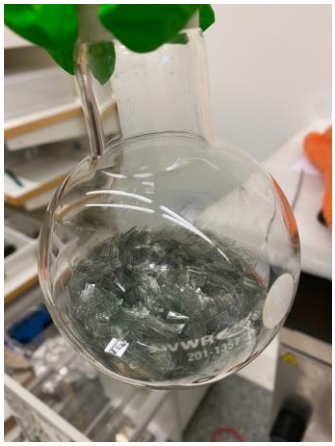

Figure 7: Coca-Cola PET used for glycolysis.

Figure 8: PET mixed with ethylene glycol before reaction starts.

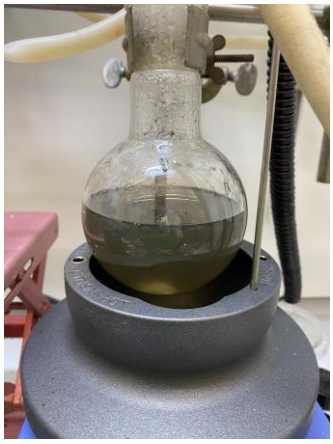

Figure 9: Mixture after glycolysis reaction.

Figure 10: BHET obtained after purification.

The images above depict the glycolysis process of Coca-Cola PET bottles. Initially, PET was manually cut into small pieces to facilitate dissolution in ethylene glycol. Upon heating the mixture overnight at 180°C, the PET fully depolymerized into a clear solution. After purification with water, BHET was recovered in solid form and subsequently dried to yield the final product. This confirms the feasibility of using post-consumer PET bottles as a viable source for BHET production via glycolysis.

4.4 Synthesis of UV curable resin

4.4.1 Methacrylation of Pure BHET (PET Pellets)

Following the complete drying of the BHET crystals, a methacrylation reaction was carried out to produce methacrylated BHET. Methacrylic anhydride was used in a 1:2 molar ratio with respect to BHET, accounting for the two hydroxyl groups available on each BHET molecule that can undergo esterification. Dimethylaminopyridine (DMAP) was employed as a catalyst at 2 wt% relative to methacrylic anhydride, while dichloromethane (DCM) was used as the solvent. The reaction was performed under a nitrogen atmosphere to prevent interference from moisture or oxygen, using a reflux setup at 60 °C with continuous stirring for 24 hours. Initially, 1 gram of BHET was used to validate the reaction before scaling up. After the reaction, the mixture appeared as a clear solution and was allowed to cool to room temperature, after which additional DCM was added to increase the volume and minimize product loss during purification. The crude product was purified through sequential washing steps to remove unreacted methacrylic anhydride and acidic by-products. The mixture was first washed three times with saturated sodium bicarbonate solution, followed by two washes with 0.5 M sodium hydroxide and two washes with 1.0 M sodium hydroxide to ensure the removal of residual acidic or anhydride species. A final wash with deionized water was performed to eliminate salts and remaining bases. The organic layer was then dried with anhydrous sodium sulfate, which was later removed by filtration. The solvent DCM was evaporated using a rotary evaporator under reduced pressure, and the viscous product obtained was further dried overnight in a vacuum oven to ensure complete removal of residual solvent (Figure 11). The final product was left under ambient conditions to solidify, yielding methacrylated BHET.

The solid methacrylated BHET was then characterized using Nuclear Magnetic Resonance (NMR) spectroscopy to confirm successful functionalization.

Figure 11: Obtained Methacrylated BHET after purification.

After confirming the success of the reaction on a small scale, the procedure was scaled up, first using 10 g of BHET then 15 g of BHET and later extended to 30 g to produce a larger quantity of methacrylated BHET.

4.4.2 Methacrylation of Coca-Cola BHET

After successfully Methacrylation pure BHET, the same reaction and purification procedures were applied to BHET obtained from Coca-Cola PET. The reaction proceeded successfully, and the formation of methacrylated BHET was confirmed using NMR spectroscopy. Figure 12 shows the reacted BHET with methacrylic anhydride before purification and Figure 13 shows the material after it has been purified and dried.

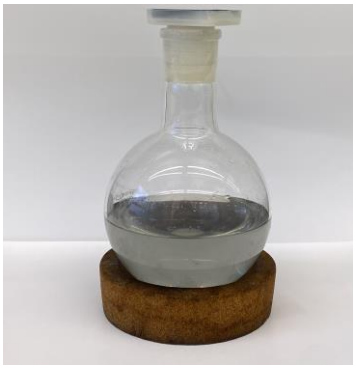

Figure 12: Methacrylated Coca-Cola BHET before purification.

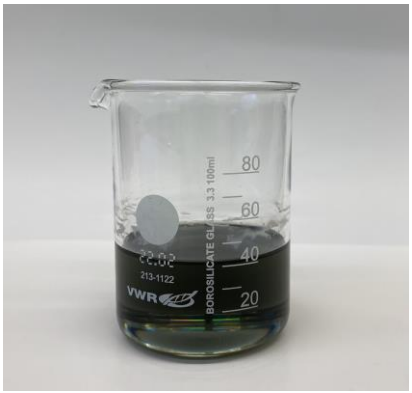

Figure 13: Methacrylated Coca-Cola BHET after purification.

4.4.3 Methacrylation of Fabrics

In a parallel experiment, polyester fabric was also used as a feedstock for the depolymerization reaction by my colleague Hedvig (Figure 14). Through glycolysis with 1,4-butanediol, she successfully obtained bis(2-hydroxybutyl) terephthalate (BHBT) (Figure 15). The reaction was conducted at 240 °C for 2 hours. The resulting BHBT was later provided to me, and I carried out a Methacrylation reaction using a procedure similar to that used for Methacrylating BHET, including the same purification steps. The reaction was successful, and the formation of methacrylated BHBT was confirmed by NMR spectroscopy. Figure 16 shows the reacted BHBT with methacrylic anhydride before purification and Figure 17 shows the material after it has been purified and dried.

Figure 14: Polyester fabric before depolymerization reaction with butanediol.

Figure 15: Obtained BHBT after the depolymerization reaction of fabrics.

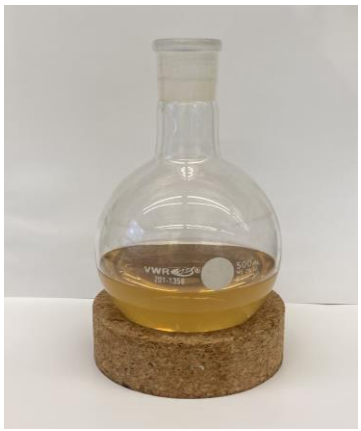

Figure 16: Methacrylated BHBT before Purification.

Figure 17: Methacrylated BHBT after purification and removal of DCM solvent.

4.4.4 Synthesis of Schiff-base (imine bonds) resin

Since the final resin is a conventional thermoset polymer cannot be reshaped or reprocessed once cured, an additional Methacrylation reaction was carried out using vanillin to produce another type of resin that is called Schiff-base resin. The Methacrylation reaction was done using a procedure similar to that used for Methacrylating BHET, including same washing

steps. The resulting methacrylated vanillin underwent another reaction with JEFM with ethanol as a solvent. The mixture was under atmosphere conditions and stirring for 5h. The product was obtained in a powder form that was filtered from the solution.

The imine bonds between vanillin and JEFM are dynamic covalent bonds. These bonds can reversibly break and reform under heat. This reaction is called Imine metathesis. This resin was then blended with methacrylated BHET and methacrylated BHBT resins in order to reduce the overall crosslinking density which gives the final resin a type of behaviour that allows the reshaping under heat after curing.

