**The microstructural evolution of cementitious, flexible
waterproofing membranes during deformation with special focus
on the role of crazing**

Marius Waldvogel^{1*}, Roger Zurbriggen², Alfons Berger¹, and Marco Herwegh¹

¹ Institute of Geological Sciences, University of Bern, Baltzerstrasse 1+3, 3012 Bern,
Switzerland

² Nouryon Chemicals AG, Industriestrasse 17a, 6203 Sempach Station, Switzerland

* Corresponding author: marius.waldvogel@geo.unibe.ch

Abstract

The initiation and evolution of deformation-induced (micro)structures in one-component, cementitious, flexible waterproofing membranes is investigated combining normed crack-bridging (EN14891) with image analysis of in-situ photos acquired by optical and scanning electron microscopy. The permanent deformation of the polymer matrix concentrates in a trapezoidal deformation volume and subdivides into an active and a passive part. During the active part, the polymer matrix stretches and fibril-void microstructures (FVM) form. The ubiquitously present heterogeneities (quartz grains, cement particles and air pores) act as stress concentrators. After FVMs reach their maximum density inside the deformation volume, straining by passive stretching until final rupturing takes over. Starting at the substrate-membrane interface, the cracking propagates through the membrane along aforementioned heterogeneities and the spatially distributed FVMs. Linking mechanical behaviour and deformation structures is therefore crucial to (i) understand the complex elasto-plastic deformation and to (ii) develop new products increasing the durability of the protective system.

Keywords

crack-bridging; waterproofing membrane; permanent deformation; (micro)structures

1. Introduction

Cracking of concrete can be induced by several mechanisms [1] and causes severe damage to concrete structures both through the cracking and the subsequent degradation by water ingress [2]. Concrete and other cement-based materials are prone to cracking as they have a low tensile strength only. In the building industry, the tensile strength of cement-based products like mortars is commonly enhanced by polymer modification because pure polymers show a high tensile strength [3,4]. Due to their improved tensile strength and extensibility [3], these polymer-modified mortars (PMMs) prevent the propagation of cracks formed in the substrate (hygrical shrinkage, thermal expansion/contraction etc.) into above laying systems (e.g. tilings) by stretching above the (micro)crack forming in the substrate and stopping its propagation out of the substrate [5–7] (Fig. 1). This behaviour, called crack-bridging ability (CBA), is the reason for the use of PMMs as waterproofing membranes at instances where constructions are in contact with water like bathrooms, swimming pools, roofings or underground facades. Modification can be done by adding the polymer as dispersion or as redispersible polymer powder (RPP) [8–10]. Addition of the polymer takes place directly prior to the production of the fresh slurry. From a logistic [8–11], environmental [8–11] and performance [8,11,12] point of view, the RPP modification is advantageous. In their hardened state, PMMs represent a composite material consisting of brittle fillers. Here quartz grains, hydrated and unhydrated cement particles, and mixing entrained air pores are incorporated in a polymer matrix. Polymer composites subdivide into two groups. The first group covers polymer matrixes containing rubber particles. The matrix is brittle and the incorporated particles are ductile [13]. The second group describes polymer matrixes with incorporated inorganic nanoparticles [13]. In this group, the filler material is more brittle than the polymer matrix. Several studies deal with the deformation behaviour and deformation structures in uniaxial tension for the respective group. For both groups, deformation relates to stress concentrations forming around the particles (rubber or inorganic) inside the polymer matrix [13–18]. Deformation structures found in the first group of polymer composites are crazing in between the rubber particles [13,19,20], void formation [15,21], shear yielding in

between rubber particles [13,15,20,22,23] and crack blunting at the rubber particles [24]. The second group deforms by debonding at the nanoparticle-matrix interface [18,19,21], plastic void growth [17,18] and craze-like microstructures [13,25]. Crazing, mentioned as deformation structure in both groups, is a deformation mechanism originally found in amorphous polymers below their glass transition temperature (T_g). It describes local plastic deformation [26–28] which starts as micro- and nano-voids [26–35] developing to an alternating sequence of fibrils and voids [28,30,36] oriented parallel to the extension direction [37] and finally resulting in fibril rupture and therefore, cracking [27,28,31,37–39]. Studies dealing with organic coating relate the CBA to the total failure of the organic coating mechanical tests [2,40,41]. Furthermore, combining data of both, dog-bone tests and crack-bridging tests, relate the crack-bridging ability with the mechanical behaviour of those organic coatings [40]. Further investigations show that the failure of the coating starts at the substrate-coating interface and migrates vertically towards the coating's surface [40]. The deformation behaviour in the present cement composites currently lacks a profound understanding. So far crack bridging tests according to norms provide the only information about the crack-bridging ability of waterproofing membranes. Studies dealing with the appearance of white spots and lines on surfaces of waterproofing membranes and relating them to domains of local strain concentrations [42,43] are the only information dealing with deformation-induced structures in waterproofing membranes. Detailed investigations of the active failure processes during crack bridging of a waterproofing membrane are missing. We close this gap by combining crack-bridging experiments with quantitative (micro)-structural analysis in order to detect the involved deformation processes. The latter is exerted on in-situ photographs, optical microscopy and scanning electron microscopy (SEM). Based on all results we suggest a subsequent progression of deformation processes with a link to the bulk mechanical behaviour of the waterproofing membrane during crack-bridging.

