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Porous polymaleimide networks

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Porous network structures were prepared by *in situ* polymerisation of a mixture of *N*-phenylmaleimide and 1,1′-(methylenedi-4,1-phenylene)bismaleimide (95 : 5 w/w) in poly(vinylidene difluoride-*co*-hexafluoropropylene) (PVDH). The mixture of the maleimide monomers was found to form thermoreversible gels with PVDH. Thermodynamic analysis of the gelation process using calorimetry data indicated the formation of complexes of *N*-phenylmaleimide and vinylidene difluoride repeat units with a molar ratio of 1 : 2, respectively. PVDH formed optically clear solutions in the mixture above the gelation temperature, observed at 80–120 °C depending on composition. Polymerisation of the maleimides was induced by increasing the temperature to 250 °C. During polymerisation, the resulting polymaleimide phase separated from the PVDH melt. A morphological study by microscopy revealed that blends with 80 wt% PVDH contained continuous networks of crosslinked polymaleimide. The porous networks were collected after removing the PVDH by solvent extraction. Thermogravimetrical analysis of the polymaleimide networks under N_2 atmosphere showed that the onset of weight loss occurred at 380 °C. These networks may thus be used to prepare thermally stable membranes.

Introduction

Maleimide polymers and copolymers have found use in the area of electronics for the aerospace and aircraft industry.[1] The general properties of this class of polymers include tractability, high thermal stability, high durability, good water resistance, fire resistance, and radiation resistance. In addition, the polymaleimides are relatively cheap materials. These characteristics make it interesting to prepare porous three-dimensional polymaleimide networks for use in, for example, membrane applications.

The present work was aimed at preparing porous polymaleimide networks by polymerisation of a mixture of phenylmaleimides in melts of a vinylidene difluoride copolymer. Phenylmaleimides were chosen primarily because of their high thermal stability and low cost. Poly(vinylidene difluoride) (PVDF), used as the polymerisation medium for the maleimide mixture, is an important polymer which has found use because of its piezoelectric and pyroelectric properties,[2] and more recently also because of its ability to form gel electrolytes for use in lithium batteries.[3] PVDF also displays several features which make it attractive as a medium for polymerisations of, for example, maleimides at high temperatures. Firstly, it is chemically inert and has a high thermal stability, with a large difference between the melting point and the decomposition temperature, ~400 °C.[2] There is thus a large range of temperatures at which polymerisation can be carried out, with little probability of chain transfer to the semi-fluorinated polymer. Secondly, PVDF has a high concentration of permanent dipoles because every second carbon in the macromolecular chain is fluorinated. As a consequence, PVDF can be expected to interact favourably with organic compounds containing polar units, such as different maleimides. PVDF has for example previously been shown to be miscible with poly(methyl methacrylate)[4,5] and to swell in various ketones and carbonates.[6] This indicates the possibilities to dissolve and polymerise quite polar monomers in PVDF. Of course, even though a monomer is soluble in PVDF, the corresponding polymer will most probably not be miscible, and thus polymerisation will result in a phase separated polymer blend. In the present study, a copolymer containing a few mol% of hexafluoropropylene was chosen because it has a lower crystallinity than PVDF. Consequently, the former polymer has a lower melting point and generally also a higher solubility. The behaviour of the phenylmaleimide mixture in PVDH was studied by calorimetry before thermal polymerisation of the monomer mixture dissolved in PVDH melt. The resulting PVDH–polymaleimide blends and the isolated polymaleimide networks were then characterised by calorimetry, microscopy, and thermogravimetrical analysis.