4.5 Synthesis of films under UV light

For the synthesis of UV-curable film materials, four different formulations were prepared. These included methacrylated BHET derived from pure PET pellets, methacrylated BHBT obtained from polyester fabric, a blend of methacrylated BHET with methacrylated vanillinJEFM, and a blend of methacrylated BHBT with methacrylated vanillinJEFM. All four materials were subjected to a series of characterization techniques to evaluate their thermal, chemical, and mechanical properties. The analyses included Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), hot press film formation, Fourier-Transform Infrared Spectroscopy (FTIR), tensile strength testing and solvent resistance.

To evaluate the UV-curing behavior of the material, an initial test was conducted using 1 g of methacrylated BHET. In this trial, 0.5 g of the material was dissolved in 0.5 mL of dichloromethane (DCM), maintaining a 1:1 ratio of resin to solvent. The photoinitiator PABO was added at 1 wt% relative to the amount of BHET. The solution was stirred until complete dissolution was achieved.

Once fully dissolved, the mixture was poured onto a flat white curing surface exposed to UV light for up to 5 minutes. The exposure resulted in successful crosslinking, forming a solid film, confirming that the material could be effectively cured under UV light (Figure 18).

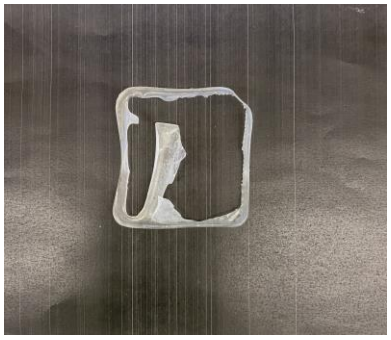

Figure 18: Successful cross-linking testing of 0.5g BHET under UV light.

Following the successful UV-curing test of 0.5 g of methacrylated BHET, the preparation of the four materials intended for characterization was carried out using the same procedure. For the formulation using only methacrylated BHET, 10 g of material was used (Figure 19), while 5 g of methacrylated BHBT was used (Figure 21) for its corresponding formulation. In the blended formulations, methacrylated BHET was mixed with methacrylated vanillinJEFM in a 1:1 ratio, using 1.12 g of BHET and 3 g of methacrylated vanillinJEFM, resulting in a total mixture of 4.12 g (Figure 20). Similarly, methacrylated BHBT was mixed with methacrylated VanillinJEFM in a 1:1 ratio, using 1.2 g of BHBT and 3 g of methacrylated VanillinJEFM, giving a total mixture of 4.2 g (Figure 22). All four formulations were successfully cured under UV light, resulting in solid films, as shown in the figures below

Figure 19: UV Cured Methacrylated BHET.

Figure 20: UV Cured Methacrylated BHET mixed with Methacrylated Vanillin JEFM.

Figure 21: UV Cured Methacrylated BHBT.

Figure 22: UV Cured Methacrylated BHBT mixed with Methacrylated Vanillin JEFM.

As an additional test to verify the success of the methacrylation of BHET derived from Coca-Cola PET, a UV-curable film was synthesized using silicone molds. The formulation was cured under UV light, and the resulting film as shown below, confirms that the methacrylated Coca-Cola BHET was suitable for UV curing (Figure 23).

Figure 23: Synthesized films with silicon molds using Coca-Cola's obtained BHET.

5. Results and Discussion

5.1 Chemical Recycling of PET PELLETS to obtain BHET

All reactions were carried out at a consistent temperature of 180°C with continuous stirring at 280 rpm overnight, unless otherwise stated.

The total amount of BHET obtained from all glycolysis experiments was 244.3g. The details of each experiment are summarized in Table 1 and Figure 24.

Table 1: Summary of Glycolysis reactions with their respective obtained BHET

Experiment Number	PET Used (g)	BHET Obtained (g)	Yield (%)
1	5.0	1.6	24.2
2	40.0	13.5	25.5
3	40.0	30.0	56.7
4	40.0	32.8	61.9
5	40.0	21.0	39.7
6	40.0	24.3	45.9
7	40.0	23.0	43.5
8	40.0	36.7	69.0
9	40.0	30.7	58.0
10	40.0	30.7	58.0

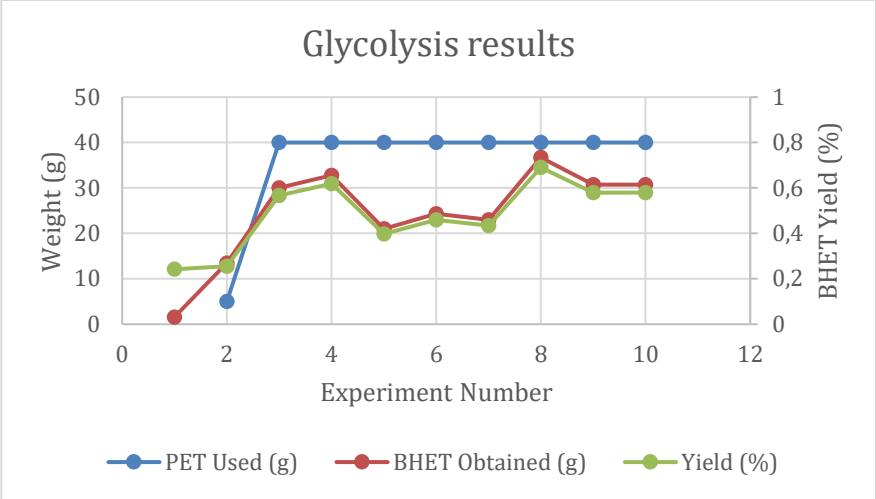

Figure 24: Results obtained of Glycolysis reaction of PET Pellets

5.2 Characterization Techniques

The characterization techniques used to evaluate each UV-cured material are selected to provide a comprehensive understanding of their chemical, thermal, mechanical, and crosslinking behavior. The results obtained from each technique help confirm successful curing, assess the degree of crosslinking, and evaluate thermal stability and mechanical performance. The table below summarizes the techniques used and the specific information derived from each.

5.2.1 NMR

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful technique in polymer chemistry because it provides detailed information about the structure of molecules. It can be used not only to identify specific chemical groups but also to measure how different parts of a polymer are connected. For example, NMR helps confirm chain ends, repeating units, and the arrangement of monomers. In cases where more than one type of monomer is used, the material is called a *copolymer*, and NMR can show how these different monomers are distributed along the polymer chain. Since the polymers and products in this work are soluble, solution-state NMR was applied to analyze their structures and confirm the success of the reactions. ^{1}HNMR and ^{13}CNMR were performed to confirm the structure of the experiments that have been performed.

