

Appendixes

A-1. Contact angle data analysis

The contact angle results were obtained from the sessile drop measurements using the geometric mean method of Owens, Wendt, and Rabel.^{46,76} They applied the Young's Equation.¹⁵⁸

$$\gamma_{sl} = \gamma_{sv} - \gamma_{lv} \cos \theta \quad (\text{A-1.1})$$

where γ refers to surface tension or surface energy, the subscripts sv , sl , and lv , refer to the solid-vapor, solid-liquid, and liquid-vapor interfaces respectively, and θ is the contact angle formed between a pure liquid and the surface of the solid as shown schematically in Figure A-1.1.

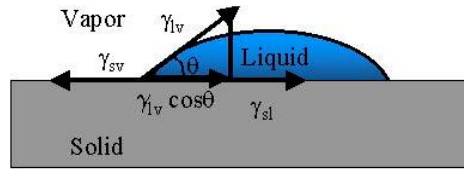


Figure A-1.1: Schematic illustration of the Young's Equation (A-1.1) at the three phase boundary of a sessile drop on a solid surface.

Together with geometric mean method the γ_{sl} value defined by Good and Girifalco in Equation A-1.2.¹⁵⁹⁻¹⁶¹

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2\sqrt{\gamma_{lv}^d + \gamma_{sv}^d} - 2\sqrt{\gamma_{lv}^p + \gamma_{sv}^p} \quad (\text{A-1.2})$$

Where d and p refer to the disperse and polar parts of the surface tension, respectively. By combining equation A-1.1 and A-1.2 leads to Equation A-1.3:

$$\frac{(1 + \cos \theta)\gamma_{lv}}{2\sqrt{\gamma_{lv}^d}} = \sqrt{\gamma_{sv}^p} \cdot \sqrt{\frac{\gamma_{lv}^p}{\gamma_{lv}^d}} + \sqrt{\gamma_{sv}^d} \quad (\text{A-1.3})$$

In Equation A-1.3 the polar (γ_{lv}^p) and the disperse part (γ_{lv}^d) of surface tension of the test liquid can be determined by using Equations A-1.4 and A-1.5.

$$\gamma_{lv}^p = \gamma_{lv} \cdot \text{polarity} \quad (\text{A-1.4})$$

$$\gamma_{lv}^d = \gamma_{lv} - \gamma_{lv}^p \quad (\text{A-1.5})$$

The square root of the ratio of the polar and disperse parts of the surface tension is used in the Owens, Wendt, and Rabel graphical data evaluation and this generates the intersection value of the x -axis. Whereas the intersection value of y -axis can be obtained by solving the left hand side of Equation A-1.3. After plotting and fitting the data by linear regression, the square of the slope ($(\gamma_{sv}^p)^{1/2}$) gives the polar part of the surface tension of the solid surface and the intercept ($(\gamma_{sv}^d)^{1/2}$) gives the disperse part of surface tension. The explanation of this calculation method is demonstrated in Figure A-1.2.

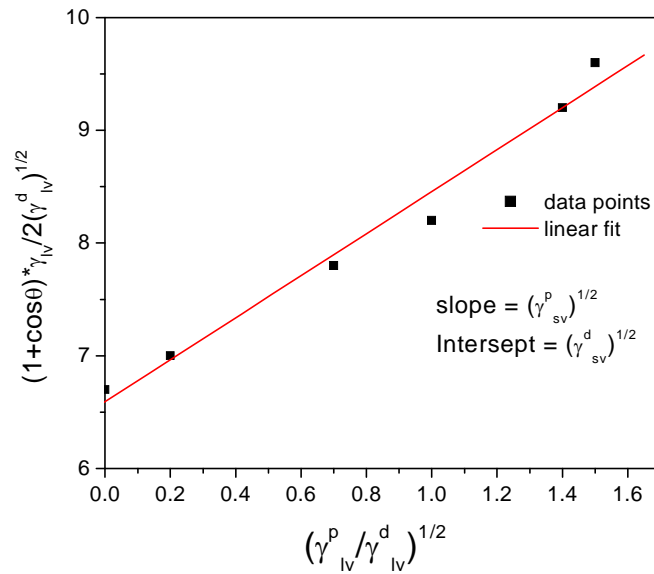


Figure A-1.2: A graphic representation of Owens, Wendt, and Rabel approach for calculation of surface tension.