2. Methods

81 This study focusses on liquid-applied, one-component, cementitious, flexible waterproofing
82 membranes. In the used standard formulation, a waterproofing membrane consists of quartz
83 grains (0.1 – 0.3 mm in diameter), Ordinary Portland Cement (OPC, 52.5 N) and an ethylene
84 vinyl-acetate (EVA) based redispersible polymer powder (RPP). The choice of the
85 appropriate amount of RPP is based on several factors: First, the optimum polymer content
86 in crack isolation floor systems is considered to be between 20-35 wt.% [44]. Second, RPP
87 contents >25 wt.% only increase the crack-bridging, while the maximum load and hence
88 stress the membrane can bear remains constant from 25 wt.% RPP onwards [45]. Third,
89 from 25 wt.% onwards, the waterproofing membrane represents the volumetrically dominant
90 phase in the composite material [45]. Therefore, it can be assured that the mechanisms
91 being active during crack bridging are governed by the mechanical behaviour of the RPP. In
92 order to produce samples for crack-bridging tests and dog-bone tests, a slurry is produced
93 by mixing the individual components (dry mix) and adding water in the appropriate amount
94 (see Tab. 1 for weight percentages of individual components). For crack-bridging samples,
95 the freshly mixed slurry is applied on both sides of two juxtaposed fibre cement boards
96 (substrate in this study) and is cured for 28 days at 23°C and 50% relative humidity.
97 Afterwards, the fibreboards are cut by a Con-Star 35/60 saw into 160 mm by 30 mm
98 samples. The application and sample preparation process is described in detail in [46] and
99 summarised in Figure 2. The volumetric composition of the hardened waterproofing
100 membrane is based on point counting of thin-sections and is provided in Table 2. In contrast
101 to the norm defining the geometry and production of crack-bridging samples as well as the
102 crack-bridging test [47], the initial gap is not produced by bending the cured sample in a jig.
103 Instead we simulate the crack by juxtaposing two substrate plates prior to the slurry
104 application. This modification was done in order to avoid bending-induced pre-damage (e.g.
105 debonding of the waterproofing membrane) as this might already influence the results of
106 crack-bridging tests significantly [41]. For dog-bone samples, the freshly mixed slurry is
107 applied as plane membrane on a plastic film and is cured for 28 days at 23°C and 50%
108 relative humidity. Afterwards, individual dog bones are punched-out by a blade. The

geometries of the dog bone are defined by type 5 of the according norm [48]. Both, crack-bridging and dog bone tests, are exerted using a Z020/TH2S by Zwick/Roell™ (Fig. 3a). Testing speeds are set to 0.15 mm/min for the crack-bridging samples and 100 mm/min for the dog-bone samples following [47] and [48] respectively. For both sample types, nominal stress is calculated by using the individual sample geometry. Furthermore, nominal strain is calculated for dog-bone samples based on their individual geometry. Every experiment is run until a total failure of the sample occurred and recorded with time-lapse photography (Fig. 3b). For the crack-bridging samples, the exact point of failure defined in [47] is determined by revisiting the acquired photographic time-lapse sequences. For all crack-bridging samples, the surface evolution of lateral strain localisation is optically traced by detecting strain whitening [42] domains in the time-lapse photographs. This image analysis is exerted using Fiji [49] modified with the Xlib and shape filter [50] plugins. On the processed images (Fig. 4 a2-d2), the width of the strain-whitening zone is measured perpendicular to its long axis along lines separated by 1 mm distance. Obtained width values are then averaged. The outermost 5 mm on each side of the sample are discarded, in order to exclude potential edge effects (red shaded areas in Fig. 4a-d) [45]. Additionally, the number of white spots and their respective widths are mapped in every tenth photograph (i.e. steps of 100 μ m displacement) along three lines (green dashed lines in Fig. 4 a2-d2) and then averaged. The spacing between the three lines is set large enough to assure that no line was counted twice (green dashed lines in Fig. 4 a2-d2). In an additional set of crack-bridging experiments, the respective experiment is stopped at a predefined displacement; the sample is stabilized allowing manufacturing of thin-sections (Fig. 3c, d). Stabilisation is done by gluing plastic wedges into the open substrate gap using a fast-setting, two-component epoxy. Due to their shape, the plastic wedges fit in all open substrate gaps without any pushing. Resulting thin-section series therefore represent snap-shots at given displacements allowing investigating damage evolution in sections parallel to the extension direction but perpendicular to the fibreboard planes (Fig. 3d, Tab. 3). Thin-sections are investigated using optical light microscopy. The surface of a piece of a strained crack-bridging sample is examined using

scanning electron microscopy (SEM, Zeiss Evo 50, variable pressure mode, gas pressure in the chamber = 21 Pa, beam current = 500 pA, acceleration voltage = 11.69 kV). Using the SEM in variable pressure mode allows observations without coating the sample. Additionally, continuous degassing of the large-sized porous, crack-bridging sample counteracts the stability of the high vacuum configuration. However, the spatial resolution is somewhat reduced in the variable pressure mode. In order to circumvent these problems, stretched samples of just the waterproofing membrane (5 mm by 2 mm, no substrate) are coated by gold and studied under high-vacuum SEM conditions (beam current = 250 pA, acceleration voltage = 6 kV). Note that all optical investigations were performed to image the deformation evolution prior to failure of the waterproofing membrane.