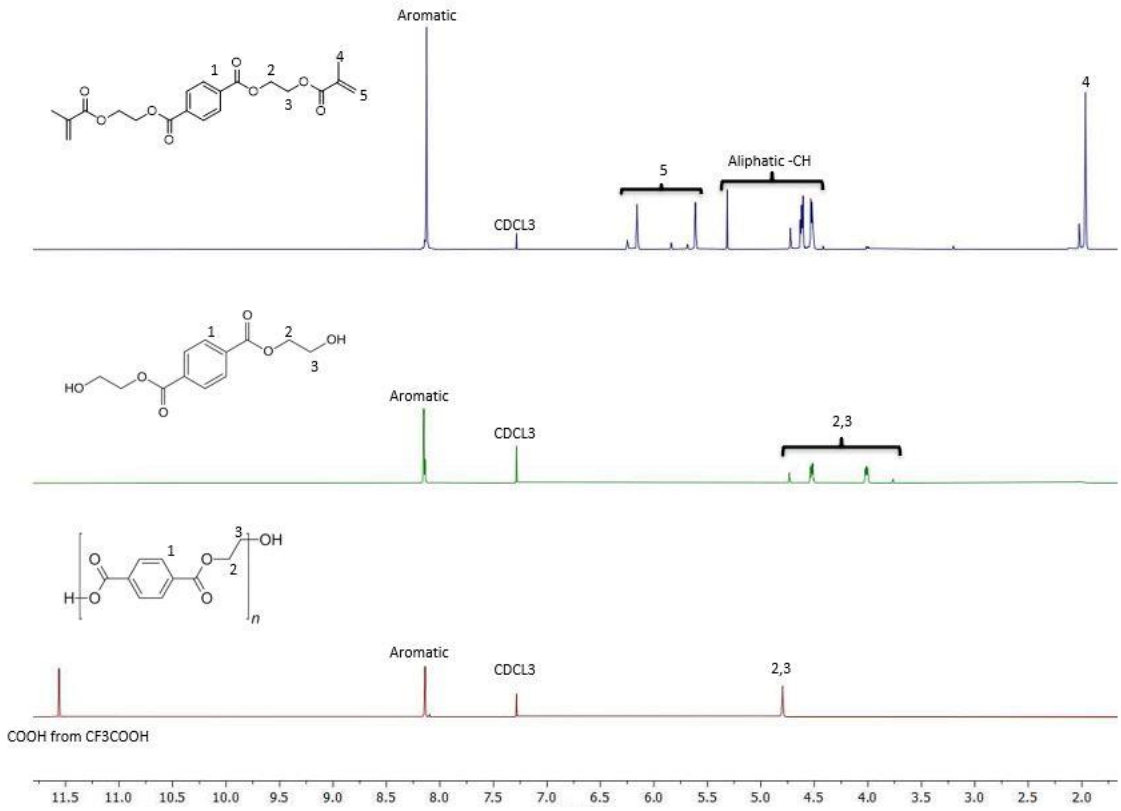

Figure 25: ^{1}H NMR spectra of (bottom) PET pellets dissolved in trifluoroacetic acid, (middle) BHET obtained from glycolysis, and (top) methacrylated BHET recorded in $CDCl_3$. For the PET pellets, a characteristic peak is observed at ~11.5 ppm corresponding to the –COOH proton from trifluoroacetic acid. In all three spectra, the aromatic protons of the terephthalate unit appear between 8.0 and 8.5 ppm. The $CDCl_3$ solvent peak is seen at 7.26 ppm. Signals from the ethylene glycol units are evident between 3.5 and 5.0 ppm in all three materials. For the methacrylated BHET, additional signals are observed at ~1.8–2.0 ppm assigned to the CH_3 group of the methacrylate and between ~5.2–6.5 ppm corresponding to the CH_2 protons adjacent to the methacrylate double bond. These features confirm the successful methacrylation of BHET.

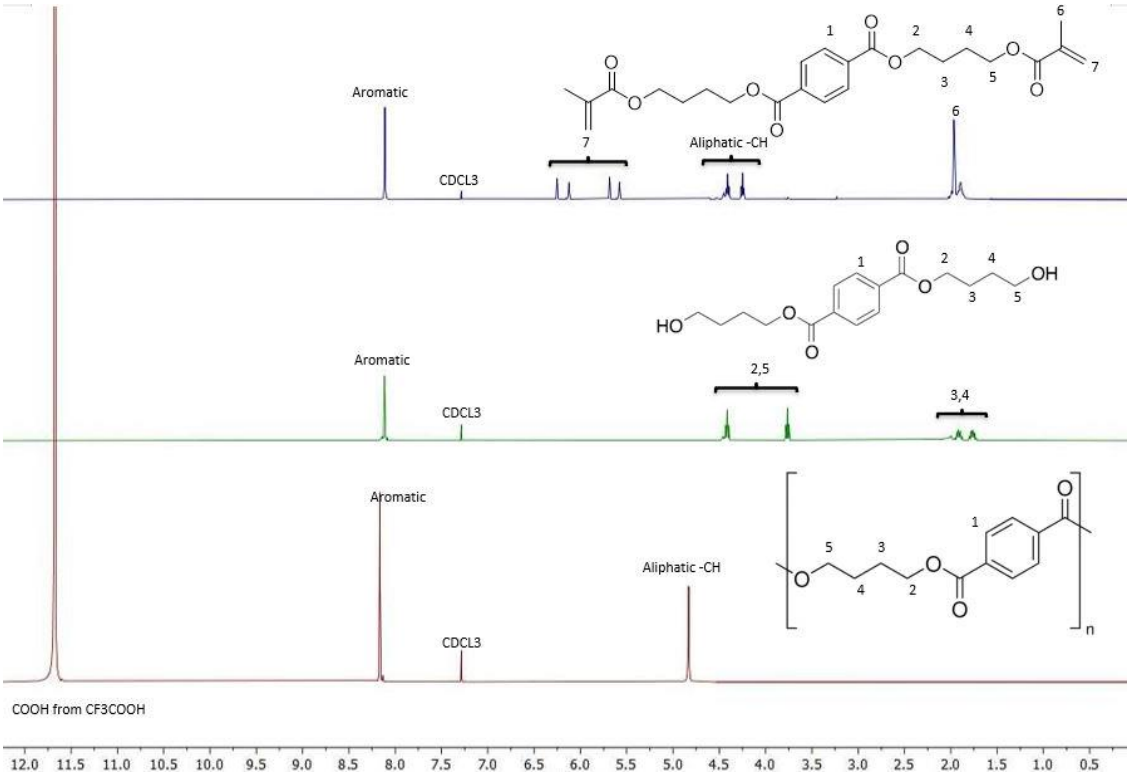

Figure 26: ^{1}H NMR spectra of (bottom) textile dissolved in trifluoroacetic acid, (middle) BHBT obtained from glycolysis of the textile, and (top) methacrylated BHBT recorded in $CDCl_3$. For the PBT textile, a characteristic peak is observed at ~11.5 ppm corresponding to the –COOH proton from trifluoroacetic acid. In all three spectra, the aromatic protons of the terephthalate unit appear between 8.0 and 8.5 ppm, with the $CDCl_3$ solvent peak at 7.26 ppm. Signals from the glycol units are present between 3.5 and 5.0 ppm. In BHBT and methacrylated BHBT, additional resonances around 1.8 ppm arise from the CH_2–CH_2 groups of the butylene spacer; although these signals are not clearly resolved in the bottom spectrum of PBT, they are still present. For the methacrylated BHBT, further peaks are seen at ~1.8–2.0 ppm assigned to the methacrylate CH_3 group and between ~5.2–6.5 ppm corresponding to the methacrylate CH_2 protons adjacent to the double bond. These features confirm the successful incorporation of the butylene glycol unit and methacrylation of BHBT.

