Replacement of monomer and catalyst in BADGE-MA/alkene coatings

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GENERAL TECHNIQUES AND CONSIDERATIONS
Chapter 2. General techniques and considerations

Abstract

In this chapter, details of sample preparation, and the synthesis and characterisation of the compounds and complexes used in this thesis are provided together with a description and discussion of the techniques used to characterise both the curing process and the cured materials. Phenomena specific to the free radical curing of resins containing cross-linking agents are addressed; the effect of initial viscosity on curing profile and refractive index changes on spectroscopic analysis.
2.1. Introduction

Commercial formulations of resins are often multi-component mixtures for which often the description of the content available from the manufacturer is incomplete, and the precise function of every component is not fully understood. It is important to know the exact composition of the resins used to understand curing of the type of bis-methacrylate/monomer mixtures studied here. Therefore the starting material was custom synthesised and the materials used were characterised in the detail and the exact composition of mixtures is reported. The cross-linker used throughout this work was provided by AkzoNobel. It is important to fully understand and characterise the material to get a full understanding of the polymerisation of this material with other monomers. Therefore in this chapter the complete synthesis and characterisation of BADGE-MA is reported. The preparation of a standard sample is described. Next to the cross-linker, the synthesis of the iron complex used in these studies, Fe(II)-bispidine, is described including a (spectroscopic) characterisation.

Secondly, in this chapter several non-trivial aspects that are relevant to curing of mixtures of cross-linker and monomer will be discussed, as these aspect have to be taken into account for most of the experiments presented in the rest of this thesis and will help understand some of the results. The effect on monomer concentration and addition of non-reactive diluents on viscosity will be discussed as well as the effect of initial viscosity on curing profile of these resins.

Finally, methods that were used in several of the following chapters to investigate and follow the curing of these resins, and the techniques used to characterise the polymer product obtained after curing will be introduced and described in detail in this chapter. This includes discussion on how spectroscopic data is obtained, e.g., time resolved Raman experiments to follow conversion in curing resins, and how the data is processed. All relevant information on how measurements were automated for the purpose of high-throughput screening will be provided, to a level that should enable the reader to build a similar system.

2.2. Sample preparation and catalyst synthesis

In this section general considerations when working with these resins are mentioned, including how to handle BADGE-MA and addition of styrene or other monomers, and when catalyst should be added and mixed. The storage (shelf-life) of the prepared resins is considered, as are the inhibitors present in the resin and those removed from reactive diluents. The amount of initiator and catalyst added and concentrations of all components are controlled.
2.2.1. Preparation of standard samples

Styrene (≥ 99.0%), cumene hydroperoxide (80%) and Co(II)(2-ethylhexanoate)$_2$ solution in mineral spirits (65 wt%) were obtained from SigmaAldrich. A solution of Mn(II)(neodecanoate)$_2$ (8 wt% on metal basis) in mineral spirits and Fe(II)-bispidine solution (Borchi®OXY-Coat 1410, 10wt% of complex in 1,2-propanediol) was obtained from Borchers, Al$_2$O$_3$ 90 active 70-230 mesh was obtained from Merck. Cumene hydroperoxide and the Co(II)(2-ethylhexanoate)$_2$ containing solution were used without further treatment. Styrene (or other monomer) was passed over a short column of Al$_2$O$_3$ to remove the inhibitor (BHT), GC-FID was used to confirm removal of the inhibitor, and the filtered styrene was stored at 7 °C for a few days at most, or used immediately.

Bisphenol-A based diglycidylether dimethacrylate, hereafter referred to as BADGE-MA, was placed in an oven at 80 °C for approximately 30 min, 10 g of warm BADGE-MA was poured into a disposable 20 ml glass vial with screw cap, to which 3.5 g (i.e., 0.35 g/g BADGE-MA resin) styrene was added and a vortex mixer (Scientific Industries, Vortex genie 2) or a SpeedMixer™ (FlackTek, DAC 330-100 SE) was used to homogenize the mixture. For samples which were difficult to mix, the glass vial was heated gently. After cooling to room temperature 0.1 wt% (based on the total resin weight) of Co(II)(2-ethylhexanoate)$_2$ solution or Fe(II)-bispidine solution was added to the homogeneous solution, resulting in concentrations of 1.9 mMolal or 0.15 mMolal, resp. The mixtures were mixed again until fully homogeneous and yielded a blue/purple solution or a yellow solution, respectively. The BADGE-MA/styrene/catalyst mixture was poured into 2 or 4 ml glass vials used for reaction monitoring. The polymerisation is initiated by the addition of typically 17 µl (0.092 mmol) cumene hydroperoxide per gram of resin and mixing thoroughly on the SpeedMixer. In the case of Co(II)(2-ethylhexanoate)$_2$, addition of the cumene hydroperoxide resulted in a change in colour from blue/purple to green.

2.2.2. Removal of inhibitors

During synthesis of BADGE-MA, 1000 ppm (4.5 mMolal) 2,6-di-tert-butyl-4-methyl phenol (BHT) is added to inhibit unwanted polymerisation during storage. In all experiments the cross-linker was used as received, that is without removal of the inhibitor. All monomers were filtered over Al$_2$O$_3$ before use. It was confirmed by GC-FID that various materials can be used to remove the stabiliser from styrene including: Al$_2$O$_3$ 90 active neutral (stage 1), Al$_2$O$_3$ 90 70-230 mesh(activity level II-III), Al$_2$O$_3$ 60 HF$_{254}$ Type E (basic), Al$_2$O$_3$ Acidic (activity level I), Celite 535, and activated Carbon. Depending on the ratio of monomer to cross-linker (typically 0.30 to 0.54 g per gram BADGE-MA) the resulting BHT concentration in a resin (BADGE-MA/monomer mix) is between 3.5 and 3.0 mMolal).
2.2.3. Choice of catalysts used

As the work carried out is this thesis is in collaboration with an industrial partner, the focus was not on catalyst/ligand design, catalyst availability of a commercial scale was of concern. With this in mind a commercially available iron complex that has been used earlier to substitute cobalt based catalysts in alkyd paints, was selected as starting point for cobalt replacement in BADGE-MA/alkene resins. Although available commercially and received as a gift as a solution, the ligand and iron(II) complex thereof was prepared also for comparison.