Experimental

Blend samples were prepared by thermally induced polymerisation of a phenylmaleimide mixture in a melt of poly(vinylidene difluoride-*co*-hexafluoropropylene) (PVDH, Elf Atochem, Inc., Kynar Flex® 2801[7]). The PVDH sample contained 88 wt% vinylidene difluoride units. The mixture of phenylmaleimides consisted of *N*-phenylmaleimide (PM, Aldrich), shown in formula **1**, and 1,1′-(methylenedi-4,1-phenylene)bismaleimide (BPM, Aldrich), shown in formula **2** at a ratio of 95 : 5 (w/w), respectively. Compounds containing this mixture and PVDH were cast from acetone solutions in Petri dishes, and annealed in closed containers at 80 °C. The overall weight fraction of polymer in the compounds (w_2) was kept at 0.20, 0.30, 0.40, 045, 0.50, 0.60, and 0.80. Samples of pure PVDH, as well as the monomer mixture, were also prepared in the same way. Weighed pieces of the samples were put into aluminium containers which were then sealed and transferred to the measuring cell of a Mettler TA 3000 differential scanning calorimetry (DSC) system under N_2 purge. The samples then were put through the temperature program shown in Fig. 1. The samples were first annealed at 180 °C for 20 min, and after cooling down to 0 °C, they were heated to 300 °C. The samples were retained at this temperature for 30 min to polymerise the PM–BPM mixture, before cooling down to 0 °C again. Finally, the samples were heated to

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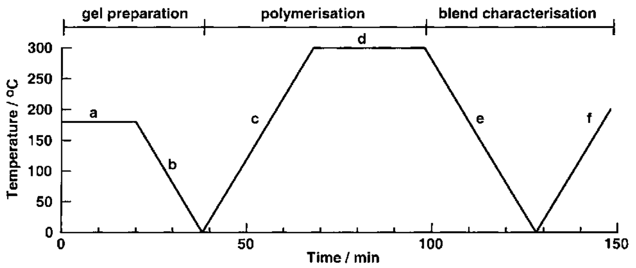
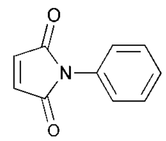


Fig. 1 The temperature sequence employed in the preparation and characterisation of the blends by DSC.

200 °C. The scan rate was in all cases 10 °C min^{-1}. Peak values were taken as melting (T_m) and crystallisation (T_c) temperatures, and the heats of melting and crystallisation were evaluated by integration of the corresponding peaks. At least six samples of each composition was prepared and analysed as described above.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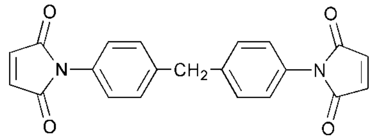
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The blends were analysed by thermogravimetrical analysis under an N_2 flow in a Mettler TGA. During analysis the temperature was increased from 50 to 650 °C at 10 °C min^{-1}.

Scanning electron microscopy (SEM) was employed to study the morphology of a blend containing 80 wt% PVDH prepared by the thermal treatment in the DSC. The specimen was prepared for analysis by extracting the PVDH phase with acetone. After drying in vacuum for 24 h at ambient temperature, the remaining crosslinked polymaleimide phase was sputter coated with a 15 Å Au/Pd layer, before analysis using an International Scientific Instruments 100A SEM operated at 15 kV.

Results and discussion

Compounds consisting of PVDH and various amounts of a monomer mixture of PM–BPM (95 : 5 w/w) were prepared by casting from acetone solutions. After drying, DSC was employed to first study the gelation process of this system, then to carry out the polymerisation of the monomer mixture to form the blends, and finally to characterise the thermal properties of the blends and networks. Fig. 1 shows the DSC temperature sequence used. The different sets of DSC traces obtained during the thermal treatment of the samples are shown in Fig. 2. The pure PVDH copolymer had $T_c = 114$ °C, and $T_m = 145$ °C, and the pure monomer mixture had $T_c = 23$ °C and $T_m = 86$ °C.

Gelation

After annealing at 180 °C for 20 min, all the compounds were optically clear, indicating that the samples were homogeneous solutions. Upon cooling, gels were formed by crystallisation-induced phase separation of PVDH. As seen in Fig. 2, scan b, the temperature of gelation for the increased progressively with the weight fraction of PVDH, w_2, from 76 to 92 °C. At ~10 °C, the maleimide mixture crystallised in the compounds with w_2 equal to 0.20 and 0.40. When the gels were heated (Fig. 2, scan c), all the samples, except the one with $w_2 = 0.80$, first showed cold crystallisation of the maleimides at $T_c = 7$–25 °C, then melting of the same phase at $T_m \sim 90$ °C. Finally the gels melted at $T_m = 110$–140 °C, depending on the composition. These results demonstrated the thermoreversibility of the gels. PVDF has previously shown to form thermoreversible gels in acetophenone, ethyl benzoate, glyceryl tributyrate, and various diesters.[8–10] This type of gelation involves physical crosslinking by the formation of crystalline PVDF regions which hold the gel together. Above the gel fusion temperature of these systems, polymer solutions are formed after melting of the crystalline regions.