3. Results

3.1 Crack-bridging samples

3.1.1 Sample's surface

Using the time-lapse photographs, four important moments during the sample's surface evolution are identified (Fig. 4). (i) *Discontinuous-Strain-Whitening* marks the moment at which a first strain whitening spot occurs on the sample's surface. (ii) *Continuous-Strain-Whitening* marks the moment at which a first line of strain whitening spans over the entire sample width. (iii) *First Failure* marks the time at which the waterproofing membrane is not watertight anymore, i.e. the occurrence of a fracture dissecting the entire membrane vertically [47]. (iv) *Final Failure* marks the displacement at a vertical continuous crack spans across the entire width of the waterproofing membrane. This defines the end of the experiment. Close-up pictures show an initially homogeneous surface of the waterproofing membrane with only air pores and quartz grains as heterogeneities (Fig. 5a). From early stages of strain whitening onwards, the whitening domains preferentially bend around quartz grains (orange rectangle in Fig. 5b) and run perpendicular to pore rims (blue rectangle in Fig. 5b). Additionally, elliptical holes start to form in polymer matrix. The long axes of the elliptical holes are parallel to the tensile loading direction (red arrows in Fig. 5b). During a late stage

of the strain whitening, aligned arrays of elliptical holes appear along strain whitening lines (red rectangle in Fig. 5c). Some of the former individual elliptical holes laterally connect with each other forming a crack with a lobate boundary (red dashed rectangle in red rectangle in Fig. 5c). This connection often starts from pore rims highlighting the role of the pores for crack initiation (pink arrow in Fig. 5c). Subsequently, cracks propagate progressively into the membrane by connecting either individual or already connected elliptical holes preserving the lobes in the perimeter (green arrow in Fig. 5d). Time-lapse photography also allows mapping the evolution of the zone in which the strain whitening occurs with increasing opening of the substrate gap. This *Strain Whitening Width* (SWW) starts to evolve (Fig. 6a), i.e. deviate from 0, with the *Discontinuous Strain Whitening* (grey line in Fig. 6). As prior to the *Continuous Strain Whitening* the white spots appear only locally on the membrane's surface, a continuous evolution is possible from the *Continuous Strain Whitening* (pink line in Fig. 6) onwards. From there, the SWW grows linearly with a steep slope (purple shaded area in Fig. 6). The growth rate decreases at a displacement around 950 μm (green shaded area in Fig. 6). This moderate slope is steady until the *Final Failure* (black line in Fig. 6) of the sample. Additionally to the growth behaviour of the zone of strain whitening, the number of strain whitening spots and their respective width change with increasing substrate gap opening and is linked to the slope of the SWW. As long as the slope is steep i.e. from the *Continuous Strain Whitening* onwards, the number of strain whitening spots increases while their respective width is constant (Fig. 6b). This characteristic of the individual strain whitening spots changes with the change in the slope of the SWW evolution. From there onwards, the number of strain whitening spots is constant but they increase in their respective width (Fig. 6c).

3.1.2 Microstructures in 2D along the membrane's thickness (Optical microscopy)

Optical microscopy of thin sections reveals an alternating arrangement of stretched polymer fibrils and elliptical shaped voids in between the individual fibrils (Fig. 7). Both, the fibrils and the long axes of the voids show an orientation subparallel to the direction of the tensile load

(Fig. 7). This fibril-void microstructure (FVM) represents straining of the polymer film; and therefore, mapping of film-related deformation structures (FVM and cracks) on photos of thin-sections (Fig. 8a-d) is crucial to understand the film-related deformation structures and evolution. The triple junction between membrane-substrate interface and artificial fibreboard crack represents the starting point for both straining (Fig. 8e) and subsequent cracking (Fig. 8f, g). With increasing opening of the substrate crack, both migrate towards the surface of the upper and lower membrane (Fig. 8g and h). FVM initiate and propagate (i) in front of crack tips (Figs. 7, 8f-h) and (ii) randomly at heterogeneities (air pores or quartz grains) inside a corridor of ca 2.5 mm to each side of the position of the substrate crack. Note that this distance coincides excellently with the strain whitening widths measured at the sample's surface (Fig. 6a). Contrarily to the randomness regarding the appearance inside the corridor, the position of the FVM at the respective heterogeneity is systematic and is revealed by observing the thin-sections in detail (red, dashed rectangle in Fig. 8c). The presence of quartz grains deviate the FVM towards the polar region (explained in discussion, see Fig. 16) of the respective quartz grain (Fig. 5b orange rectangle, Figs. 8f-h 9b, c black arrows). After approaching the respective quartz grain, the FVM propagates along the quartz grain-polymer matrix interface (Fig. 9b,c black arrows). Contrarily, air pores cause FVM propagation towards the equator (explained in discussion, see Fig. 16) of the respective air pore (Figs. 8f-h, 9d, e). When connecting two air pores, the FVM runs in the straightest possible way in between their respective equatorial region. As a function of increasing fibreboard displacement, the number of spots of strained polymer film increases (Fig. 8e-g) but decreases from the moment on once a continuous crack is present (Fig. 8h). The detailed investigation of the thin sections also shows that the perimeter of the cracks shows straight and convex parts (Fig. 9a).

3.1.3 Microstructures at high resolutions (Scanning Electron Microscopy)

Using scanning electron microscopy (SEM) reveals the deformation structures which form in a strained waterproofing membrane which macroscopically shows strain whitening (Fig.

