Robust and Highly Interconnected Polyurethane Diacrylate Based Macroporous Polymers

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Abstract

Polymerised high internal phase emulsions (polyHIPEs) have drawn extensive interest in recent years; however, industrial applications do require polyHIPEs to be tough and robust. The mechanical properties of polyHIPEs can be tuned by copolymerisation of polyurethane diacrylate (PUDA) and styrene. The resulting open-porous poly(styrene-co-PUDA)HIPEs were much less brittle and friable when compared to conventional poly(styrene-co-divinylbenzene)HIPEs. Moreover, poly(styrene-co-PUDA)HIPEs have impact strengths up to 10 times higher than poly(styrene-co-divinylbenzene)HIPEs. The styrene/PUDA ratio determines the morphology, thermal and mechanical properties of the poly(styrene-co-PUDA) macroporous polymers. The viscous PUDA promotes the formation of small pores in polyHIPEs. A high PUDA content of the copolymer results in low mechanical properties.

1. Introduction

Emulsion templating refers to a method to use emulsions, especially high internal phase emulsions (HIPEs), to produce macroporous polymers[1]. A HIPE containing monomers in the continuous phase and an inert liquid as internal/dispersed templating phase is prepared and polymerised. After the purification, macroporous polymers called poly(merised)HIPEs are produced. This method was first reported by Bartl and von Bonin[2], and has been further developed over the past 50+ years. By tailoring the formulation of emulsion templates, the properties of the resulting macroporous polymers, such as porosity, pore size, pore interconnectivity and, therefore, permeability, surface area, and morphology of the polyHIPEs can be tailored to suit various applications in/as membrane and separation technologies[3-7], hydrogen storage[8], catalyst supports[9], electrodes for microbatteries[10], oil servicing[11], as low dielectric substrates for use in the electronics industry[12] and scaffolds for tissue engineering[13, 14].

For a long time poly(styrene-co-divinylbenzene) polyHIPEs were the most thoroughly studied polyHIPEs[1]. However, they are extremely brittle and friable, which reduces the number of potential real-word applications, they can be considered for, dramatically. Preparing polyHIPEs from different monomers was therefore extensively studied to improve the mechanical properties of polyHIPEs. 1-vinyl-5-amino tetrazole based polyHIPEs were synthesised, which possessed higher elastic moduli than poly(styrene-co-divinylbenzene) polyHIPEs. PolyHIPEs based on dicyclopentadiene have been prepared

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via ring-open polymerisation within emulsion templates[16, 17]. The resultant polyH(M)IPEs possessed elastic moduli ranging from 23 MPa to 300 MPa depending on their porosity. Yet, the most commonly employed group of monomers are acrylates as they are solidified by free radical polymerisation, which is the most widely used polymerisation method in emulsion templating. A number of acrylates for example, butyl acrylate[18], ethylhexyl acrlylate and ethylhexyl methacrylate[19], has been used to improve the mechanical properties of polyHIPEs while reducing their brittleness. In our previous work, we dramatically reduced the brittleness of styrene based polyH(M)IPEs simply by replacing the stiff crosslinker divinylbenzene by the more flexible, long-chain crosslinker polyethylene glycol dimethacrylate (PEGDMA)[20]. Pulko et al.[21] prepared bendable polyHIPE membranes based on glycidyl methacrylate, ethyleneglycol dimethacrylate and ethylhexyl methacrylate. Recently, Tunc et al.[22] reported that polyHIPEs can be tailored from rigid materials to elastomers by tuning the template composition, i.e. varying the acrylate / divinylbenzene ratio within emulsion template. Gurevitch and Silverstein[23] reported polyHIPEs based on stearyl acrylate and stearyl methacrylate, which possessed shape-memory properties.

Here we show that polyurethane diacrylate (PUDA) can be copolymerised with styrene within emulsion templates. The effect of PUDA on the morphology, physical properties and mechanical properties of the polyHIPEs will be investigated.

2. Experiments

2.1 Materials.

Styrene (St), divinylbenzene (DVB), ammonium persulfate (APS) and $CaCl_2{\cdot}2H_2O$ were purchased from Sigma-Aldrich (Gillingham, UK). Polyurethane diacrylate (PUDA) with a molecular weight of 1200 Da (Ebecryl 284) by Cytec (Diegem, Belgium) and the surfactant Hypermer B246 by Croda (East Yorkshire, UK). All chemicals were used as received.