The surface energies are also linked with the failure of adhesive bond. Adhesion failure involves the creation of new surfaces and hence surface energies. The surface

energy term may be the work of adhesion (W_a) or work of cohesion (W_c) depending on whether the failure is adhesive or cohesive. These are defined as.¹⁶²

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \quad (\text{A-1.6})$$

$$W_c = 2\gamma_{lv} \quad (\text{A-1.7})$$

In terms of wetting behavior of solid surface one would expect only one value of contact angle i.e. solid/liquid, liquid/air. However, by experimental means, it is possible to measure at least two different contact angles on the same solid surface and for the same liquid, which are termed as advancing (θ_a) and receding (θ_r) contact angles. The difference between θ_a and θ_r is called the contact angle hysteresis $\Delta\theta$ (Equation A-1.8).¹⁶³

$$\Delta\theta = \theta_a - \theta_r \quad (\text{A-1.8})$$

In terms of contact angle hysteresis the surface energies can be estimated by using Equation A-1.9.^{96,97}

$$\gamma_{sl} = \gamma_{lv} (\cos\theta_r - \cos\theta_a) \frac{(1 + \cos\theta_a)^2}{(1 + \cos\theta_r)^2 - (1 + \cos\theta_a)^2} \quad (\text{A-1.9})$$

The required parameters in this Equation are:

- a) the liquid vapour surface tension (γ_{lv})
- b) advancing contact angle (θ_a)
- c) receding contact angle (θ_r).

This equation is based on the assumption that no precursor film left behind, during the receding mode of drop.

The contact angle hysteresis can be related to the work of spreading W_s of liquid on solid surface. Which can be easily calculated from the work of adhesion W_a and the work of cohesion W_c :

$$W_s = W_a - W_c \quad (\text{A-1.10})$$

In the following equation the work of adhesion can be determined from the advancing and receding contact angles.¹⁶⁴⁻¹⁶⁷

$$W_a = \gamma_{lv}(1 + \cos\theta_a), \text{ and } W_r = \gamma_{lv}(1 + \cos\theta_r) \quad (\text{A-1.11})$$

$$W_c = 2\gamma_{sv} \quad (\text{A-1.12})$$

Table A-1.1: Advancing and receding contact angles on PC/ABS-SMA plate for probe liquids measured by the tilted plate method, and the total surface free energy of the PC/ABS-SMA surface obtained from Equation A-1.9.

Liquid	Liquid surface tension [mN/m]	Advancing contact angle θ_a [°]	Receding contact angle θ_r [°]	Contact angle Hysteresis $\Delta\theta$ [°]	Total surface energy [mJ/m ²]
Water	72.8	89.5 ± 4.4	30.4 ± 4.6	59.0 ± 1.7	27.6
MDI	47.6	45.0 ± 1.0	7.7 ± 2.3	37.2 ± 1.5	37.6
PO-a	34.3	35.5 ± 1.3	10.3 ± 1.3	25.2 ± 0.1	29.7
PO-b	34.9	35.4 ± 1.1	17.7 ± 1.7	21.7 ± 1.5	30.4
PO-c	34.9	36.8 ± 2.4	12.4 ± 2.2	24.4 ± 0.5	30

Table A-1.2: Advancing and receding contact angles on SMA plate for probe liquids measured by the tilted plate method, and the total surface free energy of the SMA surface obtained from Equation A-1.9.

Liquid	Liquid surface tension [mN/m]	Advancing contact angle θ_a [°]	Receding contact angle θ_r [°]	Contact angle Hysteresis $\Delta\theta$ [°]	Total surface energy [mJ/m ²]
Water	72.8	79.2 ± 3.5	20.5 ± 3.1	58.8 ± 4.3	32.6
MDI	47.6	36.2 ± 1.2	13.2 ± 1.9	22.9 ± 0.8	41
PO-a	34.3	27.5 ± 1.5	8.9 ± 1.5	18.6 ± 1.3	31.5
PO-b	34.9	29.4 ± 1.7	10 ± 1.7	19.4 ± 1.8	31.7
PO-c	34.9	32.9 ± 3.9	11.2 ± 2.4	21.7 ± 3.1	30.9

Table A-1.3: Advancing and receding contact angles on PC/SAR-GF plate for probe liquids measured by the tilted plate method, and the total surface free energy of the PC/SAR-GF surface obtained from Equation A-1.9.

Liquid	Liquid surface tension [mN/m]	Advancing contact angle θ_a [°]	Receding contact angle θ_r [°]	Contact angle Hysteresis $\Delta\theta$ [°]	Total surface energy [mJ/m²]
Water	72.8	88.5 ± 2.0	35.3 ± 3.0	53.2 ± 3.1	27
MDI	47.6	45.9 ± 0.9	18.4 ± 1.2	27.5 ± 0.5	37.5
PO-a	34.3	42.3 ± 1.0	15.6 ± 2.7	26.7 ± 1.6	28
PO-b	34.9	41.5 ± 5.7	15.2 ± 5.5	26.3 ± 1.3	28.7
PO-c	34.9	43.1 ± 4.2	16.0 ± 1.7	27.1 ± 2.5	28.3

Table A-1.4: Advancing and receding contact angles on PC/ABS plate for probe liquids measured by the tilted plate method, and the total surface free energy of the PC/ABS surface obtained from Equation A-1.9.