10a). Overview images (Fig. 10a, b), show a rough morphology in non-strained areas. This topography is caused by quartz grains on a large scale (Fig. 10a, b) and by cement grains on a small scale (Fig. 10d, e). The topography significantly flattens in those parts of the waterproofing membrane being affected by strain whitening, i.e. the strained membrane (Fig. 10a, b). Present quartz grains govern the path of the strain whitening as the strain whitening bends around the quartz grains (Fig. 10a). The strain whitening evolves gradually from non-strained areas (Fig. 10c) over white (Fig. 10a blue arrow, d, e) to transparent (yellow arrow in Fig. 10a). The white part shows the strained polymer matrix of the waterproofing membrane still containing remnant structures of primary latex particles and cement grains incorporated in the strained matrix (Fig. 10d and e). Non-strained areas also contain remnant structures of primary latex particles (Fig. 10c). In the transparent part, the strained polymer film is smooth and free of cement particles (Fig. 10e). Additionally, the transparency of the membrane indicates a strong thinning of the film. Furthermore, voids initiate and grow inside the high strain zone. Voids initiate and terminate at heterogeneities (here cement grain, Fig. 10e-g). At initiation, voids are in the range of 150-300 nm and roundish (Fig. 10g). Very soon after initiation, their shape changes to elliptical with the long axis being oriented parallel to the tensile load direction (Fig. 10g). Mature voids show large ranges in size and are strongly elliptical with the same orientation of their respective long axis (Fig. 10b, f). Some of the mature voids are vertically continuous (blue dot in Fig. 10f) while others still show an intact polymer film beneath the voids (green dot in Fig. 10f). The mature voids are separated by strained polymer matrix. Based on these observations, we claim that the white part of the strained membrane represents an early deformation stage while the transparent part equals to a late deformation stage. At the rim of the zone representing the late deformation stage, the strained polymer film changes gradually from thin, smooth particle-free and void-containing to a strained polymer film containing latex and cement particles (Figs. 10e, 12). A SEM profile (red dot in Fig. 10a indicates the profile line in planar view) along the thickness of this strained waterproofing membrane reveals the formation of deformation structures in the third dimension. Deformation, expressed in form of an FVM,

takes place in vicinity of an air pore (Fig. 11). The FVM occurs in the equatorial region of the air pore relative to the tensile load direction, which is in agreement with the orientation of the FVM relative to air pores in the thin section (Fig. 8g and h). The size of the voids decreases with increasing distance from the pore rim which indicates that the FVM initiated at the pore-membrane interface and propagates into the polymer matrix (Fig. 11b and c). SEM of the surface of a deformed and fixed crack-bridging sample shows similar features (Fig. 12). On this surface, local FVMs oriented parallel to the tensile load direction indicate deformation. First of all, the area around the FVM is brighter than the rest of the waterproofing membrane (white ellipse in Fig. 12a) which indicates a high local straining of the polymer matrix. Second, highly-stretched parts of the polymer matrix in between the voids are smooth and thin, particle-free and show zones of darker colour which appear to be thinner and indented (black arrows in Fig. 12b). These latter features probably represent spots in which new voids will form. Zones of low-strained polymers film contain latex and cement particles and increasingly appear towards the rim of the FVM (white arrows in Fig. 12b). The alternating sequence of mature voids and strained polymer film found on a planar view, combined with the FVM found in the cross-section views in thin-sections and in the SEM profile along the thickness of the strained membrane, indicates that deformation structures in general and the FVM in particular are three-dimensional (Fig. 13).

3.2 Dog bone samples

The stress-strain data, recorded by the tensile rig, define the bulk material's mechanical response in terms of elastic and plastic deformation. As soon as a deviation from linear stress-strain behaviour occurs, the material reaches its elastic yield strength. On average, the dog bone samples yield elastically at 2 % strain and at 2.8 MPa stress (red arrow in Fig. 14). Afterwards, the bulk samples exhibit permanent deformation. Further important material parameters are the maximum stress the bulk material can withstand and the strain at which the sample fail. The average maximum stress is 4 MPa and appears at 26% strain (blue arrow in Fig. 14). Sample failure occurs at 29.9% strain (green arrow in Fig. 14) Due to

the constant monitoring of the dog bone's surface during the experiment, identification of surface features is possible. Noticeable features occurring on the dog bone surface are the *Discontinuous Strain Whitening* and the *First Failure*. The definition of these two features is the same as for the crack-bridging samples (Fig. 4a, c). The knowledge of the displacement of every recorded image allows the integration of the two observed features into the stress-strain behaviour of the bulk dog bone. The *Discontinuous Strain Whitening* appears after the elastic yield, i.e. the bulk membrane is already in a state of permanent deformation (Fig. 14). The *First Failure*, i.e. the lack of water tightness appears shortly after peak stress (Fig. 14). Post first failure deformation leads to growth of the first crack to complete sample rupture.

4. Discussion

4.1 Crazeing as deformation mechanism in waterproofing membranes

The evolution of deformation structures in tension is best known and described for amorphous, glassy polymer films. Plastic deformation initiates at heterogeneities (scratches, dust particles, imperfections, artificially induced) by the formation of nanovoids [51,52]. With ongoing deformation, the nanovoids grow resulting in a microstructure of stretched polymer fibrils with intercalated voids [28,30,31,37,39,53]. The diameter of the individual features inside one craze ranges between 5 and 50 nm [54,55]. Both, the fibrils and voids are oriented parallel to the tensile load direction [28,30,31,37,39,53]. This microstructure is known as crazes and its formation process is called crazeing. With further deformation, the fibrils stretch and elongate plastically [31,38,51,53]. The highly strained fibrils grow by drawing in material from the rim surrounding the craze microstructure [51,54]. This rim represents a locally low-strained polymer film. Outside of this structure, the polymer film is under bulk strain conditions. The fibrils rupture when their maximum stretching capacity is reached and from that moment onwards, a crack initiates and follows the craze microstructure [27,28,31,37–39]. The craze microstructure itself propagates perpendicular to the tensile load direction as nanovoids form at the craze tip [30]. Figure 15 summarises this described evolution of the deformation structure. Although well-known from amorphous,