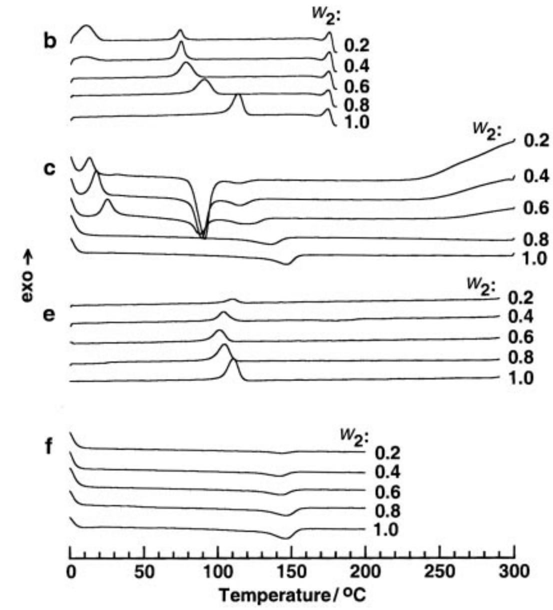


Fig. 2 DSC traces of samples with different blend compositions (w_2). The traces shown are from the temperature scans shown in Fig. 1: b (cooling scan: 180–0 °C), c (heating scan: 0–300 °C), e (cooling scan: 300–0 °C), and f (heating scan 0–200 °C). The scan rate was 10 °C min^{-1} in all cases.

Thermoreversible gelation is generally associated with enthalpy changes, and the variation of enthalpy with composition can provide important information connected with the molecular mechanism of gel formation.[9] In Fig. 3 the enthalpy of gelation, ΔH_{gel}, is plotted as a function of w_2 (circles). As seen, the function showed a positive deviation from linearity in

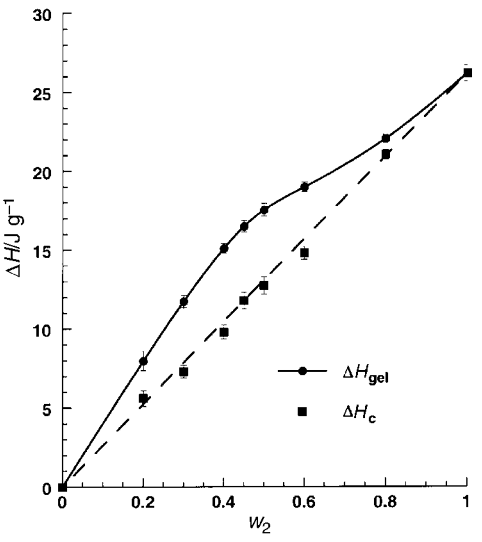


Fig. 3 Heat of gelation, ΔH_{gel}, measured before polymerisation, and heat of fusion, ΔH_c, measured after polymerisation, *versus* gel composition, w_2. Dashed line indicates $\Delta H = w_2 \Delta H_{c2}$, and the bars indicate the standard deviation obtained by analysing at least six samples.