2.2 Preparation of polyH(M)IPEs.

The emulsification setup consisted of a reactor with a glass paddle (anchor) rod connected to an overhead stirrer. The continuous and internal phases of emulsion templates were prepared separately. The internal phase was aqueous solution containing $CaCl_2{\cdot}2H_2O$ as electrolyte and contained APS as initiator. St and PUDA were mixed in the reaction vessel; the St/PUDA ratios varied from 1.66:1 to 1:1.66. To the mixture the Hypermer B246, with various concentrations, was added to formulate the continuous phase. The internal phase was added dropwise while stirring at a speed of 400 rpm. Afterwards, the emulsions were further stirred at 2000 rpm for 3 min to produce homogeneous emulsions. A control sample, containing St and DVB with a ratio of 1.66:1, was prepared using same emulsification procedure. These emulsions were transferred into free-standing polypropylene (Falcon®) tubes and placed in oven; the emulsions were heated to 70 °C for 24 h for polymerisation. After polymerisation, the samples were first washed with water for 24 h and then in ethanol. The purified samples were dried at 70 °C until constant weight.

2.3 Characterisation of polyHIPEs.

Fracture surfaces of polyH(M)IPEs S1-S9 were investigated by scanning electron microscopy (SEM, Hitachi S-3400N, Hitachi High Technologies, Mannheim, Germany). Prior to the investigation, the fracture surfaces of the samples were gold coated using an Agar Auto Sputter Coater (Agar Scientific, Essex, UK). The images were further analysed using UTHSCSA software ImageTool for pore and pore throat size measurement.

The skeletal densities ρ_s of all samples were determined using a Helium displacement pycnometer

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(Accupyc 1330, Micrometrics Ltd., Dunstable, UK). The foam densities ρ_f were measured using graphite powder displacement pycnometry (Geopyc 1360, Micrometrics Ltd., Dunstable, UK). The porosity (P) was calculated from the measured densities as follows:

$$P=\left(1-\frac{\rho_f}{\rho_s}\right)\cdot 100\% \tag{1}$$

Mechanical properties of the polyHIPEs or polyMIPEs were determined by compression testing using a Lloyds EZ50 (Lloyds Instruments Ltd, Fareham, UK) equipped with a 50 kN load cell. Prior to compression testing the samples were cut into disks with a diameter of about 25 mm and a height of about 10 mm. At least six disks per sample were measured. Charpy impact tests were performed using an Instron Ceast 9050 (Instron GmbH, Darmstadt, Germany) following the standard EN ISO 179-1-2010. The specimens were cut into 80 mm × 10 mm × 4 mm and placed on a span with a span length of 62 mm. The pendulum was 166.14 g with an arm of 229.7 mm. The drop angle of the pendulum was 150° and the energy of the pendulum was 0.5 J. The impact strength a_{cU} (kJ / m^2) was calculated as follows:

$$a_{cU}=\frac{E_c}{h\cdot b}\cdot 10^3 \tag{2}$$

where E_c is the energy (J) adsorbed by breaking the specimen; h and b are the thickness and width (mm) of the specimen, respectively.

The thermal properties of the samples were investigated using dynamic mechanical thermal analysis (DMTA, RSAG2, TA Instrument, Eschborn, Germany). Samples with a dimension of 10 mm × 10 mm × 5 mm were compressed with a frequency of 1 Hz while being heated at a rate of 4°C / min from 25°C to 175°C.

3. Results and Discussion

The HIPE templates used to produce control polyHIPE contained 75 vol.% internal phase and were stabilised by 20 vol.% of the surfactant Hypermer B246 with respect to the continuous phase volume; the resulting polyHIPE possessed a porosity of approximately 78%. The control polyHIPE possess an open porous structure, characterised by an average pore and pore throat size of about 2.8 μm and 0.4 μm, respectively. The control polyHIPE did not exhibit a glass transition temperature (T_g) within the temperature range from 25°C to 175°C due to the high crosslinking density. Correspondingly, it failed in a brittle manner during compression testing and had an elastic modulus of 70 MPa and a crush strength at break of 4.8 MPa.

PUDA was used as the crosslinker instead of the previously used DVB; all other components and their ratios as well as the emulsification conditions were identical to that of the control. Unsurprisingly, the resulting polyHIPE (77% porosity) and the control polyHIPEs had similar porosities since the emulsion templates used to make them had identical internal phase volume ratios and it possessed an open-porous structure (Fig 1.) with an average pore size of 1.2 μm and an average pore throat size of 0.4 μm. Since the formulations of PUDA-St sample and the control sample only differed with respect to the crosslinker used, the reduced pore size of the PUDA-St polyHIPE compared to that of the control polyHIPEs must be due to the presence of PUDA in the HIPE template of PUDA-St. The PUDA-St based polyHIPE remained permanently deformed when compressed to 10% of its original height but did not break; it is clearly less brittle than the St-DVB based control polyHIPE. The elastic modulus and crush strength of PUDA-St were lower than those of control. This was due to the flexibility of the PUDA chains as well as the lower crosslinking degree in the PUDA-St polyHIPE. The latter was a result of the lower PUDA molar concentration than DVB in the emulsions. However, PUDA-St polyHIPE did have a 3 times higher

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impact strength compared to the control because the flexibility of the PUDA chains enhanced the energy adsorption upon impact. This leads to a much tougher polyHIPE compared to the poly(Styrene-co-DVB)HIPE.