2.3. Synthesis of BADGE-MA

2.3.1. Experimental

The BADGE-MA used in the studies reported in this thesis was kindly provided by AkzoNobel and was prepared by R. van Gemert. Acid numbers were determined according to ISO2114, however the toluene/ethanol (1:1) solvent mixture was replaced by a xylene (mixture of isomers)/ethanol (1:1) mixture. The epoxy number was determined according to ISO3001. Epikote 828 is a commercially available glycidyl ether of bisphenol A, which has an initial epoxy value of 292 mg KOH/g.

\((\text{propane-2,2-diylbis(4,1-phenylene)})\text{bis(oxy)}\)\text{bis(2-hydroxypropane-3,1-diyl)}\text{bis(2-methylacrylate)} \text{(BADGE-MA).} \)

A 3 l three-necked round bottom flask was equipped with mechanical stirrer, thermocouple and reflux condenser, to which 1376.32 g (3.68 mol) Epikote 828, 623.68 g (7.24 mol) methacrylic acid, and 2 g butylated hydroxy toluene (BHT) (9 mmol) were added. The mixture was purged with air for 30 min at room temperature followed by heating to 100 °C and addition of 1.4 g ethyl triphenyl phosphonium bromide (4 mmol). The mixture was heated to 110 °C and the reaction was monitored through its acid value according to ISO standard ISO02114. After 7 h, the acid value had decreased to 47.7 mg KOH/g and the mixture was cooled to room temperature and left overnight. The mixture was heated in 60 min to 115 °C. After 10 h of total reaction time, the acid and epoxy value were determined and 67 g of Epikote 828 added to the mixture to make up for the difference in the measured acid and epoxy value. After 8 h the mixture was cooled to room temperature and left overnight. On day 3, the viscous mixture was heated slowly to 115 °C, with stirring possible only after reaching 66 °C. When an acid value of 7.9 was reached the mixture was cooled and poured into 100 ml containers and stored at 7 °C until use. The final
acid and epoxy values are 6.57 and 10.7 mg KOH/g, resp. $^1$H-NMR spectroscopy was used to confirm the presence of the acrylate groups.

### 2.3.2. CHARACTERISATION

Three methods are demonstrated that can be used to gain insight in the number of repeat units in the BADGE-MA cross-linker.

First, the number of repeat BPA units in the BADGE-MA was determined by $^1$H-NMR spectroscopy, Figure 2.1. $^1$H-NMR (400 MHz, Chloroform-d) δ 7.19 – 7.07 (m, 5H), 6.82 (d, J = 8.5 Hz, 5H), 6.15 (s, 2H), 5.61 (s, 2H), 4.58 – 3.61 (m, 10H), 2.79 (s, 2H), 1.96 (s, 6H), 1.63 (s, 7H). The ratio of the integral of the $\text{CH}_3$ singlets at 1.96 and 1.63 was used to determine the number of repeat units, yielding a value of $n = 1.2$. Alternatively, the ratio between the sum of the area of the aromatic proton signals at 7.19-7.07 and 6.82 ppm and vinylic protons at 6.15 and 5.61 ppm can be used: $(\frac{4.59 + 4.59}{8})/(\frac{1.95 + 1.88}{4}) = 1.20$.

![Figure 2.1: $^1$H-NMR spectrum of BADGE-MA in CDCl$_3$.](image)

Secondly, Gel Permeation Chromatography (GPC) was performed on a Hewlett & Packard 1100 system equipped with three PL-gel 3 lm MIXED-E columns in series. The columns were operated at $40$ °C using THF as eluent and with a flow rate of 1 ml/min. A GBC LC 1240 RI detector was used at $35$ °C. The system was calibrated on polystyrene standards. 10 mg of BADGE-MA was dissolved in 2 ml of THF in a GC vial. Toluene (5-10 µl) was added as internal standard and the solution was passed through
2.3.2. Characterisation

a 0.20 µm PTFE syringe filter. GPC has only limited use in determining the molar mass of the BADGE-MA as several factors can affect the retention time on the column, unless the calibration is made specifically for the compound measured. The resulting molar mass is therefore an indication. GPC shows that there are oligomers of several chain lengths and the dispersity of the compound/oligomer (D = 1.2) determined corresponds well with the distribution calculated by $^1$H-NMR and FTIR spectroscopy (see appendix).

Finally, a method based on ATR-FTIR spectroscopy was used, by which a drop of BADGE-MA dissolved in acetonitrile was deposited on an ATR crystal and a spectrum recorded after evaporation of the acetonitrile. A calibration curve was prepared using a series of mol ratio mixtures of the model compounds 4,4’-(propane-2,2-diyl)bis(ethoxybenzene) and 2-hydroxyethyl methacrylate (HEMA) dissolved in acetonitrile. The diethyl ether of BPA was prepared as reported below. BPA (≥ 99.0%) and HEMA (≥ 99.0%) were obtained from SigmaAldrich and used as received. The ratio of the areas of the C-O stretch band at 1244 cm$^{-1}$ and the carbonyl band at 1715 cm$^{-1}$ of a BADGE-MA solution in acetonitrile allowed for the ‘n’-value to be determined to be 1.2 by interpolation.

![Figure 2.2: ATR-FTIR spectrum of BADGE-MA recorded from a solution of 50 mg/ml in acetonitrile drop cast on the ATR crystal. Solvent bands are removed by scaled subtraction.](image)

The following procedure was adapted from Jaballah et al.\textsuperscript{1} 4,4’-(propane-2,2-diyl)bis(ethoxybenzene). 20 ml DMF was added to Bisphenol A (2.28 g, 10 mmol) and potassium carbonate (3.48 g, 25 mmol) in a round bottomed flask. Ethyl bromide (1.87 ml, 2.72 g, 25 mmol) was added at room temperature to the stirred mixture. After 16 h, the reaction mixture was poured into distilled water and extracted three times with dichloromethane. The extract was washed with water, dried over Na$_2$SO$_4$ and the solvent was removed \textit{in vacuo}. The product was recrystallized