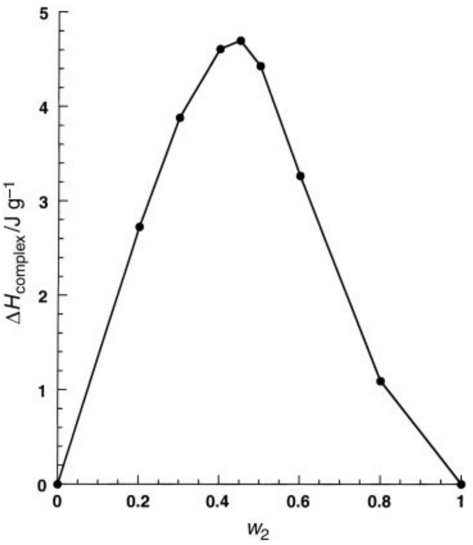


Fig. 4 Plot of $\Delta H_{complex}$ *versus* gel composition, w_2 [$\Delta H_{complex}$ was calculated from eqn. (2)].

the full composition range. The enthalpy of gel formation can be considered to have three components:[8]

$$\Delta H_{gel} = w_1 \Delta H_{c1} + w_2 \Delta H_{c2} + \Delta H_{complex} \quad (1)$$

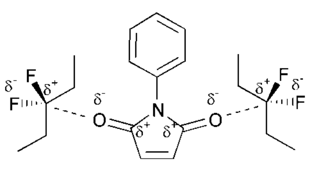
where w_1 and w_2 are the weight fractions of solvent and polymer, respectively, ΔH_{c1} and ΔH_{c2} are the heat of crystallisation enthalpies of solvent and polymer, respectively, and $\Delta H_{complex}$ is due to the formation of any organised structure in the gel. The latter term is typically connected to the formation of polymer–solvent complexes. In the present case the first term is zero because the PM–BPM mixture did not crystallise in the temperature region of interest. Consequently:

$$\Delta H_{complex} = \Delta H_{gel} - w_2 \Delta H_{c2} \quad (2)$$

is obtained. $\Delta H_{complex}$, which represents the deviation from linearity in Fig. 3, is shown as a function of w_2 in Fig. 4. The shape of the curve indicated the formation of a solvent–polymer complex at gelation,[8–10] and a maximum in $\Delta H_{complex}$ was observed very close to $w_2 \approx 0.45$. Taking into account that PVDH contained 88 wt% vinylidene difluoride, the stoichiometry of w_2 at the maximum indicated the formation of a complex with approximately 2 vinylidene fluoride repeat units per maleimide molecule, that is, one vinylidene fluoride unit for each maleimide carbonyl group. The most probable structure of the complex is shown in formula **3**, where the polar carbonyl groups of the maleimide are interacting with the -CF_2- carbons of the vinylidene fluoride units. It was noted that the molar concentration of hexafluoropropylene units is too small to draw any conclusions regarding their role in the complex formation. Previously, the stoichiometry of the vinylidene difluoride unit–solvent complexes has been found to be 3 : 1, 2 : 1, and 1 : 1 for glyceryl tributyrate,[9] diethyl adipate,[8] and ethyl benzoate[9] respectively. The results in these cases also indicated the formation of complexes with one vinylidene difluoride unit per carbonyl group. However, a study of a number of diethyl esters showed that the molar ratio of the vinylidene difluoride unit and diester varied between 2 : 1 and 4 : 1 depending on the particular ester investigated.[10]

Polymerisation and blend formation

After the temperature had reached ~250 °C during scan c in Fig. 2, polymerisation of the PM–BPM mixture was initiated thermally. The heat flow of all samples was constant after retaining the samples at 300 °C for 30 min, indicating that the polymerisation was completed. Only crystallisation and melting of PVDH was detected during scan e and f, respectively, in Fig. 2. Furthermore, the PVDH phase in all the blends had T_m equal to that of the pure copolymer (145 °C). This indicated the consumption of the monomers, and the formation of polymer blends and networks. The enthalpy of melting of the PVDH as evaluated from the last heating scans is plotted in Fig. 3 *versus* w_2 (squares). The results showed that ΔH was equal to $w_2 \Delta H_2$ after the polymerisation of PM–BPM mixture and, as expected, there were no indications of complex formation.



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The PVDH phase of the blend with $w_2 = 0.2$ was extracted with acetone in order to study the morphology and to collect the polymaleimide network. Fig. 5 shows a micrograph from the subsequent microscopy study. It can be concluded that the polymaleimide formed a continuous crosslinked porous network in the PVDH melt at the polymerisation. The largest polymaleimide ribbons in the network had a thickness of ~0.5–1 μm, while the smallest were ~0.1 μm thick. The largest pores found in the network were estimated to be ~2 μm from the micrographs.

