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Expanding and recycling a water-resistant bioderived rigid foam using CO_2-responsive amines and carbonated water

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Rigid foams such as expanded polystyrene (EPS) packing have become common when transporting or storing valuable items. EPS is an inexpensive, lightweight, and robust protective material that can be easily moulded into a desired shape. Economically, EPS is an excellent choice for packaging; however, it puts a significant strain on the environment. It is made from petrochemicals, uses smog-forming organic solvents as blowing agents, and is rarely recycled because it is expensive to recycle. Biobased foams have been developed to try and mitigate the environmental impacts of EPS production and end-of-life but have poor water resistance during use, which is a key feature in packaging. We have developed a rigid foam material from vanillin that addresses the environmental issues of EPS and the lack of water resistance of current biobased foams. Adding a tertiary amine group to a vanillin-derived polymer made it possible for the polymer to be CO_2-responsive, as polymers containing tertiary amines can alter their properties in the presence or absence of CO_2 and water. This CO_2-responsive feature allowed the polymer to be hydrophobic during use but dissolve in carbonated water at the end of life. The dissolved polymer in carbonated water can be re-expanded back into a foam by rapid heating, which allows the polymer to have improved recyclability compared to EPS and avoid organic solvent blowing agents. This bioderived CO_2-responsive rigid foam can be recycled back into new rigid foam materials with a 98% material recovery efficiency. Recycling had an impact on the foam mechanical properties but the foam maintained water resistance even after 5 recycling cycles. A bioderived CO_2-responsive rigid foam such as this may, after further development, be a greener substitute for EPS packing materials.

Green foundation

1. This work describes an alternative to expanded polystyrene foam (EPS). The new material uses CO_2-responsive functionality to address specific environmental concerns that are caused by EPS.
2. This CO_2-responsive rigid foam was synthesized using bioderived chemicals, and uses carbonated water as the polymerization solvent, recycling and reprocessing solvent, and blowing agent (instead of pentane). The material can be easily recycled back into new foam products by dissolution back into carbonated water and re-expansion by rapid heating.
3. Further optimization of the reaction conditions and introduction of flow chemistry would be particularly useful in limiting reagent use, reducing waste generation, and minimizing energy consumption.

Introduction

Consumer goods are more often than not contained within some sort of plastic packaging that is discarded after serving its purpose, often ending up in landfills or the environment.[1] Packaging is a societal necessity but also an environmental burden. A widely used plastic packaging material is expanded polystyrene (EPS) foam. Approximately 7 million tonnes of EPS foam were manufactured globally in 2022.[2] It is a desirable material for packaging as it is inexpensive, lightweight, and provides excellent physical properties that protect both high-value and commodity items. However, EPS has several key environmental problems that have lowered its popularity amongst the ever-growing, environmentally conscious world. EPS is prepared from a non-renewable plastic, polystyrene (PS), which in its foamed state is typically classified as non-recyclable because it is not economically feasible to recycle it, result-

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ing in its disposal in the environment.[3,4] In addition to these issues, the manufacture of EPS requires the use of organic solvents as blowing agents to expand the foam to the desired size, shape, and density.[5] In some countries, these organic solvents are directly emitted into the atmosphere, leading to greenhouse gas effects and smog formation.[6,7] Alternative foam packaging needs to provide similar properties to EPS foam but address the environmental concerns of poor recyclability, the use of organic solvent blowing agents, and preparation from non-renewable starting materials. EPS foam packaging provides the desired properties for protecting goods, but comes at the cost of harming the environment during production and at the end of life.

Discarded EPS foam packaging itself causes damage to the environment with the generation of microplastics[8] and chemical leaching,[9,10] but the manufacturing process of the starting materials also contributes to environmental and human harm. Styrene, the monomer used in the production of EPS foam, is produced through a multi-step process starting from crude oil. Benzene and ethylene are isolated from crude oil and reacted, producing ethylbenzene.[11,12] Following isolation, ethylbenzene is converted to styrene by direct dehydrogenation, which accounts for 85% of commercial styrene production.[11] Each of these molecules poses significant hazards. Ethylbenzene is a possible carcinogen, whereas benzene and styrene are known carcinogens.[13–15] Besides being carcinogenic, these chemicals are also extremely hazardous to handle; their dangerous properties like flammability, toxicity, and volatility have led to several industrial accidents in recent years.[16,17]

The manufacturing of EPS from styrene also poses risks of harm to worker health and the environment. Styrene is suspended in water and polymerized into PS beads. After polymerization and separation, these beads are permeated with pentane to act as a blowing agent in the expansion step. The treated beads are exposed to steam, causing rapid evaporation of the pentane, leading to the expansion of the beads. The expanded beads are matured by allowing residual moisture and pentane to off-gas, leaving behind pristine EPS beads. The matured beads are then moulded into a shape.[5] Without a sufficient capture system, up to 85% of the pentane used during production can be lost, which equates to 14 tonnes per year of pentane being released into the atmosphere, causing smog formation and greenhouse effects.[18] The release of volatile gases also puts workers at risk of central nervous system depression and fires; pentane is highly flammable, with a flash point of −49 °C.[19] The use of a blowing agent is important for achieving low-density EPS foams, but the use of organic solvents as blowing agents is detrimental to workers and the environment.

Researchers and industry have realized the environmental issues with EPS foam packaging and have developed some biobased alternatives, such as starch and cellulose packing foams.[20,21] The preparation of these foams is different from EPS and from each other. Starch-based foam (SBF) is manufactured by preparing a slurry of starch and polyvinyl alcohol in water and then extruding it above 100 °C.[20] This technique uses the evaporation of water as the blowing agent to generate SBF in a consistent peanut shape. SBF packaging is the most well-known biodegradable foam. Cellulose-based foam (CBF) is prepared by dispersing cellulose fibres in water using a surfactant. The mixture is stirred rapidly to incorporate air to generate the foam. The foamed mixture is then drained of water and dried to produce the CBF.[21] These alternative foams have environmental benefits as they are prepared from renewable resources, avoid organic solvent blowing agents, and can biodegrade. However, there are performance trade-offs to directly using starch and cellulose in foam materials. Some of the desired physical properties that EPS foam possesses are missing from these biobased alternatives, notably good water resistance.[22] Poor water resistance in a foam packaging material may result in a loss of cushioning performance or damage to the valuable item. This undesired property is a consequence of the chemical structures of the biomass and additives used to prepare the foams (Fig. 1). While SBF and CBF materials do have environmental benefits compared to EPS packaging, consumers and industry prefer materials that have better performance features.

The environmental benefits of using biomass as an alternative in foam come at the expense of water resistance. Biobased foams such as SBF and CBF are extremely hydrophilic due to their chemical structure of glucose or cellulose units. The easy dissolution of starch-based foams at the end of life is a fantastic feature but any exposure to water during use is detrimental to the structural integrity of the SBF. CBF, while slightly more resilient when exposed to water than SBF, is still hydrophilic and disintegrates with water exposure.[21] There have been solutions created for this water resistance issue, such as applying hydrophobic coatings[23] or crosslinking.[24] These solutions address the lack of water resistance but may compromise the biodegradability, and recyclability of these biobased foam materials.

The chemical structure of the starch and cellulose-based foams also offers the ability for them to biodegrade. The biodegradability of materials is an excellent and environmentally conscious feature to have in a material and is the main draw towards using such a material. However, marketing biodegradability more so than recyclability gives the impression that

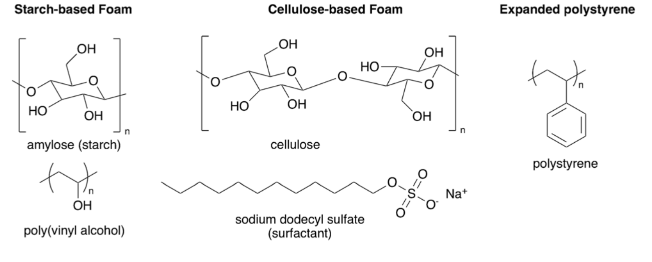

Fig. 1 Components in biobased and petroleum-based foams. (Left) Starch-based foam is comprised of starch and the polymeric stabilizer polyvinyl alcohol. (Center) Cellulose-based foam contains cellulose and a surfactant (SDS given as an example). (Right) Expanded polystyrene only contains polystyrene.

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these materials should be used once and then discarded into a landfill. These biobased foams, once discarded or damaged, should be recycled back into new foam products in a closed-loop system. This would reduce the amount of new biobased foam that needs to be produced, thereby conserving the resources needed to make it. However, for SBF, recycling is not common due to the ease of disposal by simple dissolution into water. CBF recycling is done more than SBF, using the intensive pulping process.[24] Biobased foams should be designed to be easily recyclable using simple processes, rather than easily discarded after a single use.

The use of biomass directly for foam packing materials has been demonstrated as a substitute for EPS foam but requires additional modifications to only partially improve water resistance. Rather than relying on additives or post-modifications to address the shortcomings of SBF and CFB materials, an alternative approach is to design a specific bioderived polymer that, once foamed, can almost mimic EPS physical properties. This would require using small molecules extracted from biomass that can be converted into styrene analogs with additional functional groups. The additional functional groups need to assist in improving the environmental concerns of EPS foam production and end-of-life processing, as well as the lack of water resistance in current biobased foam alternatives. Ideally, this new bioderived alternative foam can serve as a functional alternative to EPS while addressing the environmental harm caused by it.

Vanillin may serve as an intermediate towards a biobased substitute for petrochemical monomers like styrene (Fig. 2). Vanillin is a mass-produced commodity compound that presents promise for developing bioderived materials. Approximately 20 000 tonnes of vanillin are produced annually, with 15% of that coming from lignin.[25] In the 1980s, 60% of synthetic vanillin was produced from lignin but advances in synthetic procedures since then have shifted vanillin production more towards petrochemically derived sources.[27] However, with a global shift towards greener manufacturing and more sustainable materials, there may be a reemergence of large-scale production of vanillin from lignin.