\[ \text{Figure 2.2: ATR-FTIR spectrum of BADGE-MA recorded from a solution of 50 mg/ml in acetonitrile drop cast on the ATR crystal. Solvent bands are removed by scaled subtraction.} \]
from ethanol/water (3:1) to yield a white crystalline solid (0.87 g, 30%)
The experimental procedure was adopted from a publication by Börzel et al.\textsuperscript{4} Dimethyl 3-methyl-9-oxo-2,4-di(pyridin-2-yl)-7-(pyridin-2-ylmethyl)-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate (2, or bispidine). 1 Was ground to a powder using pestle and mortar and (14.0 g, 36.5 mmol) was added to a round bottom flask equipped with magnetic stir bar and reflux condenser and subsequently suspended in 200 ml ethanol. 2-(Aminomethyl) pyridine (4.74 g, 4.50 ml, 43.8 mmol) and a 37% aqueous formaldehyde solution (6.52 ml, 87.6 mmol) were added to the suspension. The suspension was heated at reflux for 30 min after which a clear brown solution was obtained. The solvent was removed and a sticky brown oil was obtained. The oil was dissolved in 25 ml ethanol while heating at reflux and cooled to -18 °C. The product precipitated as a brown precipitate, was collected by filtration and recrystallized from ethanol. After 12 days clear crystals were collected by decanting the brown liquor and washing with small portions of ice cold ethanol. The final product (2) was obtained as slightly yellow crystals with a yield of 48.4%. \textsuperscript{1}H-NMR (400 MHz, Chloroform-d) \( \delta \) 8.60 (d, \( J = 4.9 \) Hz, 1H), 8.43 (d, \( J = 4.7 \) Hz, 2H), 8.11 – 7.97 (m, 1H), 7.94 – 7.83 (m, 1H), 7.75 (t, \( J = 7.7 \) Hz, 2H), 7.65 – 7.49 (m, 3H), 7.31 (t, \( J = 6.4 \) Hz, 2H), 5.90 (s, 2H), 4.35 (s, 2H), 3.99 (s, 2H), 3.75 (s, 6H), 3.45 (s, 2H), 2.39 (s, 3H).

Fe(II)-bispidine \( \text{FeCl}_2 \cdot 4\text{H}_2\text{O} \) (500 mg, 2.51 mmol) was added to 100 ml MeOH. The ligand bispidine (2) (1.74 g, 1.05 eq, 2.64 mmol) added in 100 ml MeOH both mixtures were stirred for 10 min at room temperature (RT). The fully dissolved ligand was added in one aliquot to the stirred \( \text{FeCl}_2 \cdot 4\text{H}_2\text{O} \) solution and the mixture was stirred for 1 h at RT to yield a deep yellow coloured solution. The solvent was removed in vacuo to obtain a sticky yellow oil. EtOAc was added (twice the volume of methanol used) and the flask was sonicated for 60 min until the sticky oil transformed into a yellow powder. The product was filtered over a (P4) glass filter, washed three times with EtOAc and subsequently three times with diethyl ether. 1.61 g (>99%) of a yellow
powder was obtained as final product. $^1$H-NMR (400 MHz, D$_2$O, tip angle = 90°) δ 198.27 (s, 2H), 189.91 (s, 2H), 187.80 (s, 1H), 164.57 (s, 1H), 71.20 (s, 4H), 64.01 (s, 1H), 58.79 (s, 3H), 54.86 (s, 3H), 46.79 (s, 1H), 42.51 (s, 2H), 35.39 (s, 3H), 22.33 (s, 2H), 5.88 (s, 6H), -12.31 (s, 1H). HRMS (ESI-pos.) theoretical (C$_{28}$H$_{29}$ClFeN$_5$O$_5$): 606.12012, found: 606.11968, 624.13023 and 638.14571. Where the other masses found correspond to H$_2$O and methanol adduct, i.e., (hemi)acetal, (theoretical: 624.13068 and 638.14633, resp.). CHN analysis: Expected: C:52.36, H:4.55, N:10.90, C/N = 4.804 (complex); C:50.93, H:4.73, N:10.61, C/N = 4.800 (H$_2$O adduct); C:51.65, H:4.93, N:10.39 C/N = 4.971 (methanol adduct). Found: C:49.875, H:4.930, N:10.135 C/N = 4.921. The C/N ratio measured is between that expected for complex and for the methanol hemiacetal, which indicates a mixture, which is consistent with the HRMS data.

Figure 2.4: $^1$H-NMR spectrum of compound 1 in CDCl$_3$. The spectrum is complicated by the two positions at which enolisation can occur, with a resultant loss of symmetry. Furthermore, there are four stereocenters in this compound which results in 24 possible stereoisomers. Unreacted starting material (aldehyde) is not observed in the spectrum.
2.4.1. Experimental

**Figure 2.5:** $^1$H-NMR spectrum of compound 2 in CDCl$_3$. Here the total number of signals corresponds to that expected. The absence of enolisable positions means the compound has higher symmetry and the two -CH$_3$ (ester) groups merge to one singlet, with integration 6.

**Figure 2.6:** $^1$H-NMR spectrum of the high spin Fe(II)-bispidine complex in D$_2$O with pw = 90°and d1 = 100 ms. The total number of signals corresponds to that expected. All signals are shifted by pseudo contact shift from the S = 2 Fe(II)-centre.
Figure 2.7: $^1$H-$^1$H COSY-NMR spectrum of compound 2. Coupling with vicinal protons was only observed in the aromatic region.

Figure 2.8: HRMS (ESI-pos.) of Fe(II)-bispidine. Expansion shown below.
Figure 2.9: HRMS of Fe(II)-bispidine with expansion of range showing m/z of 606 and 624. All spectra show measured (top) and calculated (bottom) spectra.
Figure 2.10: HRMS of Fe(II)-bispidine with expansion of range showing m/z of 638. Measured (top) and calculated (bottom) spectra shown.

Figure 2.11: UV/vis absorption spectrum of Fe(II)-bispidine in water (0.075 mM) (left) and solid state Raman spectrum of Fe(II)-bispidine ($\lambda_{exc}$ 785 nm) (right).
2.5. Impact of initial viscosity on the curing profile of BADGE-MA/styrene resins

Where styrene is substituted for different monomers, with a different viscosity, the initial viscosity of the resin will inevitably be affected. In this section the importance of initial viscosity on curing will be discussed.

2.5.1. Introduction

The reaction of BADGE-MA/alkene resins can be divided in four periods following addition of initiator, which will be referred to as the ‘reaction profile’ throughout this thesis, Figure 2.13. As auto-acceleration is dependent on limiting diffusion of the growing polymer chains, thereby slowing termination by radical radical coupling, the progress of the reaction is expected to be dependant on microscopic viscosity.