Liquid	Liquid surface tension [mN/m]	Advancing contact angle θ_a [°]	Receding contact angle θ_r [°]	Contact angle Hysteresis $\Delta\theta$ [°]	Total surface energy [mJ/m²]
Water	72.8	90.2 ± 2.9	32.2 ± 7.1	58.0 ± 5.4	26.5
MDI	47.6	39.9 ± 1.5	10.9 ± 2.0	29.0 ± 0.7	39.6
PO-a	34.3	36.7 ± 1.9	14.7 ± 2.0	21.9 ± 1.2	29.5
PO-b	34.9	35.5 ± 1.3	15.4 ± 2.6	20.1 ± 1.4	30.4
PO-c	34.9	35.8 ± 1.9	15.7 ± 1.9	20.1 ± 0	30.3

Table A-1.5: Advancing and receding contact angles on PC/ABS-GF plate for probe liquids measured by the tilted plate method, and the total surface free energy of the PC/ABS-GF surface obtained from Equation A-1.9.

Liquid	Liquid surface tension [mN/m]	Advancing contact angle θ_a [°]	Receding contact angle θ_r [°]	Contact angle Hysteresis $\Delta\theta$ [°]	Total surface energy [mJ/m ²]
Water	72.8	78 ± 4	21.3 ± 4.6	56.8 ± 5.5	33.8
MDI	47.6	30 ± 4	6.8 ± 4	22.8 ± 0.6	42.9
PO-a	34.3	31.4 ± 1.7	10.5 ± 1.2	20.9 ± 0.9	30.7
PO-b	34.9	31.9 ± 2.5	12.4 ± 2.8	20.2 ± 0.9	31.2
PO-c	34.9	31.2 ± 3	11.9 ± 2.7	20.1 ± 0.9	31.3

A-2. Investigations on the reaction of isocyanate (MDI) with maleic anhydride

The idea behind this experiment was to use maleic anhydride (MA) as adhesion promoter.¹⁶⁸ In order to follow the reaction process of isocyanate with MA first the FTIR spectra of both pure reactants (MDI and MA) were recorded and are shown in Figure A-2.1. The MA spectrum (Figure A-2.1a) shows the two distinct carbonyl peaks at 1855

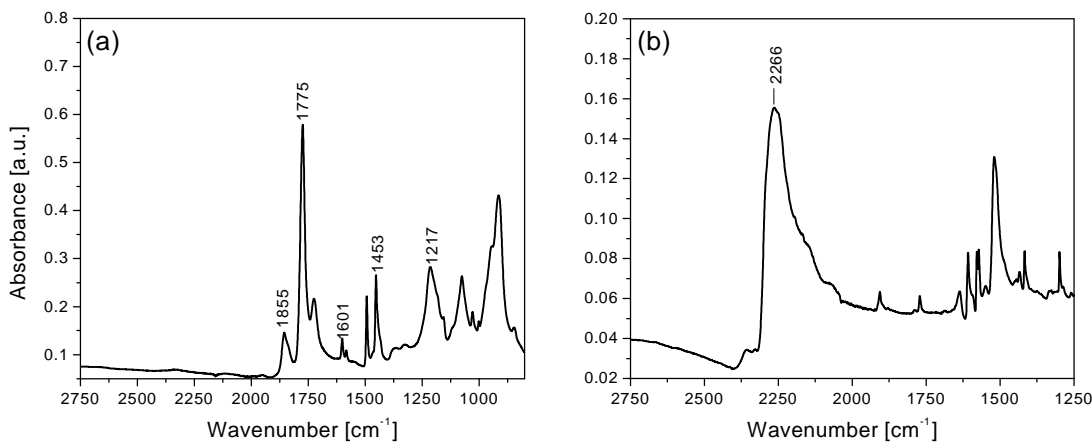


Figure A-2.1: FTIR-ATR spectra of (a) pure maleic anhydride and (b) pure MDI. The isocyanate (2266 cm⁻¹) and acid anhydride bands (1855 and 1775 cm⁻¹) are labeled in the Figure respectively.

and 1775 cm^{-1} (both peaks are linked to the MA carbonyl groups). The MDI spectrum (Figure A-2.1b) shows a very prominent isocyanate peak at 2266 cm^{-1} . The other peaks in the spectrum of both materials were not of much interest. Therefore, they are not interpreted here.