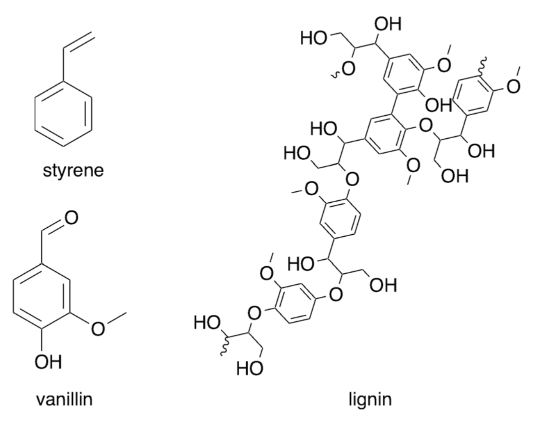
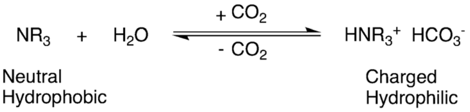


Fig. 2 The structures of styrene and vanillin and a representative structure for lignin.[26]

Preparing bioderived styrene analogs from vanillin has been demonstrated using the classical Wittig reaction but also with a Knoevenagel condensation, which is certainly more atom economical and likely a greener method.[28,29] The Knoevenagel method requires the use of malonic acid and an amine base. The only byproducts from the reaction are carbon dioxide and water, whereas in a Wittig reaction, the byproducts consist of triphenylphosphine oxide and a bromide salt. These byproducts require extensive separation to ensure a high-purity product. Using the Knoevenagel condensation for converting vanillin into a vinyl phenol is a simple, less wasteful synthetic method towards bioderived styrene analogs. While Knoevenagel condensation can produce bioderived styrene analogs from vanillin, these analogs have primarily been studied for their polymer properties, not for specific applications like foam packaging.[29] This reaction pathway provides a route towards bioderived styrene analogs without using wasteful and hazardous methods like the Wittig reaction.

Using the Knoevenagel condensation method, structurally similar molecules to styrene can be prepared but the switch to a bioderived styrene analog does not address the other harmful aspects of EPS, such as the use of organic solvent blowing agents. The manufacturing method of EPS uses the rapid evaporation of pentane to expand PS to an extremely low density. The lowest reported densities of commercial EPS foam packaging are 0.0032–0.004 g cm^3 for loose-fill peanuts.[30] For SBF and CBF, there are low densities reported, 0.019–0.026 g cm^3 and 0.011–0.045 g cm^3, respectively.[20,21] However, these reported densities are a magnitude higher than EPS, meaning that more foam material is being used to fill the same volume. Water evaporation is a capable blowing agent but the addition of an auxilary blowing agent may help lower the density further. An auxiliary blowing agent that can remain in the polymer after permeation and rapidly evaporate upon heating would be ideal but it needs to be non-hazardous, inexpensive, and abundant. CO_2 has been demonstrated as a blowing agent for foam materials but in its supercritical form.[31,32] CO_2 meets the criteria of non-hazardous, inexpensive and abundant but requiring supercritical CO_2 for foaming is an expensive method and potentially dangerous approach given the need for pressurized equipment. However, a simple alternative to using supercritical CO_2 is to use CO_2-responsive materials. These are materials that can interact with CO_2 at just 1 bar of pressure. This interaction causes a change in the material's properties. This mechanism provides a method to coordinate CO_2 to the polymer, which can then be released upon heating, similar to how EPS is manufactured.

Common CO_2-responsive materials contain a functional group of appropriate basicity, such as an amidine, amine, carboxylate anion, or phenolate anion, although tertiary and bulky secondary amines are most commonly used.[33] When CO_2 is dissolved into water, it forms dissolved CO_2 and a small amount of carbonic acid, both of which are acidic. When a tertiary amine is exposed to carbonated water, it becomes protonated, forming a trialkylammonium bicarbonate salt (Scheme 1). However, if CO_2 is removed from the system by



Scheme 1 The reaction between an amine, water and CO_2. When CO_2 is bubbled into water, carbonic acid and hydrated CO_2 are generated. These can protonate an amine, generating the bicarbonate salt. Removal of CO_2 by heating or purging with another gas will cause the reaction to reverse, generating the neutral amine.

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heating (~>60 °C) or purging with air, the trialkylammonium cations will deprotonate, becoming neutral amines again.[34] This easily reversible process can be used to dissolve a hydrophobic material containing amine groups into carbonated water, and then precipitate it out of solution by removing the CO_2.[35] Using this mechanism, materials that are traditionally water-insoluble can be made soluble in carbonated water by the addition of amine moieties.

Using CO_2-responsive materials presents a unique solution to the environmental problems of EPS and the water-resistance problem of SBF and CBF materials. Combining CO_2-responsive functional groups to bioderived styrene analogs would make it possible to (a) easily recycle to bioderived CO_2-responsive foam by dissolving into carbonated water, (b) use the rapid evaporation of CO_2 and water as blowing agent instead of pentane, and (c) allow the bioderived foam to have good water resistance after being blown because the neutral foam would be hydrophobic. A bioderived CO_2-responsive foam material that can mimic the physical properties of EPS foam as closely as possible while improving the negative aspects of EPS and current biobased foam that come from the preparation, use, and end-of-life stages, would be environmentally beneficial without sacrificing performance.

Herein, we report the design, synthesis, and testing of a new bioderived CO_2-responsive polymer that can be expanded into a rigid foam using the rapid evaporation of water and CO_2. Vanillin was modified using a one-pot Knoevenagel condensation to produce a vinyl phenol, which was further modified to install either a CO_2-responsive moiety or an acetyl group. The prepared monomers were then polymerized in carbonated water to produce high molecular weight polymers that were used without purification. The bioderived CO_2-responsive polymers were then foamed and tested for water resistance and compression strength. Afterwards, the foam was recycled using carbonated water and expanded into a new foam material. The recycled foam was again tested for water resistance and compression to compare the properties of the virgin and recycled bioderived CO_2-responsive foam to EPS foam.

Experimental methods and materials

Materials

Vanillin (99%), Amberlyst 120-ir H form, anhydrous sodium bicarbonate, toluene (ACS grade), hydrochloric acid (36.5%, technical), and anhydrous magnesium sulfate were purchased from Fisher Scientific. Acetic anhydride (99.5%), malonic acid (99%), piperidine (99%), *N*,*N*-(diethylamino)ethyl chloride hydrochloride (99%), sodium hydroxide (≥98%), hexanes (ACS grade), triethylamine (≥99%), and ethyl acetate (ACS grade) were purchased from MiliporeSigma. Potassium *tert*-butoxide (97%) was purchased from VWR International. The thermal initiator 2,2′-azobis[2-(2-imidazolin-2-yl)propane] (VA-061) was purchased from Fujifilm Wako Chemicals and recrystallized from ethanol to remove impurities. Carbon dioxide gas (CO_2, 3.0) was purchased from Linde Canada. All chemicals were used as received, except as otherwise noted.

Synthesis of 2-methoxy-4-vinylphenol (MVP)

To a 250 mL round bottom flask, 90 mL of toluene was added, followed by vanillin (9.13 g, 60 mmol), malonic acid (6.86 g, 66 mmol), and piperidine (5.92 mL, 60 mmol). The flask was fitted with a Dean–Stark apparatus and then placed into a 120 °C oil bath and magnetically stirred for 2.5 h. Afterwards, the flask was cooled to room temperature. Amberlyst 120-ir H form (25 g) was added to the flask and magnetically stirred for 16 h at room temperature to remove the piperidinium salt. The mixture was filtered through glass wool. The filtrate, a toluene solution of MVP, was used for the syntheses of DEAEMS and MVPA without further purification (yield 80%). The yield of MVP in the solution was determined by ^1H NMR spectroscopy using 99.9% acetone as the internal standard. The amberlyst 120-ir H form was regenerated by stirring it in 100 mL of 2 M hydrochloric acid for 2 h. The resin was then washed with deionized water (DI) 3 times, using 100 mL for each wash. The resin was dried in a vacuum oven at 60 °C for 24 h and reused. ^1H NMR of MVP (499.86 MHz, $CDCl_3$) δ 6.95 (d, J = 1.9 Hz, 1H), 6.93 (dd, J = 8.1, 1.9 Hz, 1H), 6.89 (d, J = 8.1 Hz, 1H), 6.65 (dd, J = 17.5, 10.8 Hz, 1H), 5.70 (s, 1H), 5.61 (d, J = 17.5 Hz, 1H), 5.14 (d, J = 10.8 Hz, 1H), 3.91 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR of MVP (125.81 MHz, $CDCl_3$) δ 146.72, 145.77, 136.76, 130.41, 120.18, 114.49, 111.55, 108.19, 55.99 ppm. The observed ^1H and ^{13}C $\{^1H\}$ NMR spectra match those reported in the literature.[29]

Synthesis of 4-diethylaminoethoxy-3-methoxystyrene (DEAEMS)

In a glovebox, potassium *tert*-butoxide (KO*t*-Bu, 16.2 g, 144 mmol), was weighed into a 500 mL Schlenk flask. The flask was sealed, removed from the glovebox, and transferred to a Schlenk line. Under an inert atmosphere, the 90 mL toluene solution containing MVP (7.20 g, 48 mmol) was added *via* cannula. The mixture was stirred at room temperature for 1 h to deprotonate MVP. After 1 h, under an inert atmosphere, *N*,*N*-(diethylamino)ethyl chloride hydrochloride (12.4 g, 72 mmol) was added to the flask. The flask was sealed under an inert atmosphere and then placed into a 60 °C oil bath for 24 h. Afterwards, the mixture was cooled to room temperature and washed with 1 M sodium hydroxide solution (5 × 50 mL, under air). The organic phase was dried using magnesium sulfate ($MgSO_4$) and then filtered. The filtrate was concentrated by rotary evaporation. The residue was purified by column

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chromatography using 95 : 5 hexanes : triethylamine by volume as the eluent and silica as the stationary phase. The product was concentrated by rotary evaporation, and a faintly yellow oil remained (yield 70%). ^{1}H NMR of DEAEMS (499.86 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.92 (d, J = 8.2 Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H), 6.63 (dd, J = 17.9, 10.7 Hz, 1H), 5.60 (d, J = 17.6 Hz, 1H), 5.13 (d, J = 11.0 Hz, 1H), 4.08 (t, J = 5.6 Hz, 2H), 3.87 (s, 3H), 2.91 (t, J = 5.7 Hz, 2H), 2.62 (q, J = 6.7 Hz, 4H), 1.05 (t, J = 7.0 Hz, 6H) ppm. ^{13}C {^{1}H} NMR of DEAEMS (125.81 MHz, $CDCl_3$) δ 149.48, 148.45, 136.59, 130.94, 119.52, 112.87, 111.85, 109.14,67.61, 55.98, 51.73, 48.02, 12.06 ppm. Calculated $M + 1 = 250.18016$ g mol^{-1}, observed $M + 1 = 250.18097$ g mol^{-1}.