Thermogravimetry was used in order to examine the thermal stability of the porous polymaleimide networks and the blends. Fig. 6 shows the results of the thermogravimetric analysis of the blend samples and the neat porous polymaleimide network, as well as neat PVDH. As seen, the neat polymaleimide network had a thermal decomposition temperature of ~380 °C, and the neat PVDH sample started to decompose at ~420 °C. The latter value corresponded well with the data given by the producer of the PVDH.[7] Poly(*N*-phenylmaleimide) prepared by radical initiated polymerisation has previously been reported to have a decomposition temperature of 364 °C.[11] Copolymerisation with PM is a common method to increase the thermal stability of vinyl and styrenic polymers.[12,13] The high decomposition temperatures demonstrated the high thermal stability of both the polymaleimide networks and the PVDH. The blends all had decomposition temperatures in between those of the respective components. The degradation occurred in two steps, as evident after differential analysis (not shown), one for the polymaleimide

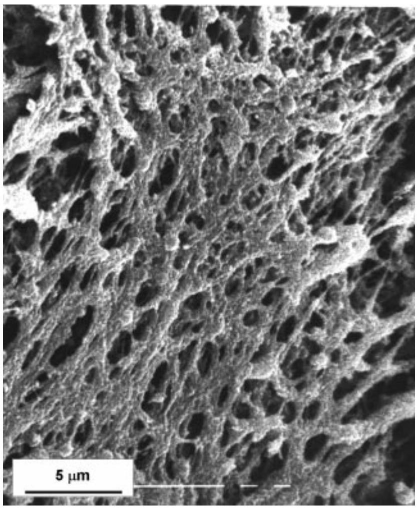

Fig. 5 SEM micrograph of a crosslinked porous polymaleimide network collected after extraction of the PVDH phase by acetone. The original blend had $w_2 = 0.8$.

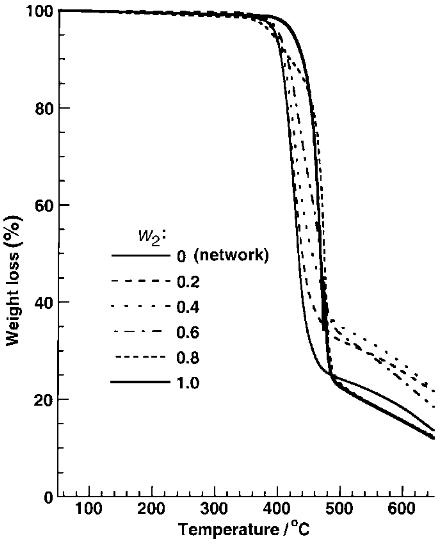

Fig. 6 Traces from the thermogravimetrical analysis of the neat porous polymaleimide network ($w_2 = 0$), the blends ($w_2 = 0.2$–0.8), and PVDH ($w_2 = 1$). The heating rate was 10 °C min^{-1}.

phase and one for PVDH phase. This was most clearly seen for the blend with $w_2 = 0.8$. The decomposition steps of the other blends were more overlapped. However, the degradation of the blends seemed to occur slower the more PVDH the blend contained.

Conclusions

Calorimetry results showed that PVDH formed thermoreversible gels in phenylmaleimides. When samples were heated above the gelation temperature, PVDH dissolved in the mixture of phenylmaleimides. Polymerisation began when these solutions were heated above ~250 °C, resulting in the formation of phase separated polymer blends. The PVDH melt proved to be an effective and thermostable dielectric medium for the thermally induced polymerisation of the maleimides. The large difference between the gel melting points and the decomposition temperature of PVDH provided a large temperature span in which to carry out the polymerisations. After polymerisation, porous polymaleimide networks were readily collected after extraction of the PVDH phase in the blends using acetone. This way of preparing polymer blends by *in situ* polymerisation of maleimides in PVDH melts may be useful when it comes to producing porous networks for use as thermally stable membranes. However, further studies are needed in order to evaluate the properties of the porous networks.

Acknowledgements

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