The reaction of isocyanate with MA was monitored by the disappearance of the characteristic peaks (Figure A-2.2) of isocyanate group at 2266 cm^{-1} and acid anhydride carbonyl at 1848 cm^{-1} . The spectra at 70°C show the initial spectra before the imide formation has occurred. The spectra taken after 110 min at 70°C did not show any observable change in the IR bands of MDI and MA. Then the temperature was increased to 90°C and the spectra were recorded at regular intervals, there was an indication of appearance of imide formation after 160 min of reaction time. After 210 min the IR bands for isocyanate and MA groups disappeared and new band at 1713 cm^{-1} appeared that could be assigned to the imide formation. The disappearance of strong -NCO absorption peak at 2268 cm^{-1} and C=O stretching vibration peak of acid anhydride at 1848 cm^{-1} in the IR spectra is an evidence that the reaction has taken place between isocyanate and MA.

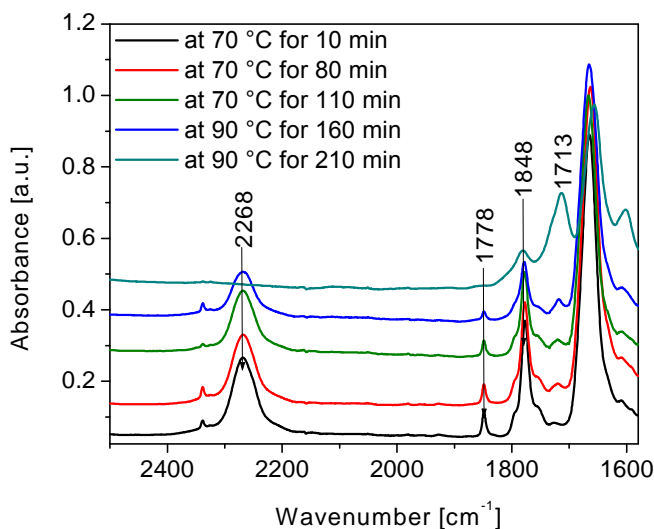


Figure A-2.2: FTIR-ATR spectra taken during the reaction of MDI and MA. The spectrum taken after 10 min is the beginning of the reaction and the spectrum taken after 210 min is the end of reaction. The IR bands linked with isocyanate (2268 cm^{-1}), acid anhydride (1848 and 1778 cm^{-1}) and imide (1713 cm^{-1}) are labeled on the respective peak for each functional group.

In order to calculate the imide content from reaction product of isocyanate and MA a calibration curve was constructed. Concerning this, different concentrations of bismaleimide (BMI) were prepared in dimethyl sulphoxide (DMSO) and then FTIR spectra were recorded for each concentration. The obtained FTIR data for imide peak at 1713 cm^{-1} were used in the calibration curve as shown in Figure A-2.3. The evaluated imide content from the reaction product was 0.147 [mol %]. These studies have shown that MA reacts with isocyanate and give a reasonable amount of the reaction product (imide formation).

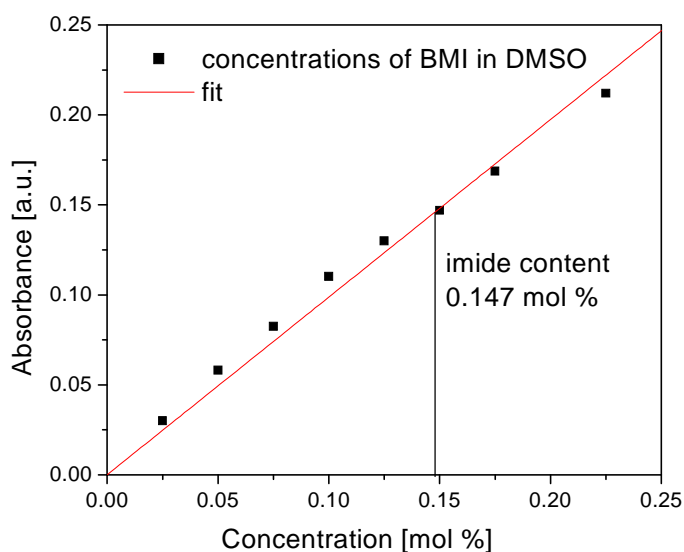


Figure A-2.3: Calibration curve for the calculation of imide content. The absorbance of imide band at 1713 cm^{-1} is plotted against different concentrations of BMI in DMSO. A linear fit of data was used to calculate the imide content from the reaction of MA and isocyanate.