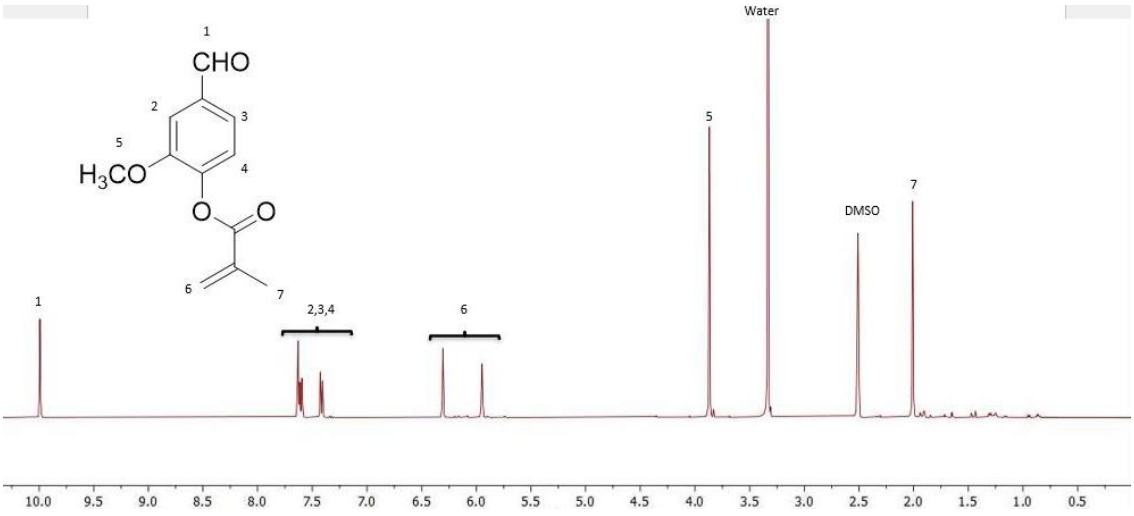

Figure 27: ^{1}H NMR spectrum of methacrylated vanillin recorded in DMSO-d_6. The aromatic protons of the vanillin ring appear between 6.7–7.8 ppm. The methacrylate group shows two sets of vinyl proton signals at approximately 5.6–6.3 ppm and a methyl group at 1.8–2.0 ppm. The –OCH_3 (methoxy) group of vanillin resonates near 3.7–3.9 ppm. The phenolic –OH (if still present) typically appears as a broad signal around 9.5–10 ppm. The DMSO-d_6 solvent peak is observed at 2.50 ppm, and the residual water peak in DMSO-d_6 appears at about 3.3 ppm. These resonances confirm the presence of both the vanillin aromatic structure and the methacrylate functionality.

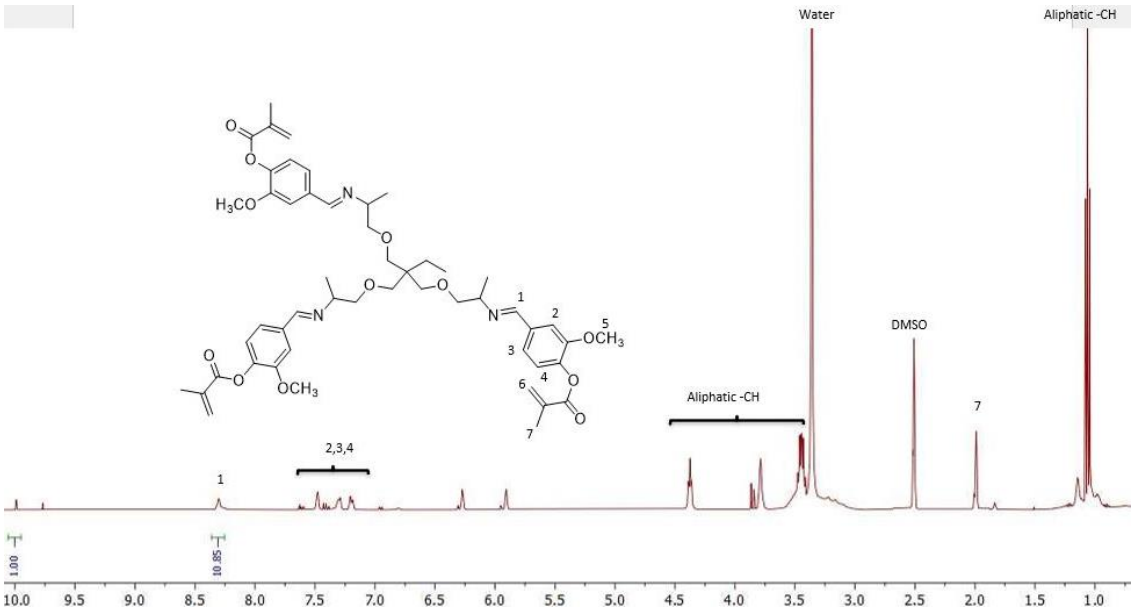

Figure 28: ^{1}H NMR spectrum of methacrylated vanillin JEFM (Schiff base) recorded in DMSO-d_6. Compared with methacrylated vanillin, the characteristic aldehyde proton signal at ~9.7–9.9 ppm has almost completely disappeared, while a new imine (C=N) proton resonance appears around 8.2–8.5 ppm, confirming successful Schiff base formation. The aromatic protons of the vanillin ring are observed between 6.7 and 7.8 ppm, and the methoxy (–OCH_3) group of vanillin resonates near 3.7–3.9 ppm. The methacrylate group shows two sets of vinyl protons at approximately 5.6–6.3 ppm and a methyl group at 1.8–2.0 ppm. In addition, aliphatic CH protons introduced through the imine modification appear dispersed at different positions between 1.0 and 4.0 ppm. The DMSO-d_6 solvent peak is seen at 2.50 ppm, with the residual water peak near 3.3 ppm. These resonances together confirm incorporation of the methacrylate group and successful formation of the Schiff base from vanillin.

5.2.2 FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) is an essential tool in polymer and materials characterization because it provides direct information about the functional groups present in a sample. By detecting specific vibrational frequencies of chemical bonds, FTIR allows researchers to confirm whether targeted reactions have taken place. For example, in this work, FTIR was used to verify the methacrylation of PET-derived monomers by monitoring the disappearance of hydroxyl and aldehyde peaks, and the appearance of characteristic ester and methacrylate C=C stretching bands. During UV curing, FTIR is also important for tracking the conversion of double bonds, as the reduction of the C=C absorption band indicates crosslinking of the resin. This makes FTIR a quick and reliable technique to confirm both chemical modifications and the curing efficiency of polymer networks.

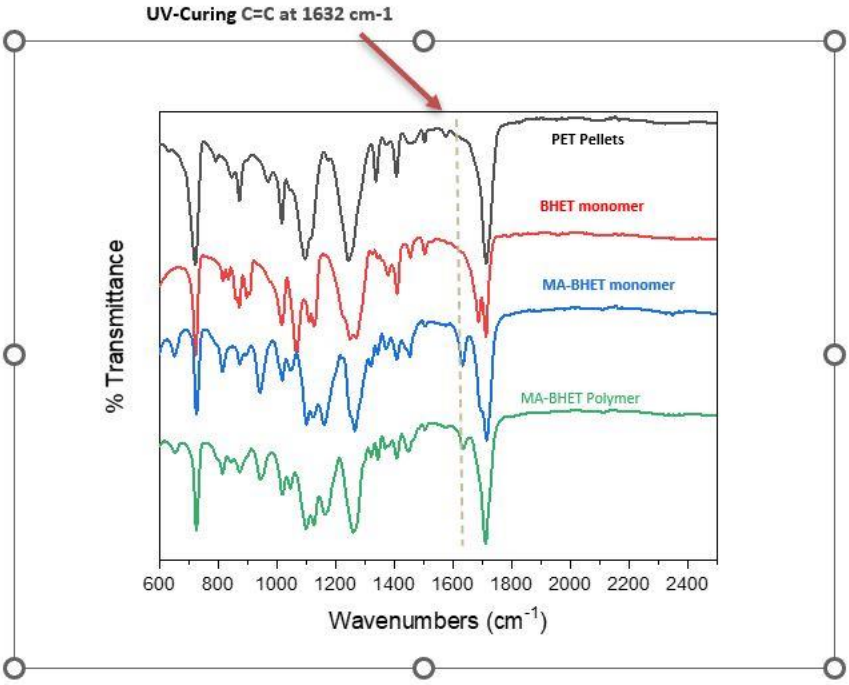

Figure 29: FTIR spectra of the PET materials. The black spectrum corresponds to the original PET pellets, while the red spectrum represents the BHET monomer obtained from PET depolymerization, showing no C=C double bond as expected. The blue spectrum corresponds to the methacrylated BHET (MA-BHET), where the appearance of a distinct band at approximately 1632 cm^{-1} confirms the presence of C=C bonds, indicating that the methacrylation reaction was successful. In the green spectrum, which represents the UV-cured MA-BHET polymer, this C=C peak decreases significantly, demonstrating the consumption of double bonds during the curing process.