![Figure 2.12: ATR-FTIR spectrum of Fe(II)-bispidine (left) and expansion of the region 2000-550 cm\(^{-1}\) (right)]

![Figure 2.13: Alkene conversion over time for an ideal BADGE-MA/alkene polymerisation](image-url)
Specifically, stage III (the rapid acceleration phase) is triggered by the formation of a gel in which the growing polymer chains are sufficiently cross-linked to become immobile and the solution forms a gel, with an increase in macroscopic viscosity. The decreased mobility of growing chains is in contrast to the monomer (styrene) and unreacted methacrylate, both of which can still move freely within the gel by diffusion. This leads to a decrease in termination of radical chain ends and therefore an acceleration of the reaction, known as the Trommsdorff-effect, Trommsdorff-Norrish, or gel-effect. Phase IV is reached when the $T_g$ of the mixture reaches the temperature of the reaction itself with the solution becoming rigid forming a so called glass. At this point monomers can no longer diffuse through the ‘solution’ and further chain extension is inhibited. It was shown that increasing the temperature above the $T_g$ lead to further growth of the polymer until again the $T_g$ of the mixture again reaches the temperature of the sample.\(^5\)

In this section, the effect of diluents, \textit{i.e.}, changing the initial viscosity of the mixture, on the reaction progress is explored. The initial viscosity of the resin can modified using an unreactive diluent such as 1,2-propanediol, which is the solvent used in the addition of the Fe(II)-bispidine complex. Although the main focus of the thesis is to replace styrene, the data obtained with styrene is critical in understanding and appreciating the interaction between components in the BADGE-MA/alkene systems that has to be replicated in styrene free formulations.

### 2.5.2. Effect of non-reactive diluents on reaction profile

Addition of ca. 5-20 weight\% of a solvent has a substantial effect on reaction progress, Figure 2.14. A trend was noted in that the transition from slow to fast phase is delayed by an increase in non-reactive diluent concentration. This effect is more pronounced for low viscosity solvents, \textit{i.e.}, the effect becomes more pronounced when 1,2-propanediol is substituted with its monomethyl ether and even more with its dimethyl ether. (Viscosities (kin): 1,2-propanediol: 40 mPa s, 1-methoxy-2-propanol: 1.8 mPa s, 1,2-dimethoxypropanol: < 1 mPa s). As the catalyst concentration changes when unreactive diluent is added, a further investigation into the effect of catalyst concentration was warranted; data shown in chapter 3, from which we concluded that variations in the concentration of Fe(II)-bispidine, in this range, does not effect the curing profile.
2.5.2 Effect of non-reactive diluents on reaction profile

Figure 2.14: BADGE-MA/styrene polymerisation initiated by the decomposition of cumene hydroperoxide catalysed by 0.16 mM Fe(II)-bispidine. Reaction conditions: sample held in a 4 ml vial at 19 °C in a temperature controlled room. The reaction is followed by Raman spectroscopy ($\lambda_{exc}$ 633 nm with carousel). Solvents added before the initiator: A) 1,2-propanediol, B) 1-methoxy-2-propanol, C) 1,2-dimethoxypropane. Part of data omitted due to misalignment of sample.

The effect of added solvent on the reaction progress was determined by varying the amount of 1,2-propanediol added while keeping a constant catalyst concentration (Figure 2.15 and 2.16). 1,2-propanediol was chosen as solvent of choice as the commercial Fe(II)-bispidine (Borchi OXY-Coat 1410) is dissolved in this solvent. Addition of $< 1$ wt% of 1,2-propanediol to the system does not show a significant effect on the reaction progress, however addition of $> 1$ wt% has a pronounced effect. Specifically, the rate of the slow phase (phase II) is unaffected, but the point at which the reaction switches from phase II to phase III shifts to longer times. Neither the rate during the fast phase (III) nor the final conversion are affected significantly. The dependence on diluent concentration supports our hypothesis that addition of diluent, i.e., decreasing the initial viscosity of the reaction mixture, delays the formation of a gel and therefore the point of acceleration.
2.5.3. Repeatability of curing experiments

The repeatability of the reaction profile in the iron-catalysed polymerisation was tested by following the curing of six vials simultaneously, with BADGE-MA/St resin from one batch, Figure 6. This data shows that the acceleration, the length of the fast phase and the extent of conversion are the same in all six samples. Between different batches or measurements on different days larger variations are expected.

Figure 2.15: BADGE-MA/styrene polymerisation initiated by the decomposition of cumene hydroperoxide by Fe(II)-bispidine (0.16 mMolal) with various amounts of 1,2-propanediol added. Reactions were conducted in 4 ml vials at 25 °C in a temperature controlled sample holder. The reactions were monitored by Raman spectroscopy, \( \lambda_{\text{exc}} \) 785 nm.
2.5.4. Dilution of BADGE-MA/styrene samples catalysed with Co(II)-soap

The data obtained with the Fe(II)-bispidine showed a pronounced dependence of the time at which phase III starting on initial solvent viscosity. With Co(II)(2-ethylhexanoate)$_2$ as catalyst, addition of 1,2-propanediol to the resin results in a colour change from purple to pink, indicative of coordination of the solvent to Co(II), which could potentially deactivate the Co(II) catalyst and indeed resin mixtures did not cure when 1,2-propanediol concentrations exceeded that of the catalyst. Hence $p$-xylene, due to its similarity in polarity with styrene, was added to the resin with a range of 20 to 100 $\mu$l $p$-xylene/g resin, i.e., 1.7 - 8.6 wt%. The delay in the onset of acceleration was observed in the Co(II) catalysed system, and is more pronounced than with the Fe(II)-bispidine catalysed resins. In the range of 20-60 $\mu$l $p$-xylene/g resin (1.7 - 5.2%) a delay in the onset of acceleration and with higher concentrations of non-reactive diluent the polymerisation behaves more like a solution polymerisation without a clear change in reaction rate, Figure 2.17.