Synthesis of 2-methoxy-4-vinyl phenyl acetate (MVPA)

MVP (7.20 g, 48 mmol) in 90 mL of toluene was placed into a 250 mL round bottom flask under air. Anhydrous sodium bicarbonate ($NaHCO_3$) (8.06 g, 96 mmol) was added to the MVP solution, followed by acetic anhydride (13.6 mL, 144 mmol). The reaction was sealed and stirred for 24 h at room temperature. After 24 h, 100 mL of aqueous saturated $NaHCO_3$ was added to neutralize the remaining acid. The mixture was stirred vigorously for 30 min. The mixture was subsequently poured into a separatory funnel, separated and then the organic layer was washed twice with 100 mL of aqueous saturated $NaHCO_3$. The organic layer was subsequently washed with 100 mL brine once, dried over $MgSO_4$, and filtered through glass wool. The filtrate was concentrated by rotary evaporation. The residue was purified by column chromatography using 60 : 40 hexanes : ethyl acetate by volume as eluent and silica as the stationary phase. The product was concentrated by rotary evaporation, and a clear colorless oil remained (yield 80%). ^{1}H NMR of MVPA (499.86 MHz, $CDCl_3$) δ 7.05–6.94 (m, 3H), 6.69 (dd, J = 17.6, 10.9 Hz, 1H), 5.70 (d, J = 17.6 Hz, 1H), 5.25 (d, J = 10.9 Hz, 1H), 3.86 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C {^{1}H} NMR of MVPA (125.81 MHz, $CDCl_3$) δ 169.09, 151.19, 139.55, 136.75, 136.38, 122.85, 119.02, 114.17, 110.01, 55.91, 20.73 ppm. The observed ^{1}H and ^{13}C {^{1}H} NMR spectra match those reported in the literature.[29]

Polymerization of DEAEMS

In a 50 mL round bottom flask, a 25 wt% mixture of DEAEMS in deionized (DI) water was prepared. The mixture was bubbled with 1 bar of CO_2 using a 22-gauge stainless steel needle for 1 h to protonate the DEAEMS thereby making it soluble in carbonated water. After 1 h, 0.5 mol% relative to monomer of 2,2′-azobis[2-(2-imidazolin-2-yl)propane] (VA-061) was added to the flask. The solution was bubbled with CO_2 and stirred for 30 min at room temperature to dissolve the VA-061. After 30 min, the needle supplying the CO_2 gas was raised out of the solution and remained in the headspace for the duration of the experiment. Simultaneously, the vent needle used to allow CO_2 bubbling to occur was removed, leaving the flask closed but with a constant supply of CO_2 being delivered to the round-bottom flask. To avoid over-pressurization, the CO_2 supply line had a mineral-oil bubbler attached to allow excess pressure to escape. The flask was placed into a 50 °C oil bath for 16 h. After the reaction was complete, the solution was continuously bubbled with CO_2 to evaporate water until the solids content increased to 40 wt%. The resulting 40 wt% polymer solution was used for generating foams without purification.

Copolymerization of DEAEMS and MVPA

In a 50 mL round bottom flask, a 40 wt% mixture of DEAEMS : MVPA at a mol ratio of 70 : 30 in DI water was prepared. The mixture was bubbled with CO_2 using 22-gauge stainless steel needle for 1 h to protonate the DEAEMS making it soluble in carbonated water. MVPA remained a separate liquid phase. After 1 h, 0.5 mol% relative to total monomer of VA-061 was added to the flask. The mixture was bubbled with CO_2 using a 22 gauge stainless steel needle and magnetically stirred for 30 min at room temperature to dissolve the VA-061. After 30 min, the needle supplying the CO_2 gas was raised out of the solution and remained in the headspace for the duration of the experiment. Simultaneously, the vent needle used to allow CO_2 bubbling to occur was removed, leaving the flask closed but with a constant supply of CO_2 being delivered to the round-bottom flask. To avoid over-pressurization, the CO_2 supply line had a mineral-oil bubbler attached to allow excess pressure to escape. The flask was placed into a 50 °C oil bath for 16 h. After 16 h, the flask, while still under a CO_2 gas supply, was removed from the oil bath and left to spontaneously cool to room temperature. The flask was supplied with CO_2 for 24 h to fully saturate the carbonated polymer solution. The resulting polymer solution was used for generating foams with no purification.

Polymer property determination

The molecular weights and dispersities were obtained by gel permeation chromatography (GPC) calibrated against monodisperse PS standards. Samples were dried in a vacuum oven at 25 °C for 24 h, dissolved in tetrahydrofuran (THF) at a concentration of 5 mg mL^{-1}, and filtered using a 0.22 μm Chromspec filter before injection. A Waters 2695 separation module equipped with a Waters 410 differential refractometer used THF as the eluting solvent at a flow rate of 0.3 mL min^{-1} through Waters Styragel HR (4.6 × 300 mm) using 4, 3, 1 and 0.5 separation columns. Differential scanning calorimetry (DSC) was performed using a TA Instruments Q100 DSC to determine polymer glass transition temperatures (T_g). N_2 flow was set to 50 mL min^{-1}. A DSC cycle was performed starting at −70 °C and heating to 150 °C, followed by an isothermal hold for 5 min, then cooling back to −70 °C and heating back to 150 °C. All heating and cooling rates were 10 °C min^{-1}. The PDEAEMS and P(DEAEMS-*co*-MVPA) samples were dried under vacuum for 24 h prior to analysis.

The thermogravimetric analysis (TGA) of the polymers was performed using a TA Instruments TGA Q500. Samples were dried under vacuum for 24 h at 25 °C. Samples were then placed onto a tared platinum pan. The autosampler proceeded to place the sample onto the microbalance hook and the oven was raised around the sample. Nitrogen gas was flowed

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through the oven at flow rate of 50 ml min^{-1}. The TGA cycle was started by raising the temperature to 100 °C at a rate of 10 °C min^{-1}. When the temperature was reached, an isothermal hold was done for 10 min to remove residual water. After 10 min, the temperature was increased at a rate of 10 °C min^{-1} to 800 °C. After the cycle was complete, the sample was then cooled and removed from the oven. The analysis of the thermogram was done using the TA Universal Analysis software.

Foaming and recycling procedure

To prepare a foam, 1.5 g of the 40 wt% polymer solution was shaped into a sphere and placed into a cylindrical glass mould. The mould dimensions were 5.0 cm long by 2.5 cm in diameter. A 1600 W heat gun was used for approximately 10 s to rapidly heat the polymer solution up. Once the polymer solution changed from translucent to opaque and the sphere began to expand, the glass mould was then placed into a vacuum chamber. The pressure was reduced to −1 bar of gauge pressure for 24 h at room temperature. After 24 h, the foam was removed from the vacuum chamber was characterized for bulk density, porosity, internal cell structure, and compression strength. Afterwards, the foam beads were placed into a 20 mL vial and crushed to increase their surface area. DI water was added to prepare a 40 wt% mixture. The mixture was bubbled with CO_2 for 24 h to allow complete saturation and dissolution to occur. The polymer solution was then foamed again using the established method.

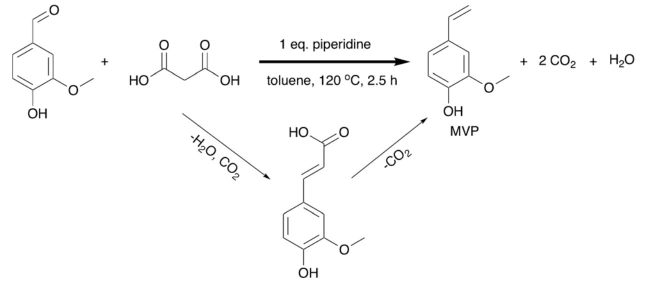
To prepare a foam for smaller-scale testing, 0.25 g of 40 wt% polymer solution was shaped into a sphere and placed onto a glass slide. The polymer solution was heated directly with a 1600 W heat gun for approximately 5 s and then placed into the vacuum chamber. The pressure was reduced to −1 bar of gauge pressure for 24 h at room temperature. Afterwards, the expanded foam beads were used for observation in optical microscopy and water resistance testing.

Foam characterization

The average bulk foam density was evaluated by cylindrical foam samples in triplicate. The average bulk volume of each sample was determined by measuring the length and circumference of the foam in triplicate. The circumference was used to determine the cross-sectional area. The volume was then calculated using the average length of the cylinder multiplied by the average cross-sectional area. The average bulk density of the foam was calculated by dividing the average mass of the foam sample by the average total volume. To determine porosity, the ratio of the volume of void space to the total volume was calculated. To find the volume of void space, the volume of the polymer was subtracted from the total volume. To calculate the volume of polymer required the density of the bulk polymer to be determined. The density of the polymer was determined by measuring the mass of three solid spheres in triplicate and then determining their volume by water displacement measurements. The water displacement measurements were done in triplicate. The volume of the polymer in a foam specimen was then determined by dividing the mass of the foam by the density of the polymer. To identify the foam morphology, an optical microscope at 20× magnification was used to observe and record images the foams.