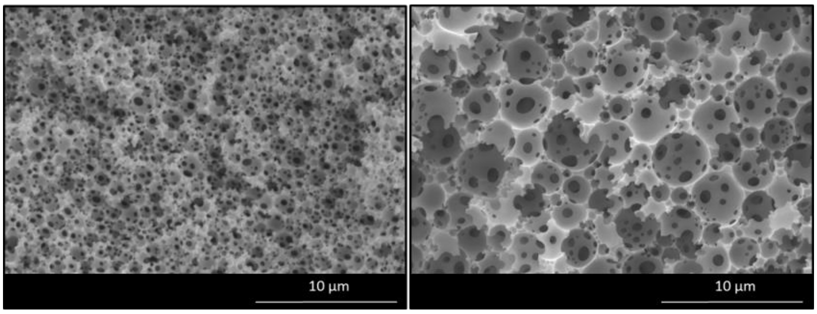

Figure 1. Morphology of PUDA and St based polyHIPEs: PUDA-St, left and PUDA-St-L, right.

Lower surfactant concentrations were used for the preparation of the emulsion template for PUDA-St-L. The densities and porosities of PUDA-St-L are identical within error to the PUDA-St polyHIPE, which is due to the identical monomer composition and the internal phase volume ratios in their HIPEs. PUDA-St-L possessed also open-porous structures just like PUDA-St: as expected the pore sizes increased due to the reduction in surfactant concentration used to stabilise the HIPEs. Although the polyHIPEs PUDA-St-L and PUDA-St have identical St/PUDA ratios, the T_g of PUDA-St-L increased with decreasing surfactant concentration used to stabilise the HIPE templates. The elastic moduli and the crush strengths of PUDA-St-L increased as compared to PUDA-St polyHIPE. The increase in the stiffness of PUDA-St-L probably due to the increase in the pore sizes, which has been reported by Maheo et al.[24] and Ceglia et al.[25, 26]. The impact strengths of PUDA-St-L also increased (to 10 times higher as the impact strength of the control polyHIPEs), indicating that tougher polyHIPEs were produced when less surfactant was used to stabilise the emulsion templates.

A group of MIPEs having an internal phase level of 60 vol.% and a gradually increasing PUDA content was polymerised to prepare polyMIPEs. The average pore size decreased with increasing PUDA content. This indicates that the droplet size of the emulsion templates decreased with increasing PUDA fraction, therefore, the increasing viscosity of the continuous HIPE phase. The skeletal densities of PUDA-St-M1 to PUDA-St-M3 increased slightly because of the gradual concentration increase of PUDA, which has a higher density than styrene. However, as expected the variation of the St/PUDA ratios had no influence on the foam densities and porosities of the samples; they are identical within error. The mechanical properties of PUDA-St-M1 to PUDA-St-M3 decreased: the elastic moduli and crush strengths both decreased to half and the impact strengths decreased almost to one third. This was probably due to the formation of flexible PUDA-rich segments and more rigid St-rich segments in the PUDA-St-M3 polyHIPE.

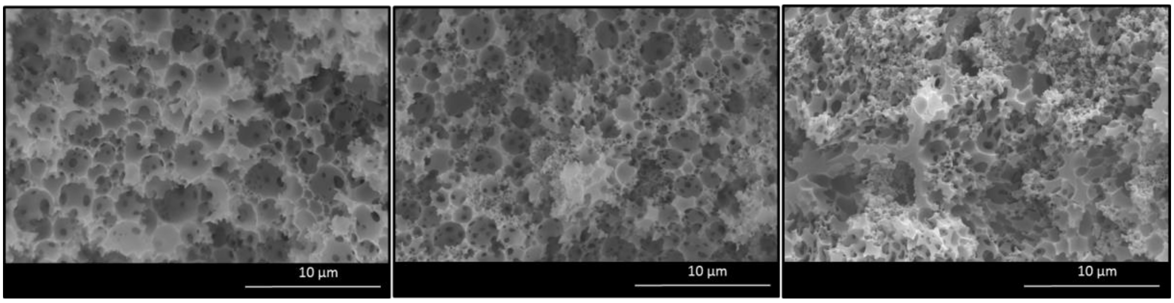

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Figure 2. Morphology of PUDA and St based polyMIPEs: PUDA-St-M1, left, PUDA-St-M2, middle and PUDA-St-M3, right.

4. Conclusion

Polyurethane diacrylate was copolymerised with styrene within emulsion templates to produce macroporous polymers. The PUDA-St based polyHIPEs is less brittle than the one based on St-DVB. The PUDA promoted the formation of small droplets in the emulsion templates and subsequently small pores in the polyHIPEs. The styrene/PUDA ratio influenced the mechanical properties of the macroporous polymers.

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