Figure 2.16: Repeatability of curing profile within one batch BADGE-MA/styrene. Concentration of Fe(II)-bispidine catalyst: 0.18 mMolal. Reaction at 25 °C.
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2.5.5. Viscosities of resin mixtures with non-reactive diluents

The rheology of BADGE-MA/styrene-resins with two concentrations of styrene (27 and 36 wt%, corresponding to 0.3 and 0.4 ml/g BADGE-MA, resp.) were studied. 0.1wt% Fe(II)-bispidine stock solution (BOC1410) was added, which gives a concentration of 0.17 mMolal, and after thorough mixing, the resins were divided over vials. These batches were diluted with 0, 50 or 100 µl 1,2-propandiol/g resin. Rheology was performed at 25 °C on a TA Instruments Rheometer Discovery 3 equipped with a Peltier heating plate and solvent trap filled with deionised water. A parallel plate setup with 20 mm top and bottom geometries (suitable for samples of high viscosity) were used for the measurements and the gap was set to 300 µm. Cumene hydroperoxide was not added to the resins. Each sample was measured four times by taking a fresh aliquot of resin from a glass vial, Figure 2.18.

The initial decrease in viscosity is an artefact of the measurement, which was observed at the other extreme of the graph when the shear rate was varied from high to low. The difference in viscosity with the addition of roughly 50 to 100 µl non-reactive diluent/g is remarkable, with the viscosity of the resin dropping from 1200 mPa s to approximately 510 mPa s. These data show that the viscosity of BADGE-MA/styrene resins changes substantially even when only small amounts of (non-) reactive diluent are added. This effect has implications in regard to the search for alternatives to styrene, as the reaction profile of the resin will depend on physical parameters (molecular weight, density and viscosity) of the alkene used.
2.5.6. Concluding remarks on the effect of viscosity on curing

The concentration of the catalyst Fe(II)-bispidine in the BADGE-MA/styrene mixture does not affect reaction progress significantly as demonstrated when varying the catalyst concentration, while holding the amount of 1,2-propanediol constant. In contrast, the amount of 1,2-propanediol added at a constant catalyst concentration shows a change in the time at which the reaction goes from phase II to phase III. Therefore, we can conclude that viscosity is an important parameter in tuning the curing kinetics of these resins. Since viscosity has such a large effect on these systems and because the viscosity changes substantially even with small changes in the composition of the resin, replacing styrene for another monomer will lead to different curing behaviour than one would initially expect. Monitoring viscosity changes and/or determining (perhaps changing) the initial viscosity will be crucial to find a suitable replacement for styrene. A key question, however, is as to how good a relation can be determined between dynamic viscosity at the start of the reaction and the change in diffusion rates of polymer and monomer as the reaction progresses.
2.6. TECHNIQUES USED THROUGHOUT THIS WORK

In this section an overview is made of the primary techniques and methods of analysis used in this thesis.

2.6.1. RAMAN SPECTROSCOPY

In this section an overview of the spectra of BADGE-MA and styrene is provided together with an assignment of the most relevant bands in regard to reaction progress monitoring. Furthermore, the approach to spectral processing, in particular normalization will be discussed.

2.6.1.1. RAMAN SPECTRA OF COMPONENTS

![Raman spectra](image)

*Figure 2.19: Raman spectra ($\lambda_{exc} 785$ nm) of neat styrene and BADGE-MA.*

Small fluctuations in laser intensity, temperature, or amount of sample in the confocal volume (e.g., due to small pocket of air in the sample), and changes in the confocal volume itself (due to changes in refractive index) can result in a variation in the absolute intensity of Raman spectra. These variations are especially relevant for experiments carried out over extended periods (e.g., following resin curing over several hours), and when comparison of band areas at different moments in the curing process are required. A normalisation procedure on a raw dataset has to be applied, to compensate for these variations. A suitable band for normalisation is one that does not show overlap with bands that change in intensity over time, and it should be unaffected by polymerisation. Which means that the bond corresponding to the vibration observed should, to state the obvious, not involve displacements of atoms in bonds that are changing in the polymerisation, but also not be too close to the part where bonds are formed/broken, as this can effect the shape and intensity (polarisability) of adjacent bonds also. See as
2.6.1. Raman spectroscopy

an example the change in shape and intensity of the BADGE-MA carbonyl \( (v_{\text{str,C-O}}) \) at 1712 cm\(^{-1} \), Figure 2.21, making it unsuitable as internal standard, despite that the carbonyl is in principle not ‘involved’ in the polymerisation.

The band at 1112 cm\(^{-1} \) from (aryl-C stretch) BADGE-MA does not overlap with any band from styrene, furthermore the band is unaffected by polymerisation, vide infra. Therefore this band was used as internal standard for normalisation of all data presented in this thesis, unless mentioned otherwise.

2.6.1.2. Carousel

The term ‘carousel’ refers to a rotating 3-D printed circular holder with a total of twelve slots that fit 4 ml glass vials, that was mounted on a stepper motor, and was controlled with an Arduino. Although in the early stage it was used for kinetic measurements, the carousel offered no control over temperature and was not sturdy, resulting in less than ideal conditions for recording high quality data. The design was superseded by the multi-stage, vide infra, which was used throughout this thesis. Raman spectra at 633 nm were obtained using a 35 mW HeNe Laser coupled to a Raman probe (Avantes) with an optical fibre. The Raman scattering collected were feed to a Shamrock163 spectrograph by a round to line fibre bundle (100 µm fibre diameter) and dispersed by a 1200 l/mm 500 nm blaze grating onto an iDus420-OE CCD (Andor Technology).

2.6.1.3. Multi-stage for automated screening

Time dependent Raman spectra were recorded using a Quantum Northwest (QNW) sample holder that can hold a maximum of six 4 ml glass vials with a Peltier element to control temperature (ca. -20 to 160 °C). The temperature control and position change were controlled by a VT100 TC1 temperature controller (Figure 2.20). The temperature controller was modified by the manufacturer (QNW) to transmit a 5V TTL pulse of the appropriate length to external trigger input of the CCD camera. Care was taken to match the impedance of the controller with that of the iDus-420-OE CCD (Andor Technology) camera, which enabled the VT100 controller to regulate temperature, sample position, and control when a spectrum was recorded. Raman spectra were recorded using a home built probe with a 35 mm focal length planoconvex lens (25 mm diameter). Excitation was provided by an ONDAX RO free space laser module at 785 (75 mW at source) passed through a laser line clean up filter, and directed into the optical path by a dichroic mirror (45°) (Semrock Di02-R785) to the sample via the planoconvex lens. The Raman back scattering passed through the dichroic mirror and a Rayleigh line rejection filter and was focused into a 100 micron multimode optical fibre connected to a Shamrock163i spectrograph with a 600 l/mm 830 nm blazed grating and a idus-420-OE CCD camera (Andor Technology). Spectra were acquired with Andor Solis. Spectra were calibrated with cyclohexane (ASTM E 1840). Spectra of BADGE-MA/alkene mixtures were obtained with 1 accumulation/2 s exposure each. The cosmic ray removal option in the ANDOR SOLIS software was disabled when running time resolved experiments, especially when using different mixtures, as it resulted in artificial removal of bands in the spectra. The system was used typically to measure overnight with ca. 1 min time interval between measurements when all 6
positions were used.