Results and discussion

The preparation of the bioderived monomers, MVP, MVPA and DEAEMS began with the modification of vanillin using the Knoevenagel condensation (Scheme 2). The precursor monomer MVP was prepared using a modified literature method.[28] Using toluene as the solvent, vanillin (60 mmol) was reacted with malonic acid (66 mmol) in the presence of piperidine (60 mmol) to produce MVP in quantitative yield. The only byproducts were CO_2 and water, which were removed *in situ* using a Dean Stark apparatus and an unsealed vessel. Traditionally, aldehydes are converted to vinyl groups using the Wittig reaction, as it is an effective method for producing vinyl groups. However, it produces a large amount of waste and has an extensive purification process. This Knoevenagel transformation provides the desired vinyl product with CO_2 and water as the byproduct rather than the bromide salt and triphenylphosphine oxide produced from the Wittig reaction. There have been several reports of producing MVP using the Knoevenagel condensation method, all with different conditions and levels of success.[28,29,36] The method described by Simpson *et al.* was selected over other methods as it was the only method that produced the desired product in 4 h with 100% conversion using a single-pot reaction. Other reports required two-pot synthesis, purification of the intermediate to proceed to MVP, or had low conversions. Other reaction conditions were assessed, such as reducing the piperidine loading to 0.5 and 0.75 eq. but this resulted in worse conversion so 1 eq. was used. The reaction time was reduced from 4 h to 2.5 h as ^1H NMR analysis of the crude mixture at 30 min intervals indicated the reaction was complete after 2.5 h. The temperature was not lowered as the second decarboxylation step would not progress to completion at lower temperatures. This was a common occurrence during testing and was also reported in the literature.[37]



Scheme 2 Reaction pathway for the synthesis of MVP. The reaction follows a two-step, one-pot process starting with a Knoevenagel condensation, followed by a thermal decarboxylation using piperidine as the amine catalyst.

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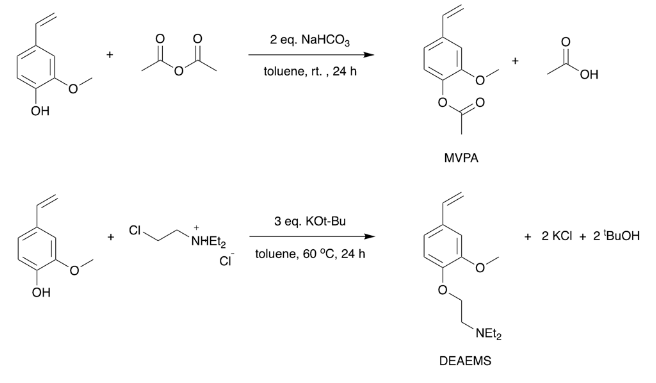
In an effort to improve process efficiency, reduce waste, and lower reagent consumption, common purification methods, such as precipitation, extraction, and column chromatography, were avoided. A simpler purification method was chosen instead, which used an acidic exchange resin that could be regenerated and reused after the process was complete. After the reaction was completed, the toluene solution contained the product MVP as its piperidinium salt. The addition of Amberlyst 120-ir H form converts the phenolate anion to the neutral phenol, whereas the piperidinium cation becomes the counter ion in the ion exchange resin. MVP was separated from the resin through filtration, producing an orange solution. ^{1}H NMR spectroscopy confirmed the production of MVP and that all the piperidine had been removed from the solution. The remaining product was not isolated from the orange solution, as it was prone to oxidation and was used in the next reactions without further purification. The ion exchange column was regenerated and reused using acidic washes to reprotonate the resin and remove the piperidinium cation.

Without isolating MVP from the toluene solution, the second monomer MVPA was synthesized (Scheme 3, Top). Again, a literature method was used and modified.[37] Acetic anhydride was added to the MVP solution in 3-fold excess to ensure complete conversion to MVPA. Anhydrous $NaHCO_3$ was added to neutralize the acetic acid produced during the reaction. The mixture was left to react at room temperature for 24 h. During the course of the reaction, the orange colour increased in intensity. However, after purification, a clear colourless monomer was obtained. Lower quantities (1.1–2.5 eq.) of acetic anhydride were explored to reduce material consumption but resulted in incomplete conversion of MVP to MVPA in 24 h. A 3-fold excess was found to be the minimum required to have complete conversion within 24 h. A similar result was reported by Lugemwa *et al.*[37] However, they report 5-fold excess as the minimum amount of acetic anhydride needed for complete acetylation of vanillin. The lower quantity of acetic anhydride needed for complete conversion of MVP may be caused by the increased nucleophilicity of MVP compared to vanillin, as the vinyl group is an electron-donating group rather than an electron-withdrawing group like the aldehyde in vanillin. The observed change in orange colour was thought to be further oxidation of MVP; however, under inert conditions, the same result occurred. The original method was kept with no alterations as the inert conditions did not produce a higher yield. The purpose of this reaction was to produce an air-stable monomer, which was obtained after purification. ^{1}H and ^{13}C {^{1}H} NMR spectra confirmed the structure of MVPA and matched the literature.[29]



Scheme 3 Synthetic routes for MVPA and DEAEMS.

As mentioned in the introduction, amines and phenolate anions are both known to be CO_2-responsive functional groups. Because MVP is a phenol, it would be tempting to simply deprotonate it and then use its conjugate base as a CO_2-responsive monomer. However, that strategy is not likely to be successful. Anionic CO_2-responsive materials like phenolates and carboxylates operate in reverse to amine CO_2-responsive materials, using the presence of CO_2, rather than its absence, to produce the neutral form. Phenolate or carboxylate switchable species would therefore not be suitable for a CO_2-responsive foam because we propose using CO_2 loss, not CO_2 addition, to simultaneously generate the neutral polymer and blow it to a foam. The other problem with using an anionic switchable molecule would be the salt accumulation generated during the addition of CO_2 into the system; neutralizing the material with carbonated water causes the auxiliary base to remain as a bicarbonate salt which will remain within the material, producing undesired properties. Thus, an amine group is preferred over a phenolate or carboxylate group as the CO_2-responsive functional group in the proposed packing foam.

Using a separate batch of MVP in toluene, the CO_2-responsive monomer DEAEMS was prepared (Scheme 3, bottom) using a Williamson ether synthesis with *N*,*N*-(diethylamino)ethyl chloride hydrochloride. An excess of KO*t*-Bu was used to completely deprotonate both MVP and *N*,*N*-(diethylamino)ethyl chloride hydrochloride. Typically, Williamson ether syntheses are performed in more polar solvents to facilitate the reaction. However, MVP was stored in toluene; the reaction was performed in the toluene containing MVP to avoid unnecessary solvent removal and replacement. Despite the use of a non-ideal solvent, the reaction progressed to completion over 24 h and remained orange throughout the reaction. After purification, a faintly yellow oil remained.

Synthesis and characterization of PDEAEMS

The preparation of PS beads for use in EPS is done through suspension polymerization using stabilizers to maintain droplet integrity throughout the polymerization. This polymerization technique is known to produce polymers with molecular weights in the hundreds of thousands of daltons. High molecular weight polymers typically have good mechanical properties, which is desired in foam materials. A similar approach was taken in the preparation of PDEAEMS.[38] However, to avoid adding auxiliary components like a stabilizer to the polymerization, it was thought that DEAEMS could act as both the monomer and stabilizer. It has been reported that CO_2-responsive monomers are capable of serving as both a

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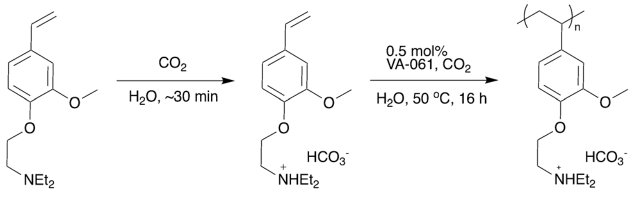
monomer and a stabilizer in the preparation of emulsion polymerizations.[39] Achieving a stable suspension polymerization requires water as the continuous phase, a dispersed oil phase, a stabilizer, and an initiator. In this case, carbonated water was the continuous phase. The dispersed oil phase was neutral DEAEMS as it is not particularly water-soluble. The stabilizer was protonated DEAEMS, which is expected to prevent the coalescence of the unprotonated DEAEMS, keeping the droplets suspended. The thermal initiator was VA-061, a CO_2-responsive azo initiator. To prepare the polymerization, DEAEMS and VA-061 were added to deionized water, creating a mixture. The solution was sparged with CO_2 for 30 min using a stainless steel needle to protonate DEAEMS and VA-061, causing them to dissolve. At room temperature (~20 °C) all the components are dissolved. However, the reaction occurs at 50 °C (Scheme 4). The elevated temperature lowers the solubility of CO_2 in water, shifting the CO_2 more into the gas phase. This, and possibly shifts in other equilibria in the system, causes deprotonation of some of the DEAEMS, leading to phase separation. With a mixture of protonated and deprotonated DEAEMS, it was thought that this polymerization may behave similarly to suspension polymerization (Fig. 3). However, this was not observed. GPC analysis was performed on the resulting polymer and the M_w for PDEAEMS was determined to be 29 kDa rather than the 100–400 kDa observed in PS suspension polymerization (Table 1). The polymerization of DEAEMS was performed at 25 wt% of monomer in carbonated water and had quantitative conversion confirmed by ^{1}H NMR spectroscopy after 16 h.

Table 1 Properties of bioderived CO_2-responsive polymers compared to commercial PS

Polymer	M_n [c] kDa	M_w [c] kDa	Dispersity ($Đ$)	T_g [d] (°C)
PDEAEMS[a]	9.5	29	3.0	25
P(DEAEMS-*co*-MVPA)[b]	29	111	3.8	44
Commercial EPS[42]	—	100–200	—	100

[a] Polymerized using 25 wt% DEAEMS in water, 0.5 mol% VA-061 (relative to monomer), reacted for 16 h at 50 °C, under a CO_2 atmosphere. [b] Polymerized using 40 wt% monomers in water, 70 : 30 feed ratio of DEAEMS : MVPA, 0.5 mol% VA-061 (relative to total monomer), reacted for 16 h at 50 °C, under a CO_2 atmosphere. [c] Determined using GPC analysis. [d] Determined using DSC analysis.

During and immediately after the reaction, the solution's viscosity had an appearance similar to that of water. This was caused by a portion of the polymer being deprotonated, which leads to the polymer being hydrophobic and phase separated from the water (Fig. 4a). As the reaction cooled, CO_2 was bubbled through the solution. Visually, the viscosity of the solution began to increase substantially after just 2 h as the polymer was protonating, which increased interactions with carbonated water. CO_2 was continuously bubbled for 24 h to remove water and raise the solids content to 40 wt%; this further increased the viscosity of the polymer solution as all the carbonated water was trapped in the charged polymer



Scheme 4 Polymerization of DEAEMS in carbonated water using VA-061 as the thermal initiator.