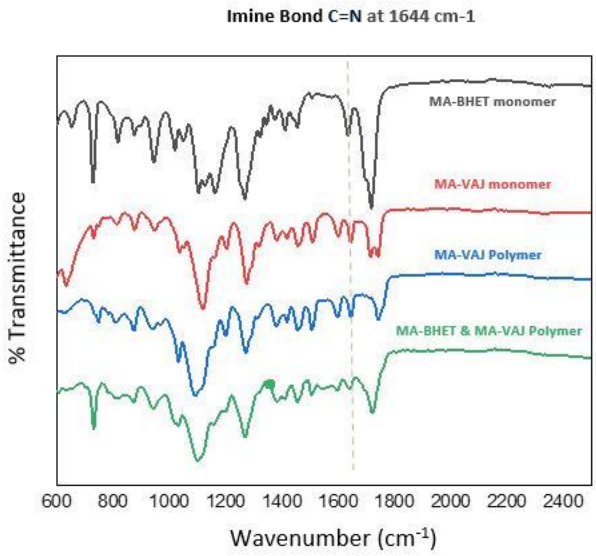

Figure 30: FTIR spectra of the textile materials. The black spectrum corresponds to the methacrylated BHET (MA-BHET) monomer, while the red spectrum represents the methacrylated vanillin JEFM (MA-VAJ) monomer. Both spectra exhibit a characteristic C=C stretching band at around 1632 cm^{-1}, confirming the successful methacrylation reaction. In addition, the MA-VAJ monomer shows a distinct band at approximately 1644 cm^{-1}, corresponding to the C=N bond, which confirms the formation of the Schiff base. After UV curing of the MA-VAJ material, the C=C peak at 1632 cm^{-1} disappears, indicating the consumption of double bonds and confirming successful curing and crosslinking.

5.2.3 Hot Press

Hot press experiments are important for evaluating the reprocessability and homogeneity of thermoset materials. By applying heat and pressure, these tests reveal whether polymer networks containing dynamic covalent bonds can reorganize and form uniform films after multiple processing cycles. The changes in film appearance, such as improved transparency and uniformity after repeated pressing, directly demonstrate the effectiveness of dynamic bond exchange. This makes hot press testing a practical way to assess material recyclability, reshaping ability, and overall processing performance.

Figure 31: Methacrylated BHETJEFM after 1st hot press cycle (cloudy, less uniform).

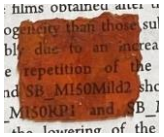

Figure 32: Methacrylated BHETJEFM after 2nd hot press cycle (more transparent and uniform)

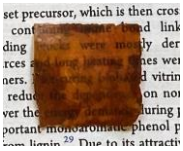

Figure 33: Methacrylated BHBTJEFM after 1st hot press cycle (cloudy, less uniform)

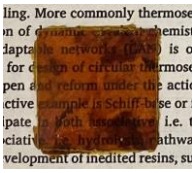

Figure 34: Methacrylated BHBTJEFM after 2nd hot press cycle (more transparent and uniform)

The hot press experiments clearly demonstrate that both methacrylated BHETJEFM (Figure 31 and 33) and methacrylated BHBTJEFM (Figure 32 and 34) can be reprocessed, which was not possible for the corresponding methacrylated thermosets before the introduction of imine bonds. For both systems, the first hot press cycle resulted in cloudy and less uniform films (Figure 31 and 32), while the second cycle produced films with much higher transparency and more uniform appearance (Figure 33 and 34). This improvement confirms that repeated pressing allows the polymer networks to reorganize, leading to better homogeneity. The reprocessing ability arises from the presence of dynamic imine (Schiff-base) bonds, which are reversible and enable bond exchange under heat and pressure. These dynamic linkages allow the materials to maintain their crosslinked structures while still being reprocessable. Similar behavior has been reported in vanillin-based imine thermosets, where the incorporation of imine bonds enabled malleability, reprocessability, and self-healing (Liguori et al., 2022).

5.2.4 TGA

Thermogravimetric Analysis (TGA) is an essential tool for evaluating the thermal stability and degradation behavior of polymeric materials. By measuring weight loss as a function of temperature, TGA provides valuable information on decomposition temperatures, thermal resistance, and the effect of chemical modifications on material stability. For thermoset resins, this analysis helps determine their suitability for high-temperature applications, assess the impact of reprocessing or dynamic bond incorporation, and compare the

performance of different formulations. Ultimately, TGA is crucial for linking thermal stability to material durability and long-term performance.

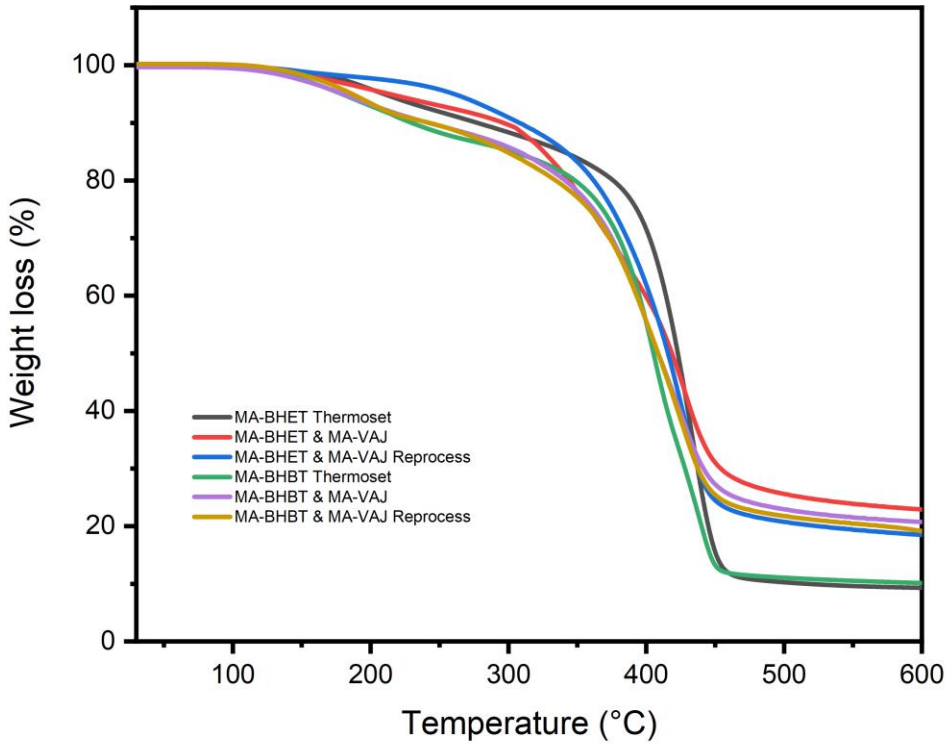

Figure 35: Thermogravimetric analysis (TGA) curves of methacrylated materials. The plot shows weight-loss profiles of MA-BHET thermoset (black), MA-BHET & MA-VAJ blend (red), reprocessed MA-BHET & MA-VAJ (blue), MA-BHBT thermoset (green), MA-BHBT & MA-VAJ blend (purple), and reprocessed MA-BHBT & MA-VAJ (yellow). All samples remain stable up to roughly 250–300 °C before undergoing major mass loss in a single degradation step, typical for polyester-based systems. The similar onset and degradation temperatures between the original and reprocessed samples indicate that the materials largely retain their thermal stability after reprocessing.

Table 2: Thermal degradation parameters obtained from TGA for the different methacrylated systems. T_5%-deg represents the temperature at 5 % weight loss, and T_{max}-deg corresponds to the maximum degradation temperature. The data show that all materials maintain high thermal stability, with only minor changes in onset and maximum degradation temperatures after blending or reprocessing.