Figure 2.20: QNW sample holder operated by the VT100 TC1 temperature and position controller (not in photo), laser and home-built variable focal-length probe. Complete system is shown as an appendix

2.6.1.4. Kinetic measurements and data handling
A typical dataset obtained with the multi-sample Raman system described above is used to demonstrate the processing of the data obtained. The Raman spectrum of a resin mixture of BADGE-MA and styrene (1:0.3 w/w) containing 0.18 mMolal Fe(II)-bispidine, was followed, after the polymerisation was initiated by the addition of cumene hydroperoxide (92 mMolal). The temperature was held at 25 °C throughout the polymerisation.
2.6.1. Raman spectroscopy

Figure 2.21: Raman spectra ($\lambda_{exc}$ 785 nm) of a BADGE-MA/styrene resin containing 0.18 mMolal Fe(II)-bispidine, curing followed after addition of cumene hydroperoxide. Spectra plotted from violet (initial) to red (final). Both raw data (top) and data after normalisation using the band at 1112 cm$^{-1}$ (bottom) are shown. The integrated area over time of the bands at 1630 cm$^{-1}$ are shown as insets.

The raw data is shown in the top part of Figure 2.21, where several band are indicated with arrows in the raw data. From left to right: 772 cm$^{-1}$ (ring deformation ‘umbrella-mode’, styrene), 1112 cm$^{-1}$ (Aryl-C-Aryl stretch, BADGE-MA), 1202 cm$^{-1}$ (Aryl-vinyl C-C stretch, styrene), 1298 cm$^{-1}$ (CH$_2$ distortion, BADGE-MA), 1315 cm$^{-1}$ (Vinyl CH$_2$ rocking, styrene), 1410 cm$^{-1}$ (Vinyl CH$_2$ scissoring, BADGE-MA and styrene), 1597 cm$^{-1}$ (C-C ring stretch, styrene and BADGE-MA ‘breathing mode’), 1625 cm$^{-1}$ (C=C stretch, styrene and BADGE-MA). Band assignment based on literature$^{6-8}$, and on DFT calculations. The band at 1112 cm$^{-1}$ does not change during polymerisation, which makes it suitable for normalisation. Prior to a normalisation based on the area of the band from 1095 - 1135 cm$^{-1}$ range an offset correction is applied to the spectra at 1135 cm$^{-1}$. Subsequently an offset correction is applied at 1670 cm$^{-1}$, and the range from the minimum between the two bands at 1597 and 1630 cm$^{-1}$, ca. 1615 cm$^{-1}$, and 1670 cm$^{-1}$ is integrated by area.
2.6.2. Calculations

DFT calculations were used as additional aid to assign bands to Raman spectra of BADGE-MA and monomers. Calculations were done using Gaussian 16 software, version ES64L-G16RevB.01, with the basis-set and solvent model as follows (# opt=calcall freq=raman b3lyp/6-31+g scrf=(solvent=toluene) nosymm).

2.6.3. Luminescence

As noted by L.E. Eijsink, luminescence spectroscopy using rigidochromes is useful in determining the point at which microscopic viscosity increases suddenly. The change in the emission spectrum due to rigidochromic effect on \([\text{Ru(dpp)}_3](\text{PF}_6)_2\) during the formation of a glass is of particular interest in this thesis. Emission spectra were recorded on an Edinburgh Instruments FS-5 spectrofluorimeter with correction for spectral response using a SC-26: TE-Cooled Sample Holder (-50 °C to +150 °C). Samples were measured at 20 °C. Emission lifetimes were determined by TCSPC with multichannel scaling with a 450 nm (EPL-450 Edinburgh Instruments) laser diode (Edinburgh Instruments).

2.6.4. Singlet oxygen emission

NIR emission spectra were recorded with excitation at 355 nm (2 mW at sample, Cobolt lasers) or 400/445 nm (35 mW at sample) combined with the optical path of the spectrometer using 45° long pass dichroic beamsplitters and focused onto the sample with a 35 mm focal length 25 mm diameter lens. Emission was collected by the same lens and passed through the dichroic beamsplitter and a long pass filter (1064 nm, Semrock) to reject visible light and focused with a 35 mm focal length planoconvex lens into a Shamrock 193i spectrograph equipped with a idus-InGaAs diode array (Andor Technology) with a 860 nm blazed 600 l/mm grating.

2.6.5. Rheology

Rheology can be used to accurately measure the viscosity of liquids over a range of shear rates. In this thesis, the time between initiation and formation of a gel was of most interest. As a visco-elastic material is formed and eventually a glass, the term ‘viscosity’ should be interpreted loosely, in particular in the paperclip experiments.

2.6.5.1. Paperclip experiment

In industry a device called a ‘gel-timer’ is used to determine the time between initiator addition and formation of a gel. We decided to replicate that type of measurement by using a custom made spindle that is equipped to hold a small paperclip, Figure 2.22. After formation of a solid polymer, the paperclip can easily be replaced. This setup is not calibrated and thus the ‘real’ viscosity is not measured and hence interpretation of these data should be limited. A clear difference (several orders of magnitude) in the observed relative viscosity from the start until the formation of a gel is measured,
2.6.5. Rheology

which provides information of interest in the present thesis. The measurements were performed on a TA instruments Discovery Hybrid Rheometer HR-2, with the peltier set at 25 °C, 0.1 rad oscillation, 1 rad/s, measuring for 7200 s and collecting 500 data points.

Figure 2.22: Custom made spindle to fit the rheometer

2.6.5.2. Rheology-Raman-Luminescence

The change in visco-elastic properties of a curing resin was correlated to the extent of alkene polymerisation (by in-line Raman spectroscopy) and to the change in emission spectra of a rigidochromatic luminophore, *vide supra*.

Figure 2.23: Combined Raman, rheology and luminescence experiment.