glassy polymers, crazing occurs not exclusively in this material but craze-like microstructures form also in amorphous and semi-crystalline polymers above their glass transition temperature (T_g) [54,56,57] and in polymer composites [13]. The FVM observed in our experiments in both light and scanning electron microscopy (i) initiates as microvoids at rigid particles which act as heterogeneities in a pure polymer film (Fig. 8f and g), (ii) develops to fibrils and voids being oriented parallel to the tensile load direction (Figs. 8f,g, 9, 10), (iii) shows internal zonation from a high strained centre to a low strained rim in the deformation structure (Figs. 10e, 12) and (iv) ruptures in a brittle manner by breakdown of the individual fibrils. All these evolutionary steps of the FVM occur in a polymer matrix above its T_g . These observations lead to the claim that, on a micron-level, the plastic deformation in the investigated waterproofing membranes is a craze-like microstructure starting with (i) microvoid formation leading to (ii) FVM initiation and propagation and ending with (iii) brittle fibril rupture, i.e. cracking. However, the size range of the individual fibrils and voids inside the FVMs correlates better with size ranges for fibrils and voids occurring in semi-crystalline polymers than in amorphous polymers [55]. Strain-induced orientation is a known plastic deformation mechanism occurring when stretching originally amorphous polymers at temperatures above their T_g [56,58–61]. Furthermore, the strain-induced orientation can cause macroscopically observable whitening [62]. Hence, the occurrence of strain-induced whitening on the membrane's surface (see 4.3) provides another hint to a strain-induced orientation of the polymer matrix. Therefore, strain-induced orientation may precede microvoid formation and forms the very first plastic deformation structure on a sub-micron level. However, the presence of strain-induced orientation is solely based on indirect observations.

4.2 From incipient strain localisation to sample failure

Crazing requires overcoming a threshold in stress [38,51,63] or strain [64,65], so its formation appears at spots of localised plastic deformation. Hence, the mapped FVM is a proxy to investigate the initiation and propagation of plastic deformation inside the

327 waterproofing membrane. Most FVMs are found in a central corridor inside the waterproofing
328 membrane (Fig. 8g) but also randomly distributed FVMs are present. Nevertheless, all FVMs
329 form between two heterogeneities present in the polymer matrix (Figs. 8f-h, 16a). This
330 implies that the incorporated particles govern (i) the spots at which microvoids and hence
331 also the craze-like microstructures initiate and (ii) their propagation pathway. Stress
332 concentration fields forming around the incorporated particles in polymer composites during
333 deformation are the reason for this dominance [66–68]. In theory, a polymer film containing a
334 single heterogeneity deforms in uniaxial tension. The position of the stress concentration
335 depends whether the heterogeneity is empty [13,63,64,68], mechanically softer [13,69,70] or
336 harder [13,63–65,69] than the matrix. Around pores and soft particle the stress concentration
337 will form at the equator of the particle [13,66,67] (Fig. 16b1). If the particle is harder, the
338 stress concentration will form around the pole of the particle [13,19,67] (Fig.16b2). The
339 investigated waterproofing membranes contain both, hard inclusions (quartz grains and
340 cement particles) and air pores. Hence, the FVMs should form at and run towards the
341 equators of air pores and form at and run towards the poles of any hard inclusion. Slight
342 mismatches occur between the theoretical positions and positions and propagation
343 directions in reality (Figs. 9, 16a). This is due to the fact that the individual stress
344 concentration fields around two heterogeneities which are in close vicinity interact
345 constructively and form a local stress concentration field at positions away from theoretical
346 positions [15]. As the plastic deformation (microvoids and FVM) form and propagate along
347 the maximum stress concentration deviations from ideal conditions occur (Fig. 9). Mapping
348 of the FVM propagation shows the influence of the respective heterogeneity. Quartz grains
349 cause a deviation towards their polar region (Fig. 5b orange rectangle, 9b, c black arrows)
350 along the grain-matrix interface. Around cement particles, microvoids form close to the polar
351 region. These observations indicate: (i) microvoids form at positions of maximum stress
352 concentrations, (ii) crazes propagate towards the spot of maximum stress concentration
353 around a rigid particle and (iii) the adhesion between quartz grains and polymer matrix is
354 weaker compared to the intrapolymer matrix strength. Contrarily, crazes propagate towards

the equator of an air pore (Figs. 5b blue rectangle, 9d,e white arrows) and terminate once reaching the pore's interior (Fig. 9d, e). Here, (i) crazes propagate towards the maximum stress concentration present around an air pore, (ii) the interfacial tension at the pore rim between the polymer matrix and the air pore is weaker compared to the intra-polymer matrix strength leading to a propagation of localized deformation into an air pore, where (iii) the propagation stops because of dissipation of the deformational energy. This behaviour results from the inverse relation between crack tip radius and crack energy [71–73]. Practical applications of this behaviour is found, for example, by crack retardation in ceramics via artificial incorporation of air pores, since there they decrease the crack tip energy by increasing the crack tip radius [74]. A continuation of the FVM at the opposite pore rim is possible as soon as the stress concentration at this point accumulates the energy needed for the initiation and propagation of the FVM. The understanding of the FVM initiation and propagation is also crucial to understand failure as cracking follows the FVM. Similar to organic coatings [40], the initial crack in the waterproofing membrane starts at the substrate membrane interface (Fig. 8f). With ongoing deformation several further cracks form and grow (Fig. 8g, h). As the individual cracks are not connected and their start and end points do not match up, these cracks must form at individual initiation spots contemporaneously at sites where the fibrils of the FVM are stretched to their maximum. Neither the pathways nor the perimeter of the cracks are straight. The deviation from a straight pathway occurs due to the bending of the FVM around quartz grains. As crack propagation follows established FVMs and these FVMs bend around quartz grains, therefore the cracks also bend around them. The perimeter of the cracks is not straight due to the incorporation of air pores in the crack. The FVMs run straight in between air pores, blunt in them and continue. Hence, any crack following this FVM blunts in an air pore, splits the air pore and continues its propagation along the FVM. The splitting up incorporates the air pore in the crack causing a trace in the crack's perimeter in form of a lobe (pink dashed ellipse in Fig. 9a).