Material	$T_{5\%\text{-deg}}$ (°C)	$T_{max\text{-deg}}$ (°C)
MA-BHET Thermoset	211	434
MA-BHET and MA-VAJ	215	429
MA-BHET and MA-VAJ Reprocess	263	426
MA-BHBT Thermoset	179	406
MA-BHBT and MA-VAJ	181	427
MA-BHBT and MA-VAJ Reprocess	183	426

All materials exhibit high thermal stability, with negligible weight loss below about 200–250 °C and a single major degradation step between 350–450 °C typical of polyester-based systems. According to Table 2, the temperature at 5 % weight loss (T_5%) is lowest for MA-BHBT thermoset (179 °C) and highest for the reprocessed MA-BHET and MA-VAJ (263 °C), indicating that the incorporation of methacrylated vanillinJEFM (MA-VAJ) and subsequent reprocessing can shift the onset of degradation to slightly higher temperatures. The maximum degradation temperature (T_{max}) remains in the 406–434 °C range for all samples, showing only minor differences between original, blended, and reprocessed materials. This behaviour, visible in the TGA curves, demonstrates that both blending with MA-VAJ and reprocessing do not compromise the main thermal-decomposition stability of the networks, while in some cases (e.g. reprocessed MA-BHET and MA-VAJ) the onset stability even improves.

5.2.5 DSC

Differential Scanning Calorimetry (DSC) is an important tool for evaluating the thermal behavior of polymeric materials. It provides insight into key transitions such as the glass transition temperature (Tg), melting, and relaxation processes, which directly influence the material's rigidity, stability, and potential applications. For thermoset resins, DSC helps confirm their amorphous nature, assess thermal performance, and verify whether reprocessing or chemical modifications affect the polymer network.

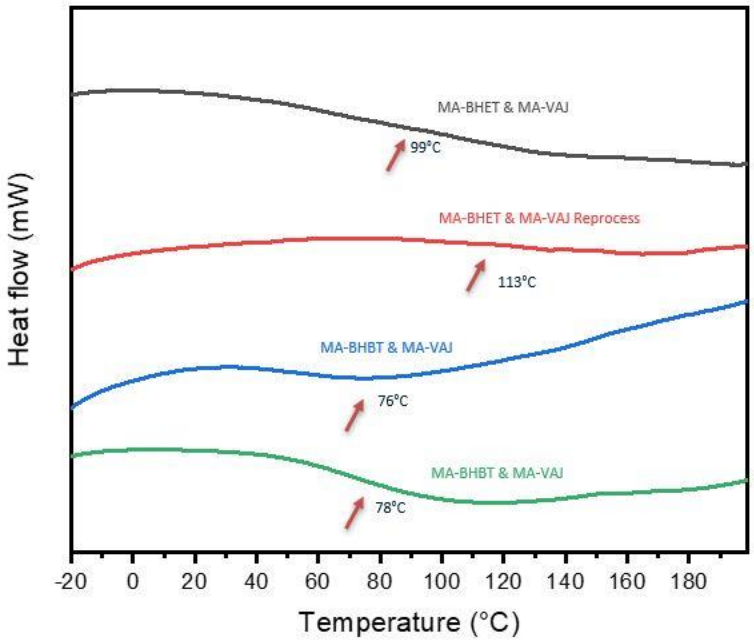

Figure 36: Differential Scanning Calorimetry (DSC) curves of methacrylated systems. The plot shows the heat-flow profiles of MA-BHET & MA-VAJ (black), reprocessed MA-BHET & MA-VAJ (red), MA-BHBT & MA-VAJ (blue), and MA-BHBT & MA-VAJ (green) as a function of temperature.

Differential Scanning Calorimetry (DSC) measurements could not be obtained for the pure methacrylated BHET thermoset and methacrylated BHBT thermoset because their highly crosslinked nature prevented the detection of clear thermal transitions. For the blend systems, the glass-transition temperature (Tg) for MA-BHET and MA-VAJ was observed at approximately 99 °C (Black Line), and for reprocessed MA-BHET and MA-VAJ at about 113 °C (Red Line). The Tg for MA-BHBT and MA-VAJ appeared near 76 °C (Blue Line), and for MA-BHBT and MA-VAJ reprocess at approximately 78 °C (Green Line).

These results show that the MA-BHET and MA-VAJ systems exhibit significantly higher glass-transition temperatures compared with the MA-BHBT and MA-VAJ systems, indicating better thermal stability at elevated temperatures — a trend that is consistent with the TGA data. The lower Tg values of the MA-BHBT and MA-VAJ samples can be attributed to the presence

of the flexible CH_2–CH_2 (butylene) spacer in BHBT, which increases chain mobility and lowers the glass-transition temperature.

5.2.6 Tensile Strength

Tensile testing was performed to evaluate the mechanical performance of the cured materials, specifically their strength, stiffness, and ability to withstand deformation under load. This test provides key information about the practical usability and durability of the materials under mechanical stress. In this work, tensile measurements were carried out only on the methacrylated BHBT blended with methacrylated vanillinJEFM (MA-BHBT and MA-VAJ) samples, as the methacrylated BHET materials were too rigid and brittle to prepare suitable test specimens and could not be reliably tested under the same conditions.

Tensile testing was performed on reprocessed methacrylated BHET blended with methacrylated vanillin (MA-BHET and MA-VAJ reprocess) so that both systems could be compared. Each formulation was tested on three replicate, and the results of these tests are presented below (Figure 37 and Table 3).

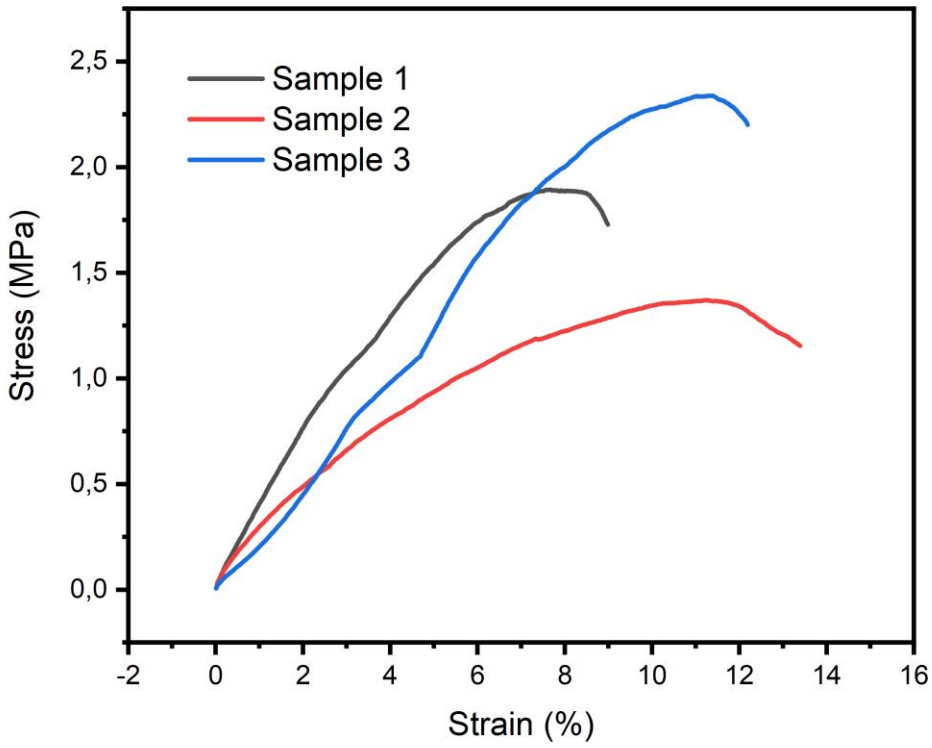

Figure 37: Stress–strain curves for the MA-BHBT blended with MA-VAJ samples. Three replicate specimens (Sample 1 – black, Sample 2 – red, Sample 3 – blue) were tested to evaluate the mechanical performance.