As a demonstration the data obtained with a BADGE-MA/4-tert-butylstyrene resin containing Co(II)(2-ethylhexanoate)$_2$ as catalyst is shown, Figure 2.24. The reaction was followed after initiation by the addition of cumene hydroperoxide. A sudden change in 'viscosity' is observed after ca 25 min, which corresponds to the formation of a gel.
A full shift in the centre wavelength of the emission of the ruthenium complex to ca. 624 nm coincides with the point at which further polymerisation was not observed, i.e., at the point a glass is formed and movement of monomer is restricted.

![Figure 2.24: Alkene conversion (Raman), rheology and luminescence data obtained from a BADGE-MA/4-tert-butylstyrene resin mixture. Reaction followed after initiation by addition of cumene hydroperoxide.](image)

### 2.6.6. Tensile testing

Six 3D-printed shapes based on ASTM standard pull-bars with dimensions of 170x23x3 mm were used to prepare a custom mold from silicone-rubber. The mold was filled with resin, with care to ensure the mold was not over/under filled and that air bubbles were not trapped in the resin. The pull-bars were cured at room temperature for 24 h. Mold bars with almost identical shapes and thicknesses could be made by this procedure.

The width and thickness of each pull bar was determined on two points to 0.05 mm accuracy, using a caliper, the averaged values were entered in the tensile test software. All measurements were performed on a Tinius Olsen H25kt using a 25kN force gauge and using a pulling speed of 5 mm/min. Raw data was saved to a .csv file, which was used to plot and extract the Young’s Modulus using a custom Python script (see appendix). The Young’s modulus was determined from the initial slope (data points 5-200), which corresponds to a strain of 0 to 0.007 (mm/mm).

Tensile testing of pull bars gives a wide spread in data and hence multiple pull bars need to be measured for each resin batch. Furthermore, the standard deviation in the data should be considered in the interpretation of differences between compositions (i.e., does the difference in the mean in two Young’s moduli exceed the standard deviation). The “n-1” method was used, which takes into account the underestimation of standard deviation when the sample size is <10, Equation 2.1.
DSC can be used to observe phase transitions in a material, such as melting, crystallisation or a transition from a glass to a rubber like state. Both exergonic and endergonic processes can be followed. In the case of a thermoset material that does not reach full conversion, it can be challenging or even impossible to determine the $T_g$ of the material with DSC, due to an overlap between the exotherm of polymerisation of residual unreacted monomer, and the phase transition. A common approach to solve this issue is by heat treating the sample (i.e., heat to a temperature well above the $T_g$ of the material, post-cure) to reach full conversion, and in a subsequent cycle to determine the $T_g$ of the material.

Arguably this approach does not provide information about the original polymer, and the physical properties (extent of conversion, $T_g$, brittleness etc.) of the material under study are changed after the heat treatment.

Superimposing a sinusoidal trajectory on the linear heating rate during DSC (modulated DSC or mDSC) may separate these two processes. Where the polymerisation is irreversible, the transition between glassy and rubbery state is reversible. With sufficient oscillations compared to the range of the transition, one can use mDSC to distinguish between these reversible and irreversible heat-flows. This approach provides more relevant data as to the $T_g$ in regard to the material and its applications. In addition to DSC, the behaviour of a material at elevated temperatures can or should be studied by Thermal Gravimetric Analysis (TGA), to ensure that a large (>5%) weight loss due to either evaporation or decomposition in the temperature range does not take place.

The measured samples were prepared by pouring resins into 4 ml glass vials with screw caps, used for reaction monitoring. The polymerisation is initiated by the addition of 17 µl (0.092 mmol) cumene hydroperoxide per gram resin and mixing thoroughly using a vortex mixer. All samples were cured at 25 °C under isothermal conditions. After the polymer reaches maximum conversion, the samples were left at room temperature for several days and the polymer is recovered from glass vial by smashing the glass.

In this work five mg of BADGE-MA/alkene polymer was loaded into a TA instruments Tzero pan to determine the glass transition temperature. The measurement was performed on a TA instruments DSC25 where the following sequence was used: equilibration at 25 °C for 5 min, heating from 25 to 200 °C at a rate of 2 °C/min, oscillation of 0.8 °C and modulation period of 60 s, cooling to 25 °C. The cycle was repeated immediately after.
Figure 2.25: As an example: mDSC of BADGE-MA/tBuSt resin cured with complex 1 (Chapter 6). Initial run in blue and second run on same sample in green (this gives T\text{g} after heat treatment). Plot shows Total (top), irreversible (middle) and reversible heat flow (bottom).

2.6.8. Alternative method for determining T\text{g} in BADGE-MA/alkene resin

The actual T\text{g} of the resin formed can be determined from the onset of further conversion as temperature is raised. The determination was deduced from the change in extent of alkene conversion by Raman spectroscopy during a slowly increase in temperature. The onset of conversion corresponds to the temperature where movement of monomer is possible again, i.e., the T\text{g}.
2.6.9. Effect of gel point and formation of a glass on refractive index

In most datasets where curing of BADGE-MA/alkene is followed by Raman spectroscopy, a shift in band position by one or two pixels can be observed. This shift is due primarily to a change in optical path through the resin, due to a change in refractive index in the material during curing. A home-built setup was used follow the change in refractive index over time, during polymerisation based on the deflection of the path of a laser beam as shown in Figure 2.27. The experimental design and construction was carried out by A. S. Sardjan and will be described in detail elsewhere. In reactions where the cross-linker co-polymerises with a reactive diluent, the apparent refractive index changes coinciding with the moment where polymerisation halts, i.e., when a glass like state is formed. Such changes in refractive index were not observed during homo-polymerisation of the cross-linker diluted in the non-reactive diluent ethyl benzene. It should be noted that the refractive index change determined with this method may be overestimated.

Figure 2.26: BADGE-MA/Styrene was cured with cumene hydroperoxide and Co(II)(2-ethylhexanoate)$_2$ (1.88 mM) at 20 °C for 3 h followed by post-curing to 80 °C (5 °C steps with 10 min intervals between steps). Initial Raman spectrum (after curing at 20 °C to spectrum at 80 °C is shown as blue to red. The area of the alkene C=C stretch band at 1630 - 1637 cm$^{-1}$ at each temperature is shown in the inset. Reproduced from Eijsink et al. 