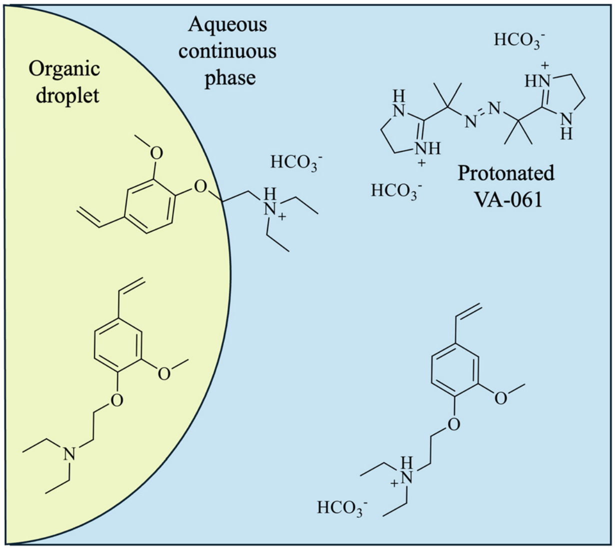


Fig. 3 Representation of the suspension polymerization of DEAEMS in carbonated water.

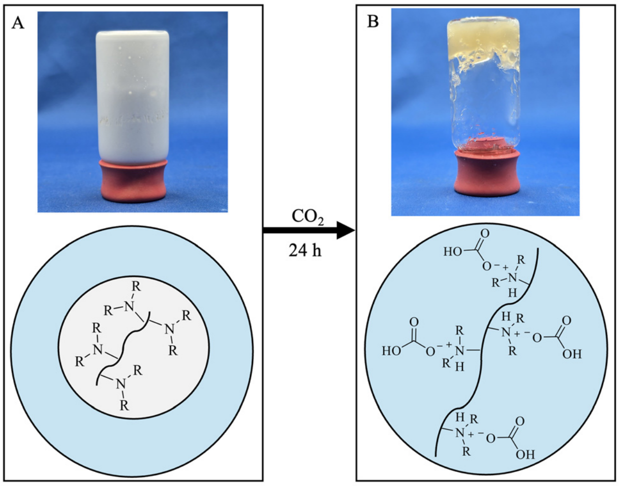


Fig. 4 Change in viscosity of PDEAEMS after 24 h of CO_2 exposure (1 bar). (A) Neutral PDEAEMS interacts poorly with neutral water so precipitates, giving a water-like viscosity. (B) Protonated PDEAEMS interacts strongly with carbonated water through hydrogen bonding. Carbonated water swells the protonated polymer matrix, resulting in the observed increase in solution viscosity.

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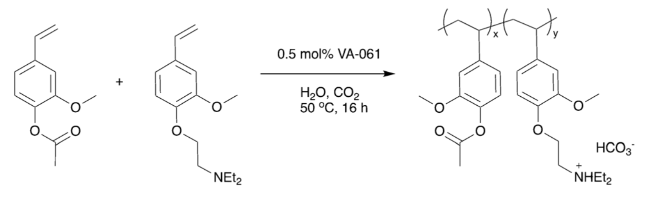
matrix. The increase in solids content, combined with strong interaction with water, caused the solution to not flow at all when inverted (Fig. 4b). The increased solids content was done because it was found that higher solid content solutions produced more consistent foams.

Ideally, DEAEMS would be polymerized at 40 wt% rather than evaporating water from a 25 wt% solution to obtain the desired final product concentration. However, polymerizing DEAEMS at a 40 wt% monomer concentration was attempted several times, but polymerization was not achieved on each attempt. Observing the ^{1}H NMR spectrum of the solution, it appeared that no reaction took place. A potential explanation for this undesired result is that the thermal initiator, VA-061, was not decomposing at 50 °C into its radical species needed to initiate the polymerization. A thermal initiator's decomposition rate is temperature dependent, but for VA-061, it has also been reported to be pH dependent as well.[40] VA-061 is a bisimidazoline azo initiator which can become protonated in carbonated water. When VA-061 is neutral it has a 10 h half life at 61 °C, but when fully protonated that temperature is lowered to 45 °C.[41] If VA-061 was not protonated sufficiently in the solution of DEAEMS and carbonated water then its decomposition temperature may have been too high to initiate the polymerization. It has been reported that when two amines with different basicities are in the same aqueous solution, they can influence the protonation of each other.[43] If DEAEMS limited the protonation of VA-061, then the reaction temperature may not have been high enough for significant initiation to occur, leading to the observed result of no reaction at 40 wt% monomer.

A key property for producing a rigid foam is that the material has a T_g significantly above room temperature. PS has a T_g of 100 °C, for example. Ideally, the bioderived CO_2-responsive polymers would have T_g values well above the temperatures that packages would be exposed to in hot warehouses or trucks. A typical maximum temperature for warehouse storage is 40 °C.[44] After analysis of the thermogram for PDEAEMS the T_g was found to be only 25 °C. This was an undesirable T_g because the foams generated from PDEAEMS were soft and susceptible to collapse if mishandled.

Synthesis and characterization of P(DEAEMS-*co*-MVPA)

Because of the unsatisfactory properties of PDEAEMS, the synthesis of P(DEAEMS-*co*-MVPA) was pursued instead (Scheme 5). Polymerizing protonated DEAEMS with the non-switchable MVPA in water was expected to produce higher molecular weights better than the homopolymerization of DEAEMS as the reaction would behave more like a true suspension polymerization; DEAEMS acting as the stabilizer and MVPA as the dispersed oil phase. Ganachaud *et al.* reported a similar polymerization method, which used permanently charged amine monomers, which acted as both surfactants and comonomers in the polymerization of styrene.[45] The polymerizations produced by Ganachaud *et al.* resulted in copolymers with M_w 100–500 kDa, which was the target range for P(DEAEMS-*co*-MVPA). MVPA is hydrophobic and poorly water soluble, so it remained phase-separated for the entirety of the polymerization; this, in combination with the protonated DEAEMS as the stabilizer, provided sufficient conditions to produce a suspension polymerization, generating higher molecular weight polymers than the homopolymerization (Table 1). The polymerization of P(DEAEMS-*co*-MVPA) was performed at 40 wt% of total monomer and progressed to quantitative conversion in 16 h. This polymerization was able to progress at a higher loading of total monomer; however, the concentration of DEAEMS in the reaction was only 30 wt% monomer. This concentration seems to be within the acceptable limit of amine-containing monomer, which allows effective polymerization to occur.



Scheme 5 Copolymerization of DEAEMS and MVPA in a 70 : 30 molar ratio in carbonated water using VA-061 as the thermal initiator.

The copolymer of DEAEMS and MVPA was synthesized to increase the polymer's T_g and hopefully produce a more rigid foam. The reported T_g of PMVPA is 104 °C.[29] A composition was prepared with a 70 : 30 molar feed DEAEMS : MVPA ratio. This feed ratio provided a sufficient amount of DEAEMS in the copolymer to allow the polymer to dissolve into carbonated water, while maximizing the potential increase in T_g. Using the Fox equation, P(DEAEMS-*co*-MVPA) was predicted to have a T_g of 41 °C (see SI for calculation). Experimentally, P(DEAEMS-*co*-MVPA) produced a T_g of 44 °C, which was slightly higher than the predicted value. The P(DEAEMS-*co*-MVPA) T_g was acceptable as it is higher than warehouse temperatures and high enough to produce a rigid foam that does not collapse when handled at room temperature.

Foam preparation and characterization

In industry, steam is used to cause the rapid evaporation of the pentane to expand the hard PS pellets. After the initial foaming using steam, the expanded foam beads are placed into a chamber to age, allowing the further release of pentane to occur. The beads are placed into a mould and heated again to expand the foam beads to the final size, shape and density. A similar process is used for foaming P($DEAEMS_{70}$-*co*-$MVPA_{30}$) but uses the rapid evaporation of carbonated water instead, similar to SBF preparation. The P($DEAEMS_{70}$-*co*-$MVPA_{30}$) polymer is dissolved in carbonated water at 40 wt% solids. The material can be handled like a soft solid, as the solution displays extreme viscosity. To prepare a P($DEAEMS_{70}$-*co*-$MVPA_{30}$) foam, a piece of 40 wt% P($DEAEMS_{70}$-*co*-$MVPA_{30}$) solution was shaped into a sphere and placed into a glass mould that is 5 cm in length and 2.54 cm in diameter. A 1600 W heat gun was used to ensure rapid and direct heating of the

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P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) solution. During the approximately 10 s heating process, the removal of water and CO_2 causes the amines contained within the polymer to deprotonate, generating the neutral, hydrophobic polymer. At the same time, the polymer is raised above its T_g, allowing the CO_2 and water vapour to expand the polymer chains and generate the foam. However, excessive heating of the polymer during the foaming process led to the collapse of the foam before the drying step was completed. To prevent this from occurring, the heat was stopped immediately after the entire polymer solution had changed from translucent to opaque. The polymer was placed into a vacuum chamber for 24 h to finish the drying process and expand the foam to its final size (Fig. 5).

Cylindrical foams were prepared to mimic traditional EPS packing peanuts. P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) was prepared at 40 wt% solids content in carbonated water. At this solids content, the polymer solution can be manipulated into spheres that can maintain their shape. At lower concentrations of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$), inconsistent foaming occurred, leading to unusable test samples. Approximately 1.5 g of the 40 wt% polymer solution was rolled by hand into a sphere to prepare the foams. The P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) solution bead was placed into the glass mould and heated for approximately 10 s until the solution changed from translucent to opaque and the bead began to expand. After, the entire mould was placed into a vacuum chamber to allow the bead to expand to its final size and remove the remaining water and CO_2. The foams produced had a similar structure and appearance to commercial EPS packing peanuts (Fig. 6).