4.3 Macroscopic deformation evolution

382 Strain whitening is the macroscopic visual expression of plastic deformation in polymer-
383 modified mortars [42,43] as well as thermoplasts [75]. Changes in the microstructure cause
384 the whitening in polymer films [62,76,77]. These changes are either changes in the crystal
385 structure [62] or the formation of voids [62,76,77]. One possible structural change is strain-
386 induced crystallinity in originally amorphous polymers [56,58–60]. When taking voids into
387 account, studies suggest that Mie scattering causes the whitening [76,77]. Hence, the voids
388 must be in a size range similar to the wavelength of visible light [76]. In the investigated
389 waterproofing membrane, strain-induced crystallinity is a suggested deformation
390 mechanism, based on the size of the individual fibrils and voids inside the FVMs (see 4.1),
391 whereas the existence of microvoids in a suitable size range is observed (Fig. 10g).
392 Therefore, the observed strain whitening represents latest the stage of microvoid formation.
393 Additionally, dog bone data show that with the occurrence of strain whitening spots the bulk
394 sample is already in plastic deformation (Fig. 14). On the surface of the waterproofing
395 membrane, the width of the strain whitening zone grows with increasing opening of the
396 substrate gap (Fig. 6a) representing the evolution of the plastic deformation. Along the
397 thickness of the waterproofing membrane, all microscopic deformation structures appear in a
398 trapezoidal zone. Fringe pattern analysis [78–80] and x-ray microscopy [81] of different
399 materials covering a substrate show that (i) plastic deformation only occurs inside this zone
400 and (ii) that the geometry of this deformation zone is strongly dominated by the gap opening
401 in the substrate these materials cover. Hence, the combination of the trapezoidal geometry
402 along the membrane's thickness and the evolution of the strain whitening width define the
403 volume of the waterproofing membrane in which deformational energy can be dissipated by
404 the formation of aforementioned microstructures. The crucial parameter of this volume is the
405 opening angle (α) of the trapeze at the substrate gap. The strain whitening width on the
406 membrane's surface provides a first order link to the evolution of this opening angle α (Fig.
407 17). The changes of α define the evolution of the deformation volume. Plotting α against the
408 opening of the substrate gap is possible from the *Continuous Strain Whitening (CSW)*
409 onwards because prior to the *CSW* the whitening spots appear dispersal on the membrane's

410 surface. The plot (Fig. 18) shows two domains: (a) a constant increase in α and (b) α being
411 continuous. Domain (a) correlates with (i) the gap openings during which the number of
412 strain whitening spots increases on the membrane's surface while their respective size stays
413 similar (Figs. 6b, 18) and (ii) the increase of number of FVMs, their propagation towards the
414 membrane's surface and the initiation and propagation of cracks establishing the trapezoidal
415 deformation zone (Fig. 18). The increase in α , in number of strain whitening spots and in
416 number of FVMs and their propagation suggest that the membrane deforms actively during
417 this period of the crack-bridging, i.e. the deformational energy is used for the evolution of
418 microstructures. Along with the domain (b) goes (i) the change of the behaviour of the strain
419 whitening spots on the membrane's surface being constant in number and increasing in their
420 respective width (Figs. 6c, 18) and (ii) the connection of cracks through the thickness of the
421 membrane and decrease of numbers of FVMs inside the deformation zone (Fig. 8h).
422 Furthermore, the growth rate of the strain whitening width matches with the tensile
423 deformation speed of the rig (dashed in in Fig. 19) which indicates that the whitening spots
424 are stretched by at the rate of the rig's pulling speed. All these observations indicate that no
425 deformation-induced microstructures form inside the membrane but existing microstructures
426 are stretched passively during this period of crack-bridging with simultaneous stress
427 relaxation inside the membrane around cracks. Studies on pure polymer films verify a
428 maximum craze density [38] which suggests that the change from active deformation to
429 passive stretching occurs as soon as the accumulation of localised strain, i.e. number of
430 FVMs inside the deformation volume reaches its maximum. From that moment onwards,
431 stretching of existing FVMs provides the only possibility to dissipate additional deformation
432 energy. The *First Failure* indicates the moment at which anywhere in the waterproofing
433 membrane fibril rupture is continuous throughout the membrane's thickness. As rupture
434 occurs when the maximum stretch of a fibril is reached, the *First Failure* must occur after the
435 change from active deformation to passive stretch (Figs. 6a, 18, 19). Also, as the *First*
436 *Failure* is a local feature, the rest of the membrane is still able to deform with passive
437 stretching until fibril rupture is continuous throughout the membrane's thickness along a line

of the length of the membrane's width inside the strain whitening zone, the *Final Failure* occurs (Figs. 6, 18, 19).