Table 3: Mechanical properties obtained from tensile testing of MA-BHBT blended with MA-VAJ. Three replicate specimens were tested to evaluate tensile strength, elongation at break, and elastic modulus.

Sample #	Tensile strength (MPa)	Elongation at break (%)	Elastic modulus (GPa)
Sample 1	1.87	8%	0.04
Sample 2	1.36	11%	0.04
Sample 3	2.33	11%	0.02
Average	1.85	10%	0.03
Standard Deviation	0.48	1.73%	0.01

The tensile test results for the MA-BHBT blended with MA-VAJ as shown in Table 3 that the material achieves an average tensile strength of about 1.86 MPa with a standard deviation of 0.48 MPa, an elongation at break of roughly 10 % with a standard deviation of 1.7 %, and an average elastic modulus of approximately 0.03 GPa with a standard deviation of 0.01 GPa. These values indicate that the network exhibits moderate strength combined with appreciable ductility, which is consistent with the presence of the flexible butylene spacer in BHBT. This flexibility contrasts with the behaviour of methacrylated BHET systems, which are too rigid and brittle to be tested under the same conditions. Overall, the results confirm that incorporating the BHBT segment produces a less brittle, more reprocessable material without sacrificing too much tensile strength.

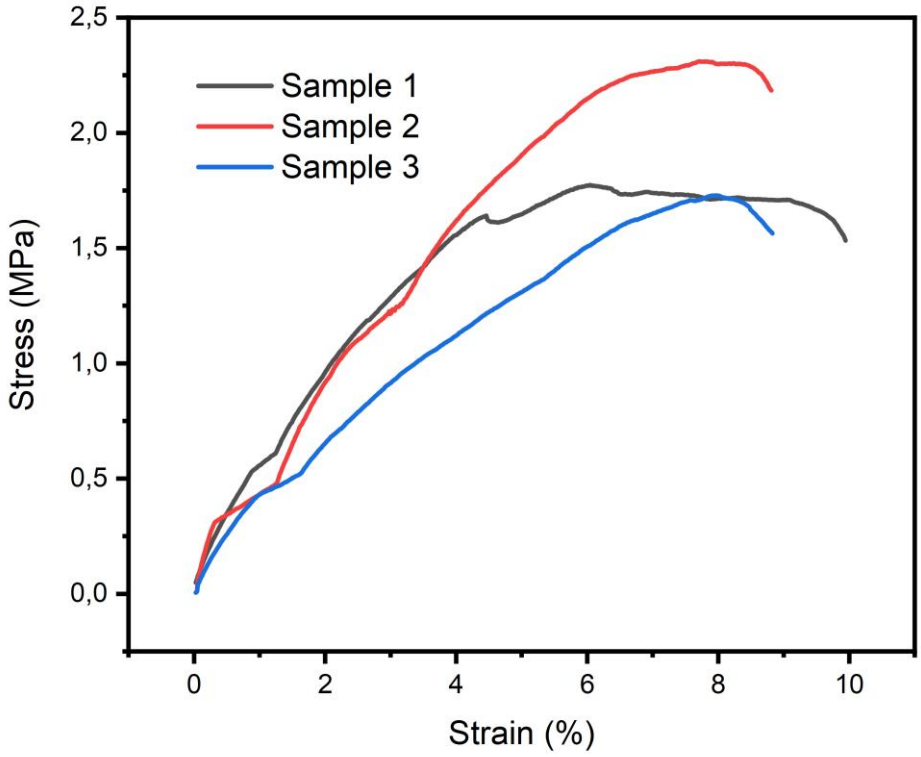

Figure 38: Stress–strain curves for the reprocessed MA-BHBT blended with MA-VAJ material. Three replicate specimens (Sample 1 – black, Sample 2 – red, Sample 3 – blue) were tested to evaluate the mechanical performance after reprocessing.

Table 4: Mechanical properties obtained from tensile testing of reprocessed MA-BHBT blended with MA-VAJ. Three replicate specimens were tested to determine tensile strength, elongation at break, and elastic modulus.

Sample #	Tensile strength (MPa)	Elongation at break (%)	Elastic modulus (GPa)
Sample 1	1.7	9%	0.06
Sample 2	2.9	8%	0.09
Sample 3	1.72	8%	0.05
Average	1.91	8%	0.07
Standard Deviation	0.33	0.71%	0.02

The tensile test results for the reprocessed MA-BHBT blended with MA-VAJ as seen in table 3, show an average tensile strength of about 1.91 MPa (standard deviation 0.33 MPa), an elongation at break of around 8 % (standard deviation 0.7 %), and an average elastic modulus of approximately 0.07 GPa (standard deviation 0.02 GPa). Compared with the original MA-BHBT and MA-VAJ material, the reprocessed samples maintain a very similar tensile strength but display a slightly lower elongation at break and a noticeably higher modulus, indicating that the material stiffens a bit after reprocessing but without a loss of strength. This demonstrates that the reprocessing step does not significantly degrade the mechanical performance of the network and that the flexible butylene spacer still imparts good ductility.

As shown in Table 3 and Table 4, The low elastic modulus indicates that the material can easily deform under applied stress, reflecting its soft and flexible nature. However, the limited elongation at break suggests brittleness, meaning it fractures before significant stretching can occur.

5.2.7 Solvent Resistance

The solvent resistance test, often carried out as a gel content analysis, is used to evaluate the degree of crosslinking in a polymer network. In this method, the cured material is exposed to a solvent in which the non-crosslinked fraction can dissolve, while the crosslinked network remains insoluble. The weight of the insoluble gel fraction is then measured to determine the extent of crosslinking. This test is important because the solvent resistance of a material directly reflects its chemical stability, durability, and suitability for applications where the polymer will encounter solvents, water, or other challenging environments. Higher gel content indicates stronger crosslinking, which improves mechanical strength, dimensional stability, and long-term performance of the thermoset material.

Table 5: Solvent resistance of methacrylated BHETJEFM and BHBTJEFM, showing initial and final weights after solvent exposure and corresponding percentage weight loss.

Solvent	MA-BHET and MA-VAJ Gel Content (%)	MA-BHBT and MA-VAJ Gel Content (%)
EtOH	100%	94%
DCM	99%	66%
THF	91%	100%
DMSO	99%	99%
Ace	95%	88%
DMF	99%	85%

NaOH (1M)	89%	74%

The gel content analysis offers insight into the chemical stability and solvent resistance of the cured materials. The gel content indicates the fraction of the polymer network that remains intact and does not dissolve in the solvent, reflecting the degree of crosslinking and overall stability. As shown table 5, the MA-BHET and MA-VAJ system demonstrated superior chemical stability compared to the MA-BHBT and MA-VAJ system in most solvents. The MA-BHET-based material consistently maintained high gel contents, reaching 100% in ethanol, 99% in DCM, DMSO, and DMF, and staying above 90% in all other solvents, with the lowest value of 89% observed in NaOH (1 M). In contrast, the MA-BHBT-based material displayed slightly lower resistance, especially in DCM (66%), NaOH (74%), and DMF (85%), suggesting that the more flexible butylene spacer in BHBT may produce a less tightly crosslinked network. Overall, the MA-BHET formulation exhibited excellent solvent resistance and crosslinking stability, confirming its stronger and more resilient network structure. The dissolving of materials in different solvents can be seen in Figure 39.