To determine the average bulk volume of each sample, the length and circumference of each foam were measured in triplicate. From the circumference measurements, the cross-sectional area was calculated and averaged. The average area was multiplied by the average length to give the average volume. The foam samples were then weighed in triplicate, and the average weight was determined for each sample. The density was then calculated using the average mass of the sample divided by its volume. The average bulk density of the prepared foams was determined to be 0.04 g cm^{-3} ± 0.006. The density of these prototype bioderived foams is a magnitude higher than that of commercial EPS peanuts, which have an average density of approximately 0.0032–0.004 g cm^{-3}.[30] The density of this P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam was similar to that of the current SBF and CBF which have densities of 0.019–0.026 g cm^{3} and 0.011–0.045 g cm^{3} respectively.[20,21] Commercial EPS beads undergo four expansion cycles to achieve this exceptionally low density. The bioderived foams only underwent one expansion cycle as a second intense heating cycle causes the foam to shrink.

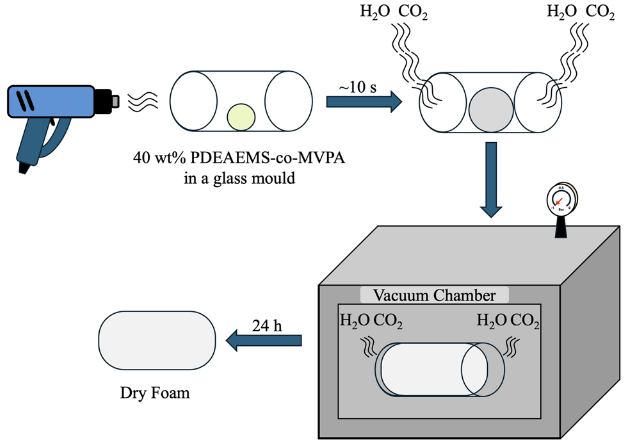

Fig. 5 Preparation method of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam.

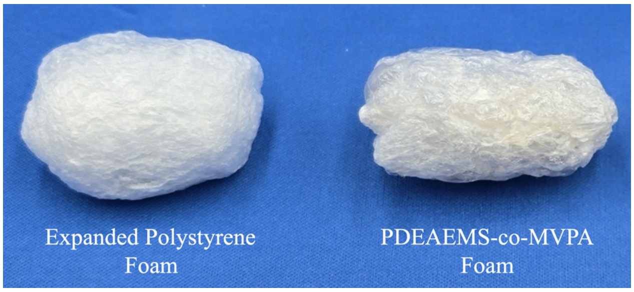

Fig. 6 Image of EPS foam peanut and P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam.

The single expansion cycle density of commercial EPS peanuts is 0.014 g cm^{-3} which is still lower than that of the P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam.[30] The foaming procedure used here for the bioderived peanuts was crude compared to the industrial processing of commercial EPS which has been optimized over decades. There is certainly room for future development of the foaming method. The demonstration of the rapid evaporation of CO_2 and water vapor as a blowing agent was achieved on multiple trials with consistent results. An optimized blowing procedure could likely attain much lower densities.

A key component of foams is their porosity. The porosity of a material is the ratio of the volume of the void space to the total volume of the material (eqn (1)).

$$\text{Porosity} = \frac{V_{\text{void space}}}{V_{\text{total}}} \times 100\% \tag{1}$$

In the case of a foam, the volume of void space is the total pore volume divided by the bulk volume of the foam structure (Fig. 7). The total volume is the bulk volume, and is easily measured. The volume of the void space is the total volume minus the volume occupied by the polymer within the foam (eqn (2)).

$$V_{\text{total}} - V_{\text{polymer}} = V_{\text{void space}} \tag{2}$$

The volume of the polymer is calculated using eqn (3).

$$V_{\text{polymer}} = \frac{m_{\text{polymer}}}{\rho_{\text{bulk polymer}}} \tag{3}$$

By dividing the mass of polymer used in the foam by its bulk density (not the density of the foam) the volume of polymer in the foam can be calculated.

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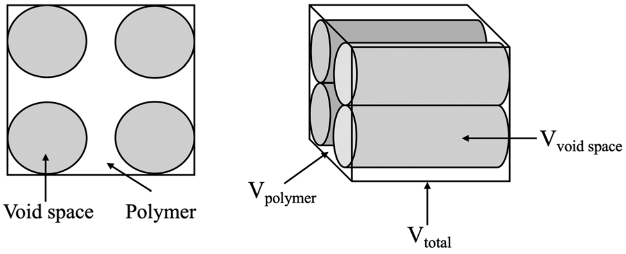

Fig. 7 Representative diagram of the internal structure of a foam. By determining the V_{polymer}, $V_{\text{Void space}}$, and V_{total}, the porosity of a foam can be calculated.

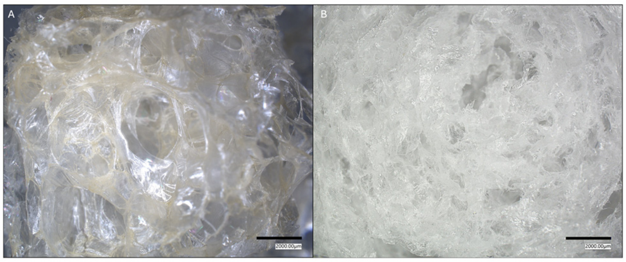

Fig. 8 Optical microscope images of the cross-section of (A) P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) and (B) EPS foam peanuts at 20 times magnification.

Since P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) is a new polymer, its bulk density had to be measured. A dry, non-foamed sample of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) was prepared by allowing 3.75 g of 40% P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) to slowly dry at ambient conditions for 7 days. This avoided foaming of the sample from occurring. After the 7 days, the polymer sample was further dried in a vacuum oven at 60 °C for 24 h to remove any residual moisture and CO_2. No foaming occurred during this drying step. The solid, dried polymer was removed from the oven and cut into thirds. The three solid P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) samples were weighed in triplicate. The volume of each polymer sample was measured in triplicate by water displacement. Using these averaged values of volume and mass, the average bulk density of the P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) polymer was then calculated to be 1.02 g cm^{-3} ± 0.003. Using this average bulk polymer density, the V_{polymer} in a foam sample can be calculated.

Three different foam samples were prepared using the established foaming methods to calculate V_{polymer}, V_{total}, $V_{\text{void space}}$ and porosity. The cylindrical foams were measured for V_{total} using a ruler and micrometre. Measurements were taken in triplicate and averaged. To determine V_{polymer}, the three foam samples were individually weighed in triplicate. The mass of each foam was averaged. Using eqn (3), the average V_{polymer} in the foam samples was calculated. With V_{total} and V_{polymer} known, $V_{\text{void space}}$ for each foam sample was calculated. Porosity was calculated using eqn (1). The average porosity of the three samples was 92% ± 1%. The porosity for EPS packing peanuts is 95–98%, depending on the manufacturer.[46,47]

EPS foams can differ in internal structure, either by having a closed-cell or open-cell morphology. A closed-cell foam morphology features individual, non-interconnected voids, whereas an open-cell foam has interconnected voids throughout the entire foam. Closed-cell foams typically have higher density and are used in insulation applications as their air and moisture permeability are low. Open-cell EPS foams are used in loose-fill packaging applications like packing peanuts.[48] To compare the internal structure of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam to a commercial EPS peanut, the foams were cut in half and the cross-sectional area was observed under optical microscopy (Fig. 8). The P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam displayed interconnected pores, resembling an open-cell foam structure. The commercial EPS peanut also presented an open-cell foam structure but the pore structure was smaller than the P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam. The evaporation of CO_2 and water during the foaming process produces an irregular open-cell structure with large pore sizes (see SI for measured pore sizes).

One of the design features of CO_2-responsive polymers is to interact strongly with carbonated water but poorly with neutral or basic water. This provides the polymer with good water resistance during use and ease of recyclability at the end of life using carbonated water. However, in some cases, the amines contained within the polymer can interact with neutral water. This occurs when the amine's basicity is strong enough to cause it to be protonated by neutral water. As the basicity of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) was unknown, a water resistance test was conducted to determine if the polymer's basicity is strong enough to interact strongly with neutral water. A strong interaction with water would lead to the degradation or dissolution of the foam, which is commonly observed in SBF and CBF materials. A small foam bead was prepared using the established method and then placed into deionized water for 5 days (Fig. 9). After 5 days, the foam bead remained floating on the deionized water, with no change in appearance or size. However, the bead settled slightly further into the water than

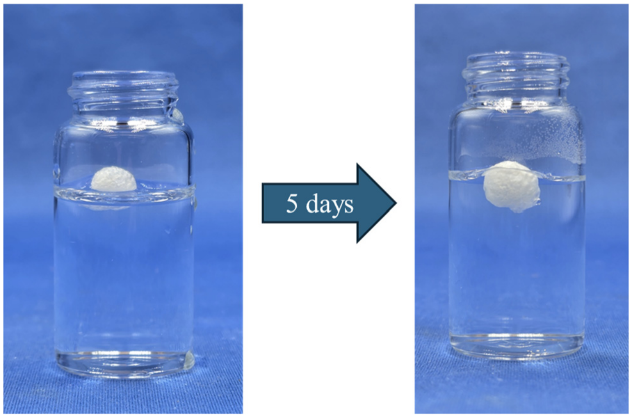

Fig. 9 Water resistance test of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam in neutral water. Over 5 days there was no observed disintegration or damage to the foam.

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at the beginning of the experiment, indicating some water had interacted with the foam. This was not detrimental to the foam as it did not lead to degradation or dissolution of the foam. The interaction between P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) and neutral water was not concerning, as the foam maintained its shape and size. Drying of the foam at ambient conditions returned it to its original state.

As P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) is designed to be used as a foam packaging material, its compression strength is an important property. P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam packing peanuts were prepared using the established method and tested for compression strength using an Instron 8521 with a 5 kN transducer load cell. The compression testing method was modified from ASTM D1621-04. Commercial EPS packing peanuts were also tested for compression strength as a comparison. Force deflection curves were obtained in triplicate for both P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) and EPS foams (Fig. 10).