4.4 Three-dimensional evolution of (micro)structures and bulk mechanics

Imaging an infinite number of either thin sections lined-up behind each other or surfaces stacked on top of each other, shows that the deformation evolution with all its related structures is three-dimensional (Fig. 20). During the ongoing displacement, the waterproofing membrane shows several microstructures at different positions inside the membrane's volume (Figs. 8, 9, 20a). Hence at a fixed displacement, several deformation mechanisms and multiple mechanical stages of the material, known from dog bone tests (Fig. 14) are active simultaneously (Fig. 20a). The active deformation occurs after the elastic yield up to peak stress (Figs. 14, 20a). Passive deformation lasts from peak stress to the occurrence of the first failure in the dog bones (Fig. 14) and represents only a short period during the stress–strain history of the material (Fig. 20). Linking the evolution of the deformation mechanisms and associated microstructures with the stress–displacement data from the dog bone tests shows that the mechanical state decreases from the substrate-membrane interface to the membrane's surface (Fig. 20a) and that peak stress coincides with the crack initiation at the membrane–substrate interface. From peak stress onwards failure migrates through the membrane. Slices at fixed displacements and therefore time (t_1 to t_3 in Fig. 20a) demonstrate the spatial distribution of deformation structures and mechanism (Fig. 20c). The slices along specific displacements (t_1 - t_3 in Fig. 20c) do not only confirm the decreasing microstructural maturity towards the membrane's surface but also show the progradational behaviour of the respective deformation mechanisms and their associated structures (Fig. 20c). Both, the passive deformation and the failure, do not propagate as a straight surface but as a progradational front containing lobes (Fig. 20c). These peaks and troughs indicate that deformation structures do not initiate and propagate simultaneously at a specific displacement but at different displacements inside the membrane. Most likely the ubiquitously present heterogeneities cause this difference in the

point of initiation. Furthermore, these heterogeneities can cause spots inside the membrane which show more mature deformation structures and mechanisms than their surrounding (crack tip in the middle of the membrane in Fig. 9). A connection between these spots and deformation structures propagating to the membrane's surface may connect and cause additional lobes.

5. Conclusions

The investigated waterproofing membranes deform in an elasto-plastic manner. During the plastic deformation, microvoids form and evolve to craze-like fibril-void microstructures (FVM) with ongoing deformation. These FVMs evolve in the active part of the plastic deformation, which is macroscopically seen in the appearance of whitening spots. During the passive part, the now existing spots become stretched, which is macroscopically detectable by the growth in their width. Plotting the strain whitening width in a width-displacement diagram allow a macroscopic detection of the active and passive part of the plastic deformation. The active part coincides with the steep slope in the diagram, while the moderate slope represents the passive part.

Fibrils inside the FVMs rupture as soon as their maximum capability in stretching is reached. This induces crack initiation and propagation. Cracking via fibril rupture initiates at the substrate-membrane interface at peak stress of the crack-bridging test. Crack propagation follows existing FVMs and a first continuous crack from interface to surface is observed shortly after the change from active to passive deformation. From this moment onwards, the membrane does not provide water tightness anymore and water might infiltrate into the substrate potentially causing degradation. Based on these observations, the evolution and growth of FVMs and subsequent fibril rupture indicates a ductile-to-brittle deformation behaviour.

Inside the waterproofing membrane, stress concentrations build up at the incorporated heterogeneities such as quartz grains, cement particles and air pores. They cause initiation

of new FVMs and deviation of existing FVMs. The position of the stress concentration, and therefore the spots where FVMS either initiate or deviate to, depends on the type of heterogeneity. Particularly, air pores act as an active retarder in crack propagation by blunting the crack tip when a crack hits an air pore.

On sample scale, the FVMs define a trapezoidal zone spanning from the substrate-membrane interface to the surface. This trapeze is the cross-section of the volume in which all deformation takes place. Based on the strain whitening width on the membrane's surface and the substrate gap opening, the opening angle α can be calculated. This angle is the crucial parameter that determines the volume in which plastic deformation accommodates. The change from the active part of the plastic deformation to the passive part possibly occurs when the maximum FVM density is reached within the trapezoidal deformation volume.

Further research should focus on the influence of intrinsic and extrinsic parameters on the crack bridging behaviour of waterproofing membranes. This includes but is not restricted to polymers of different Young's modulus, variations in temperature and/or deformation rate of the tensile rig. Additionally, the influence of changes regarding the heterogeneities requires closer investigations. The number, size and arrangement of both rigid particles and air pores may affect the number, the initiation and/or propagation of FVMs and therefore either prolong the active deformation part and/or retard crack initiation and growth. Furthermore, the number, size and arrangement of air pores may aid the crack-bridging ability by influencing the crack retardation effect positively.

6. Acknowledgement

The authors gratefully express their gratitude to Giuseppe Storti and Stefano Caimi from ETH Zurich; Josef Kaufmann and Frank Winnefeld from EMPA and Srdan Kisin, Livio Hegglin, Dragana Paripovic and Alexander Zapf from Nouryon for fruitful discussions and

input. Erwin Bühler and Hans Wicki from Nouryon are thanked for their patient introduction in sample preparation and sample testing procedures. Mr. Dettmar is thanked for the careful and well exerted preparation of the thin sections. Innosuisse, formerly known as Commission for Technology and Innovation (CTI), is gratefully thanked for the financial support of project No. 18797.1 PFIW-IW.

7. References

- [1] C.A. Issa, P. Debs, Experimental study of epoxy repairing of cracks in concrete, *Constr. Build. Mater.* 21 (2007) 157–163. doi:10.1016/j.conbuildmat.2005.06.030.
- [2] M. Delucchi, A. Barbucci, G. Cerisola, Crack-bridging ability and liquid water permeability of protective coatings for concrete, *Prog. Org. Coatings*. 33 (1998) 76–82. doi:10.1016/S0300-9440(98)00012-5.
- [3] S. Chandra, Y. Ohama, *Polymers in concrete*, CRC Press, 1994.
- [4] Y. Ohama, *Handbook of polymer-modified concrete and mortars properties and process technology*, Noyes Publications, New Jersey, 1995.
- [5] J.E. Isenbarg, J.W. Vanderhoff, Hypothesis for reinforcement of portland cement by polymer latexes, *J. Am. Ceram. Soc.* 57 (1974) 242–245. doi:10.1111/j.1151-2916.1974.tb10878.x.
- [6] V.R. Riley, I. Razl, Polymer additives for cement composites: a review, *Composites*. 5 (1974) 27–33. doi:10.1016/0010-4361(74)90016-0.
- [7] D. Van Gemert, L. Czarnecki, M. Maultzsch, H. Schorn, A. Beeldens, P. Łukowski, E. Knapen, Cement concrete and concrete-polymer composites: two merging worlds: a report from 11th ICPIG Congress in Berlin, 2004, *Cem. Concr. Compos.* 27 (2005) 926–933. doi:10.1016/j.cemconcomp.2005.05.004.
- [8] R.P. Bright, T.J. Mraz, J.C. Vassallol, The influence of various polymeric materials on