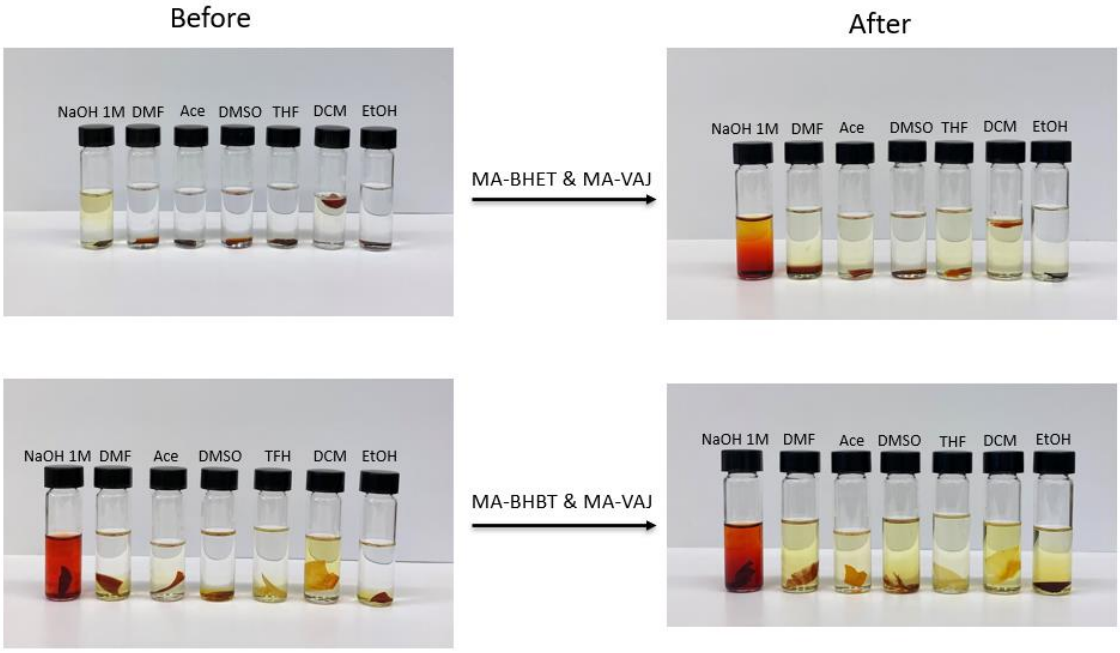

Figure 39: Visual comparison of solvent-resistance tests before and after immersion of the cured resins. The top row shows MA-BHET and MA-VAJ samples, and the bottom row shows MA-BHBT and MA-VAJ samples, each immersed in NaOH (1 M), DMF, acetone (Ace), DMSO, THF, dichloromethane (DCM) and ethanol (EtOH). The photographs on the left were taken before immersion and those on the right after 48 h exposure. MA-BHET and MA-VAJ retained their integrity with minimal colour change or mass loss across all solvents, whereas MA-

BHBT and MA-VAJ displayed more pronounced colour change, swelling or fragmentation in several solvents, indicating lower solvent resistance due to its more flexible butylene spacer.

6. Conclusions

6.1 Summary of Findings

In summary, the characterization results highlight how molecular structure and dynamic imine incorporation influence the overall performance of the synthesized materials. The MA-BHET sample exhibited clear C=C peaks in FTIR, confirming successful methacrylation, and demonstrated the highest thermal stability, with an onset degradation temperature of approximately 211 °C and a T_{max} of around 434 °C. Due to its highly crosslinked thermoset nature, no distinct glass transition temperature (Tg) was observed, and the material could not be reprocessed or hot-pressed. Similarly, MA-BHBT, characterized by the CH_2–CH_2 (butylene) spacer confirmed through ^{1}H NMR, showed slightly lower thermal stability (onset ≈ 179 °C, T_{max} ≈ 406 °C) and, like MA-BHET, did not exhibit a clear Tg or reprocessability due to its extensive crosslinking.

Upon incorporating methacrylated vanillin (VAJ) to introduce dynamic imine linkages, reprocessable thermosets were successfully achieved. The MA-BHET and MA-VAJ system displayed characteristic C=N peaks confirming Schiff base formation, alongside high thermal stability (onset ≈ 215 °C, T_{max} ≈ 429 °C) and the highest Tg among all materials (~99 °C, increasing to ~113 °C after reprocessing). Although this material was too brittle for tensile testing, it exhibited excellent reprocessability under hot-pressing and outstanding solvent resistance, with less than 10 % mass loss in all solvents tested. The MA-BHBT and MA-VAJ thermoset also demonstrated successful reprocessability, with moderate thermal stability (onset ≈ 181 °C, T_{max} ≈ 427 °C), a lower Tg of 76–78 °C due to the flexible butylene spacer, and measurable mechanical properties—tensile strength ~1.8–1.9 MPa, elongation 8–10 %, and modulus 0.3–0.7 MPa. However, its solvent resistance was comparatively lower, with up to 34 % mass loss in some solvents.

Overall, the incorporation of dynamic imine bonds effectively transformed the non-reprocessable methacrylated systems into reprocessable thermosets with enhanced chemical stability and retained thermal integrity—particularly evident in the MA-BHET and MA-VAJ network, which demonstrated the most balanced performance across all evaluated parameters.

Overall, the combined results demonstrate that methacrylated BHET blended with methacrylated vanillin JEFM forms a thermally and chemically robust but brittle network, while methacrylated BHBT blended with methacrylated vanillin JEFM yields a less brittle, more reprocessable material with slightly lower thermal stability but good mechanical performance. These findings confirm that varying the glycol segment (ethylene vs. butylene)

provides a straightforward means to tune the balance between rigidity, processability, thermal stability, and solvent resistance in upcycled methacrylated polyester-based resins.

6.2 Contributions to the Field

This research contributes to the field of sustainable polymer science and recyclable thermosets by demonstrating how methacrylated PET-derived monomers can be successfully incorporated into dynamic covalent networks. By systematically comparing the thermal, mechanical, and chemical performance of ethylene- versus butylene-based structures, the study provides valuable insights into how spacer length affects rigidity, flexibility, solvent resistance, and overall stability of reprocessable thermosets. Importantly, the work confirms that the introduction of dynamic imine bonds enables effective hot-press reprocessing, producing uniform films without significant loss of performance, which directly addresses the challenge of recycling crosslinked thermosets. The findings highlight a pathway for upcycling PET waste into value-added, reprocessable materials, thereby advancing the development of circular economy strategies.

6.3 Sustainable Development Goals

This research aligns closely with several United Nations Sustainable Development Goals by addressing the environmental challenges associated with plastic waste. Most directly, it supports SDG 12, Responsible Consumption and Production through the upcycling of PET into value-added, reprocessable thermosets, promoting circular economy practices and reducing reliance on virgin fossil-based plastics. By lowering the environmental footprint of plastic production and extending material lifetimes, the work also contributes to SDG 13, Climate Action. In addition, the reduction of persistent PET waste helps mitigate pollution in aquatic environments and landfills, thereby advancing SDG 14, Life Below Water and SDG 15, Life on Land. Finally, by developing innovative sustainable materials, the research also supports SDG 9, Industry, Innovation and Infrastructure, highlighting how scientific innovation can enable more sustainable industrial practices.

Figure 40: Alignment of this research with the United Nations Sustainable Development Goals (SDGs), highlighting contributions to innovation (SDG 9), circular economy (SDG 12), climate action (SDG 13), and the impact of plastic pollution on water (SDG 14) and land (SDG 15).

6.4 Future Work

Future work should focus on optimizing the reaction conditions from glycolysis through methacrylation, purification, and imine bond formation to reduce reaction time and improve yield. The UV-curing process also needs to be optimized to ensure full conversion and better

material performance. In addition, blending both BHET and BHBT should be investigated to combine their respective strengths. Finally, other dynamic covalent chemistries beyond imine bonds, such as disulfide, boronic ester, or transesterification, could be explored to further enhance reprocessability and material properties.

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