The compression strength of the foams was obtained when the foam reached 50% of its original length (L_o) (0.02 m on average). The compression strength was calculated using eqn (4):

$$\sigma = \frac{F}{A_o} \tag{4}$$

where σ is the compressive strength, F is the force in Newtons at 50% the sample's original height, and A_o is the original cross-sectional area of the sample. The average compressive strengths for the P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) and EPS foams are reported in megapascals (MPa) along with the standard error. The choice of determining the compression strength of the foams at 50% of its L_o was to observe the largest difference in strength before possible densification of the sample occurred. The compression strength could have been obtained at a different deformation height, such as 25% but 50% was selected for these tests. It is common to test compression strengths between 10–50% of the sample's L_o. The compressive strength of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) was 0.093 ± 0.014 MPa, which is three times higher than the EPS foams (0.031 ± 0.0027 MPa). This higher compressive strength indicates that P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) can withstand higher forces than the EPS foam, which is advantageous for packaging applications.

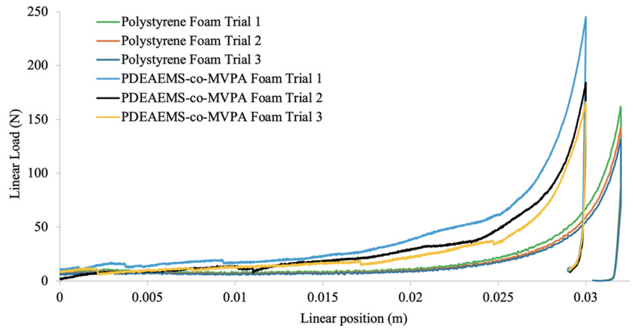

Fig. 10 Force deflection curves for P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) and EPS foam peanuts. Samples were mounted into an Instron 8521 equipped with a 5 kN transducer load cell and crushed at a rate 0.1 mm s^{-1}. The compression strength was determined by using the measured force at 50% the L_o (approximately 0.02 m) divided by the A_o of the sample.

Recycling P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam

The industrial recycling of EPS foams has been deemed uneconomical but this does not mean that EPS itself not recyclable. EPS can be recycled using either through mechanical, thermal or chemical recycling, but the properties of the materials typically degrade.[3] This leads to EPS foam typically being downcycled to lower-value materials. An alternative, non-destructive method to EPS recycling involves dissolving waste EPS into an organic solvent, followed by either precipitation or evaporation of the solvent to produce PS particles or fibers.[49] Typical solvents include toluene, xylenes, and methyl ethyl ketone.[50] Researchers have reported using a greener solvent for recycling EPS by switching to D-limonene, a solvent made from renewable resources and that is less toxic than the aforementioned solvents. While less toxic and made from renewable resources, D-limonene is cumbersome to remove from waste EPS, requiring high distillation temperatures due to its boiling point of 178 °C or multi-step washing and extraction.[49–51] A key advantage of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam is its ability to be easily recycled by dissolving it into carbonated water due to the CO$_2$-responsive amines in the polymer. P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) can also be foamed again by evaporating the carbonated water, something that is not possible using other recycling methods. If unfoamed P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) is desired, simply bubbling air into a low concentration (1–25 wt%) solution of carbonated P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) or blowing air across the 40 wt% protonated polymer will deprotonate the polymer and result in precipitation of the neutral polymer. The neutral polymer can be easily filtered from the water, a method that requires far less energy, reagents, and time than high-temperature distillations or multi-step extractions.

When recycling is desired, P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foams are crushed by hand and dissolved into carbonated water at 40 wt% solids to produce a highly viscous solution (Fig. 11a). A portion of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) solution was shaped into a sphere, placed into a cylindrical glass mould, and expanded using a 1600 W heat gun. After heating, the mould was placed in a vacuum chamber to expand the foam to its final size. The dried foam was then redissolved again into carbonated water. This was done over 5 trials (the original plus four dissolution and expansion cycles). High recovery and recycling percentages are needed to justify using bioderived CO$_2$-responsive rigid foams. Fig. 12 shows the percent recovery of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$). The average recovery is ≥98% per cycle. This high % recovery allows the rigid foams to be reused over multiple cycles with minimal losses during preparation and handling.

Effects of recycling on P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) properties

To recycle P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) required the polymer to be redissolved back into carbonated water at 40 wt% solids. This simple step of dissolving the polymer and re-foaming it does not follow the traditional recycling practices mentioned previously The act of dissolving the polymer into carbonated

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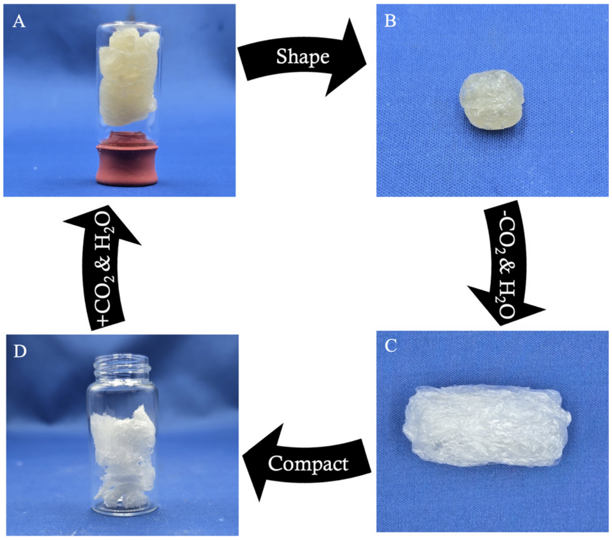


Fig. 11 Preparation and recycling of the bioderived CO_2-responsive rigid foam P(DEAEMS$_{70}$-*co*-MVPA$_{30}$). (A) P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) is dissolved in carbonated water at 40 wt% solids content. (B) The polymer solution is shaped into 1.5 cm (~1.5 g) bead. (C) The P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam after heating and drying. (D) Foamed P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) was crushed and added back to the vial. DI water was added to produce a 40 wt% mixture. The mixture was bubbled with CO2 for 24 h to dissolve the foam. The entire process was repeated four times.

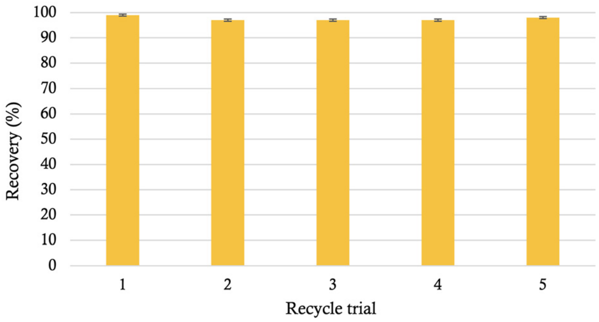


Fig. 12 Percent recovery of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) over different cycles. Percent recovery was determined by analyzing the final mass of polymer compared to the start mass of the polymer for each trial. Average recovery was determined to be ≥98%.

water is not considered chemical recycling, as the polymer is not being depolymerized.[52] The foams were crushed during recycling to demonstrate how damaged or unusable foams can be recycled back into usable foams. The P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foams were also not melted down after use, which avoided thermal degradation that could occur from this recycling technique. The properties of the P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam are expected to be maintained after recycling because it does not undergo the mechanical, thermal, or chemical recycling that is used on EPS.

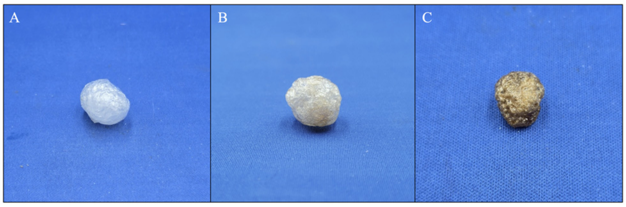
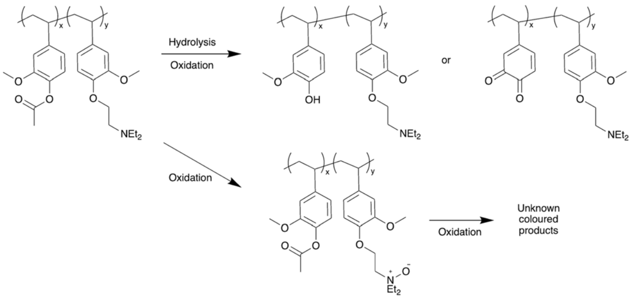


Fig. 13 Colour change of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam after recycling cycles. (A) Pristine foam, no recycling performed. (B) P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam after two recycling cycles. (C) P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam after five recycling cycles.

During the recycling process, a noticeable change in the appearance of the foams occurred. After each recycling step, the foam discoloured, transitioning from white to yellow and then to brown (Fig. 13). There are two possible causes for discolouration to occur: oxidation of the amine groups or hydrolysis and oxidation of the MVPA to quinones (Scheme 6). The immediate product of amine oxidation is amine oxides, but those are colourless. Further decomposition or oxidation is needed to obtain coloured products from amines. There is no mention in the literature on the structures of these impurities, even from relatively simple amines. Researchers have attempted to identify these coloured oxidation products but only suggested what the possible oxidation products could be.[53] The other potential source of discoloration could be the hydrolysis of MVPA and subsequent oxidation of the resulting phenol to coloured quinones.[54,55] The use of the heat gun as the direct heating source for foaming may also contribute to the oxidation of the polymer, as it is common to have degradation of polymers from thermal treatment.[56] Hydrolysis is likely to occur as the polymer is stored in acidic water. To determine whether hydrolysis of the acetate group was occurring, ^1H NMR spectroscopy was used to identify a change in the acetate peak. In Fig. 14, the ^1H NMR spectra of the virgin and 5 times recycled P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) are shown. The acetate peak for MVPA is shown in the red box. There is a clear decrease in intensity between the virgin and recycled polymers. Integrating these peaks shows a 50% decrease in the methyl protons attached to the acetate group on the recycled polymer, meaning half of the acetate groups in P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) have hydrolyzed (see SI for integrated ^1H NMR



Scheme 6 Possible oxidation pathways of P(DEAEMS$_{70}$-*co*-MVPA$_{30}$). Tertiary amines can oxidize to amine-oxides, which can decompose or further oxidize to unknown products. Hydrolysis of MVPA units produces phenols that can oxidize to quinones. Both pathways can cause colour changes in the polymer.