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Figure 2.27: Refractive index over time during curing of resin with a reactive diluent, BADGE-MA/Styrene (middle) and a non reactive diluent, BADGE-MA/ethyl benzene (right). The experimental setup is shown on the left.

2.7. Concluding remarks

In this chapter the starting materials used in resin curing studies in the later chapters are characterised, and a detailed description on how to prepare samples was provided. Parameters that can affect curing, which are not necessarily obvious, such as the effect of initial viscosity, have been discussed. An overview was provided of all the measurements used in this thesis, which enable curing to be followed over time and physical properties of the obtained polymer to be determined. Artefacts that can appear in a measurement, such as an observed shift, due to changes in refractive index of the material upon curing were discussed.

2.8. Acknowledgments

I acknowledge Oetze Staal for 3D printing of the shapes of the pullbars, Andy Sardjan for refractive index measurements, Ruben Wagenaar for assistance with the rheology studies, Rogier van Gemert for synthesis of the BADGE-MA, Wesley Browne for DFT calculations, and Yanrong Zhang for figure 2.26, on the onset of further polymerisation upon post-cure heat treatment.
Bibliography


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2.9. Appendix

Figure 2.28: Gel permeation chromatogram (GPC) of BADGE-MA in THF using toluene as internal standard. Found: Mn = 848.8 g/mol, Mw = 1043 g/mol, D = 1.18.

Figure 2.29: QNW sample holder operated by the VT100 TC1 temperature and position controller, the laser, and (raised) the spectrophotometer.
Script used for controlling multistage (QNW)

Controller Script
Interval = .6 (0.01 min)

This script will only work with T-App 1.50 or later
Note: time is in ‘centiminutes’!

___

Set temperature
___

[F1 TT S 25.00] set temperature to 25 °C
[F1 TC +] turn on temperature control
[*WCT>=25] Wait until the temperature reaches 25
[F1 CT -]
[F1 HT -]
[*CTD]
[*MSG + Press the OK if you sure you want to continue with this measurement right now]

___

set pulse width
___

[F1 T1 I] configure Output
[F1 T1 W 10.] set pulse width to 10 ms
[F1 T1 -]

[F2 PL 1]
[*D 15] this should give it enough time to move to this position

[*LS 300] number of loops

[F1 CT ?]
[F1 T1 M] pulse
[*D 5] wait 3 seconds, should be longer than accisition time!
[F2 PL 2] move to position 2
[*D 5] this should give it enough time to move to next position
[F1 CT ?]
[F1 T1 M] pulse
[*D 5] wait 3 seconds, should be longer than accisition time!
[F2 PL 3] move to position 3
[*D 5] this should give it enough time to move to next position
[F1 CT ?]
[F1 T1 M] pulse
[*D 5] wait 3 seconds, should be longer than accisition time!
[F2 PL 4] move to position 4
[*D 5] this should give it enough time to move to next position
[F1 CT ?]
[F1 T1 M] pulse
[*D 5] wait 3 seconds, should be longer than acquisition time!
[F2 PL 5] move to position 5
[*D 5] this should give it enough time to move to next position
[F1 CT ?]
[F1 T1 M] pulse
[*D 5] wait 3 seconds, should be longer than acquisition time!
[F2 PL 6] move to position 6
[*D 5] this should give it enough time to move to next position
[F1 CT ?]
[F1 T1 M] pulse
[*D 5] wait 3 seconds, should be longer than acquisition time!
[F2 PL 1] move back to position 1
[*D 15] this should give it enough time to move to next position

[*LE] end of loop

[F2 PL 1]

It is of note that a communication error between the sample holder and the controller required hard-coding every position change.

**Python script for determining Young’s Modulus**

An example of the python script used to import, plot and fit the tensile test data presented in this chapter is shown below.

2.9.0.1. **Importing packages**

```
import numpy as np
import matplotlib.pyplot as plt
from scipy.optimize import curve_fit
import pandas as pd
import ctypes
import glob
import os
```

2.9. Appendix

2.9.0.2. Parameters
# specify the path to the folder with the raw data files of the measurement
path = r‘X:\My Documents\DATA\HdB110 Pullbars L3 and L4\20221004 (tensile)\batch 3’
path_out = path
# set number of samples in dataset
n = 6
# set sample name which will be used in the legend and will be the name of the plot,
do not use ‘/’ in the name
x = ‘VE_tBuSt_Mn 1.0 mMolal_5 eq L3’

2.9.0.3. Importing .csv files
# get all the csv files in the directory
# use ‘Hugo’ to read all csvs that have a filename that start with Hugo
csvfiles = glob.glob(os.path.join(path, ‘Hugo*.csv’))

# loop through the files and read them with pandas
dataframes = [ ] # list that holds all the individual dataframes
for csvfile in csvfiles:
    df = pd.read_csv(csvfile, sep = ‘.’, decimal = ‘,’ ,skiprows = 1, header = None, skipfooter = 1, engine = ‘python’)
dataframes.append(df)

#concatenate them together
result = pd.concat(dataframes, axis = 1, ignore_index = True)

# safe combined dataframes as new csv
result.to_csv(path_out + ‘/concat.csv’)

2.9.0.4. Plotting
a = 5*n

fig, ax = plt.subplots(figsize = (4,3), dpi = 600)

for i in range(0,a,5):
    ax.plot(result[i],result[i+1], '.', label = x + " " + f‘round(1+i/5)’)

ax.set_ylabel("Stress (kPa)") # set label on y axis
ax.set_xlabel("Strain (mm/mm)") # set label on x axis
ax.set_ylim(0,65000) # if you do not want to fix the range unable this line by adding ‘#’
in front
ax.set_xlim(0,0.08) # if you do not want to fix the range unable this line by adding ‘#’
2.9.0.5. Fitting

def func(a,x):
    return a*x

param = []
llim = 5 # sets lower limit of datapoint used for fitting
ulim = 200 # sets upper limit of datapoint used for fitting
for i in range(0, a, 5):
    popt, pcov = curve_fit(func, result[i][llim:ulim], result[i+1][llim:ulim])
    print(popt[0], np.sqrt(pcov[0,0]))
    param.append([popt[0], np.sqrt(pcov[0,0])])

    plt.plot(result[i], result[i+1])
    plt.plot(result[i], func(result[i], *popt), 'r-', label=f'fit {i}')
    plt.legend()
    plt.show()

    df = pd.DataFrame(param) df.to_csv(path_out + f'//young’s moduli {x}.txt')