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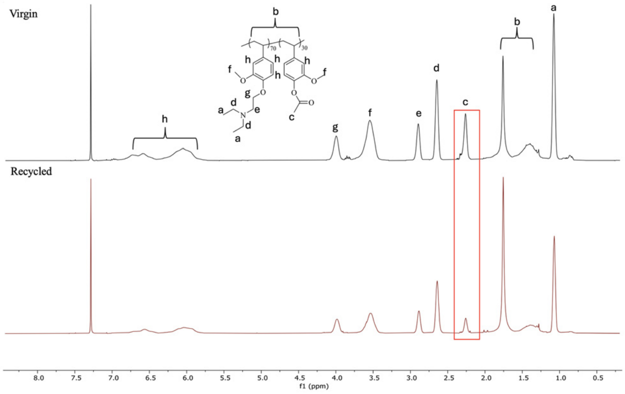

Fig. 14 Stacked ^{1}H NMR spectra of virgin and 5 times recycled P(DEAEMS$_{70}$-*co*-MVPA$_{30}$). The intensity of methyl protons on the acetate group of MVPA decreases from the virgin polymer to the recycled polymer. This indicates that a portion of the acetate groups has been cleaved off, producing a phenol.

spectra). There was no indication that amine oxidation was occurring by ^{1}H NMR analysis, but the amount occurring may be below the detection limit of the spectrometer. It is mostly like that both amine oxidation and hydrolysis of the acetate group are occurring to some extent.

During the recycling of EPS, it is typical for the molecular weights to decrease as mechanical, thermal and chemical treatments cleave the chains.[57] Since P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) is not undergoing these treatments, the molecular weights of the recycled foams should be relatively similar to those of the virgin polymer. However, the degradation of acetate groups would inherently lead to a lower observed molecular weight but not by orders of magnitude as seen in the common recycling techniques. GPC analysis of the 5 times recycled P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) was done to compare against the virgin polymer. Unexpectedly, the molecular weight was determined to be almost fivefold lower than that of the virgin polymer (Table 2). Dissolution and subsequent precipitation of the polymer from carbonated water would not be enough to degrade the polymer molecular weight by almost 80%. The more likely cause of this observed decrease in molecular weight was not from chain cleavage but from poor solubility of the recycled polymer in THF. The oxidation of the tertiary amine, the phenol generated from hydrolysis, and its formation of quinone or catechol most likely produced salts or crosslinked polymer with limited solubility in THF. During the sample preparation, the polymer solution is passed through a 0.22 µm nylon filter; larger chains containing oxidized species are filtered out of the solution, leaving only lower molecular polymers in the sample to be analyzed. The formation of oxidized species on P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) is the suspected cause that prevented the polymer from being accurately analyzed by GPC.

The T_g of the recycled P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam was examined and compared against the virgin P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam. There was a 2 °C decrease in the T_g from virgin foam to the recycled foam. Again, this observation can be attributed to the oxidation of the polymer. The recycled polymer structure differs slightly from the pristine polymer, leading to different chain interactions and resulting in a lower T_g. Oxidation can also lower T_g, as it disrupts chain interaction.[58] Any reduction in T_g is undesired but the recycled P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam maintained a T_g above 40 °C, which is the acceptable upper limit for hot trucks and warehouses.[44] The recycled P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam can still be used for packaging applications, as the slight decrease in T_g did not cause it to become soft in normal and hot working conditions. With the recycling process causing oxidation to P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam, its water resistance was retested to observe if the changes in the material negatively impacted its performance (Fig. 15). The 5 times recycled P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam bead was placed into deionized water for 5 days. Initially, the recycled foam displayed similar results to the virgin foam. However, by the end day 5, the recycled foam bead had swelled in size and was almost fully submerged in the water. It remained buoyant the entire 5 days but there was a clear difference in size compared to the virgin

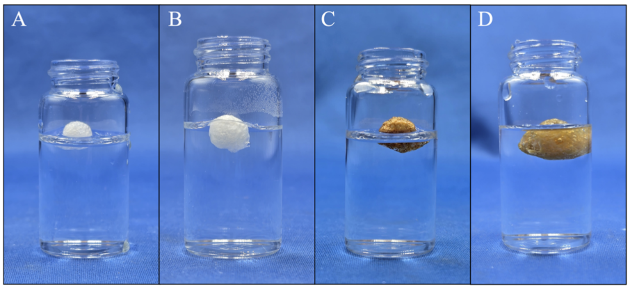

Fig. 15 Water resistance test comparison between virgin P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) and recycled P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) in neutral water. (A) Virgin P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) at time = 0. (B) Virgin P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) after 5 days. (C) Recycled P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) at time = 0. (D) Recycled P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) after 5 days.

Table 2 Properties of virgin and recycled P(DEAEMS-*co*-MVPA)

Polymer	M_n [a] kDa	M_w [a] kDa	Dispersity (*Đ*)	T_g [b] (°C)	Temperature at 50% mass loss[d] (°C)
Virgin P(DEAEMS-*co*-MVPA)	29	111	3.8	44	395
Recycled P(DEAEMS-*co*-MVPA)	9.6[c]	24[c]	2.5	42	395

[a] Determined by GPC analysis. [b] Determined by DSC analysis. [c] Molecular weights of polymer that pass through the 0.22 µm nylon filter. [d] Determined by thermal gravimetric analysis.

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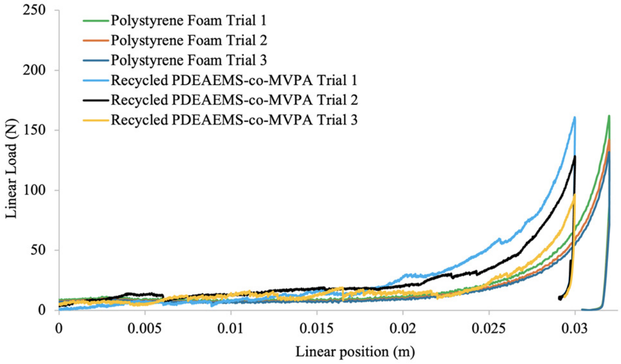

Fig. 16 Force deflection curves for P(DEAEMS70-*co*-MVPA30) and EPS foam peanuts. Samples were mounted into an Instron 8521 equipped with a 5 kN transducer load cell and crushed at a rate 0.1 mm s^{-1}. The compression strength was determined by using the measured force at 50% the L_o (approximately 0.02 m) divided by the A_o of the sample.

foam, which did not increase in size after 5 days in water. There was no observable disintegration of the recycled foam, which was a welcome result. The oxidation of the polymer did increase the hydrophilicity of the foam, but it did not cause the foam to dissolve or disintegrate when exposed to neutral water, which was the desired result.

The recycling of PDEAEMS-*co*-MVPA slightly influenced the physical properties of the polymer; this was expected to influence the compressive strength of the foam. The 5 times recycled P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) was foamed and tested for compression strength. Following the established method, the force deflection curves of recycled P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) were obtained in triplicate (Fig. 16). The compression strength was calculated using the measured force at 50% L_o. The average compression strength and standard error are reported. The compression strength of the recycled foam was 0.046 ± 0.0022 MPa, which was lower than the 0.093 ± 0.014 MPa observed from the pristine foam. The degradation of MVPA, coupled with the possible oxidation of the tertiary amines, most likely deteriorates the mechanical properties of the foam. The lower compression strength could also be a result of the recycled foam retaining more moisture, as it has increased hydrophilicity. Water can act as a plasticizer, which makes materials softer and have weaker mechanical properties. A high water content within the recycled foam could lead to weaker foam. Although the recycled foam had a lower compressive strength compared to the pristine foam, it maintained a higher compressive strength than the EPS foam peanuts, which had a compressive strength of 0.031 ± 0.0027 MPa. This demonstrates that P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) remains a valid packing material even after recycling.

Conclusions

As packaging continues to be a societal necessity, sustainable foam alternatives with good physical properties that can be easily recycled into new foam packaging are needed. Using vanillin as a starting material, a bioderived CO_2-responsive rigid foam was prepared to solve several key problems associated with EPS and current biobased foam packaging. Monomers were prepared using modified literature methods, which were improved upon to reduce unnecessary waste generation, have better atom economy than traditional reaction pathways, and use some renewable resources instead of petroleum products. The polymerization of the bioderived styrene analogs was done in carbonated water using the monomer DEAEMS as a stabilizer during suspension polymerization of MVPA and DEAEMS eliminated the need for additional stabilizers. P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) was pursued over PDEAEMS as the polymer had better properties. P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foamed easily using the rapid evaporation of water and CO_2 to act as the blowing agent, eliminating the need for pentane as the blowing agent. The average density of the foams was calculated to be 0.04 g cm^{-3}, with a porosity of 92%. The pristine P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foams foams had excellent water resistance and better compressive strength compared to EPS foam peanuts. After expansion and analysis, the rigid foams were dissolved back into carbonated water at 40 wt% solids and expanded back into a new rigid foam material. No new virgin polymer was added to the solution, making each new foam a 100% recycled material. The recovery of the polymer after each recycling step averaged 98%, making it easy to reuse and reproduce multiple rigid foams with minimal losses. The properties of the recycled foams did deteriorate slightly due to oxidation but the P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam retained its water resistance and managed to have better compressive strength than the EPS foam peanuts. Polystyrene, however, has one practical advantage; it is inexpensive. Future work on EPS substitutes must find a way to simultaneously reduce the environmental impact of packing foam, use biomass as the feedstock, facilitate recycling, and bring down the cost of production to a level that, while not necessarily being as low as EPS, is at least low enough not to be prohibitive. This P(DEAEMS$_{70}$-*co*-MVPA$_{30}$) foam demonstrates solutions to multiple environmental issues with EPS, while having better water resistance that current biobased foam packaging. This bioderived CO_2-responsive rigid foam may provide the starting point for generating sustainable rigid foams that can be recycled back into new rigid foams using simple, and potentially greener routes.

Author contributions

D. Barker: conceptualization, methodology, formal analysis, investigation, validation, writing – original draft, writing – review & editing, visualization. M. F. Cunningham: conceptualization, resources, supervision, writing – review & editing. G. Liu: conceptualization, resources, writing – review & editing, supervision, project administration, funding acquisition. P. G. Jessop: conceptualization, resources, writing – review & editing, supervision, project administration, funding acquisition.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI), which contains spectra, thermograms, microscopy photos, and the calculation of the T_g. See DOI: https://doi.org/10.1039/d4gc06165a.

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