- 541 the physical properties of a cementitious patching compound, in: L.A. Kuhlmann, D.G.
542 Walters (Eds.), Polym. Hydraul. Mix., American Society for Testing and Materials,
543 1993: pp. 44–62.
- 544 [9] J. Schulze, O. Killermann, Long-term performance of redispersible powders in
545 mortars, Cem. Concr. Res. 31 (2001) 357–362. doi:10.1016/S0008-8846(00)00498-1.
- 546 [10] H. Lutz, Waterproofing with cementitious slurries, Master Build. 3rd quarter (2005).
- 547 [11] S.I. Schneider, D.R. Dewacker, J.G. Palmer, Redispersible polymer powders for
548 tough, flexible cement mortars, in: L.A. Kuhlmann, D.G. Walters (Eds.), Polym.
549 Hydraul. Mix., American Society for Testing and Materials, 1993: pp. 76–89.
- 550 [12] J. Colville, A.M. Amde, M. Miltenberger, Tensile bond strength of polymer modified
551 mortar, J. Mater. Civ. Eng. 11 (1999) 1–5.
- 552 [13] G.H. Michler, F.J. Baltá-Calleja, Nano- and micromechanics of polymers structure
553 modification and improvement of properties, Carl Hanser Verlag, 2012.
- 554 [14] Q. Fu, G. Wang, Polyethylene toughened by rigid inorganic particles, Polym. Eng. Sci.
555 32 (1992) 94–97. doi:10.1002/pen.790320204
- 556 [15] Y. Huang, A.J. Kinloch, Modelling of the toughening mechanisms in rubber-modified
557 epoxy polymers - part I finite element analysis studies, J. Mater. Sci. 27 (1992) 2763–
558 2769. doi:10.1007/BF00540703.
- 559 [16] G.-M. Kim, G.H. Michler, Micromechanical deformation processes in toughened and
560 particle filled semicrystalline polymers: part 2. model representation for
561 micromechanical deformation processes, Polymer (Guildf). 39 (1998) 5699–5703.
562 doi:10.1016/S0032-3861(98)00169-4.
- 563 [17] C.M. Chan, J. Wu, J.X. Li, Y.K. Cheung, Polypropylene/calcium carbonate
564 nanocomposites, Polymer (Guildf). 43 (2002) 2981–2992. doi:10.1016/S0032-

565 3861(02)00120-9.

566 [18] T.H. Hsieh, A.J. Kinloch, K. Masania, J. Sohn Lee, A.C. Taylor, S. Sprenger, The
567 toughness of epoxy polymers and fibre composites modified with rubber
568 microparticles and silica nanoparticles, *J. Mater. Sci.* 45 (2010) 1193–1210.
569 doi:10.1007/s10853-009-4064-9.

570 [19] G.-M. Kim, G.. Michler, Micromechanical deformation processes in toughened and
571 particle-filled semicrystalline polymers: part 1. characterization of deformation
572 processes in dependence on phase morphology, *Polymer (Guildf)*. 39 (1998) 5689–
573 5697. doi:10.1016/s0032-3861(98)00089-5.

574 [20] C.B. Bucknall, Applications of microscopy to the deformation and fracture of rubber-
575 toughened polymers, *J. Microsc.* 201 (2001) 221–229. doi:10.1046/j.1365-
576 2818.2001.00838.x.

577 [21] L.C. Tang, Y.J. Wan, K. Peng, Y.B. Pei, L. Bin Wu, L.M. Chen, L.J. Shu, J.X. Jiang,
578 G.Q. Lai, Fracture toughness and electrical conductivity of epoxy composites filled
579 with carbon nanotubes and spherical particles, *Compos. Part A Appl. Sci. Manuf.* 45
580 (2013) 95–101. doi:10.1016/j.compositesa.2012.09.012.

581 [22] Y. Huang, A.J. Kinloch, Modelling of the toughening mechanisms in rubber-modified
582 epoxy polymers - part II a quantitative description of the microstructure-fracture
583 property relationships, *J. Mater. Sci.* 27 (1992) 2763–2769. doi:10.1007/BF00540703.

584 [23] R.A. Pearson, A.F. Yee, Toughening mechanisms in elastomer-modified epoxies -
585 part 2 microscopy studies, *J. Mater. Sci.* 21 (1986) 2475–2488.
586 doi:10.1007/BF01114294.

587 [24] G.H. Michler, Micromechanics of polymers, *J. Macromol. Sci. Part B.* 38 (1999) 787–
588 802. doi:10.1080/00222349908248139.

- 589 [25] Z.J. Tao, S.D. Ping, Z. Mei, Z.P. Cheng, Microstructure deformation and fracture
590 mechanism of highly filled polymer composites under large tensile deformation, J.
591 Phys. Conf. Ser. 419 (2013). doi:10.1088/1742-6596/419/1/012014.
- 592 [26] E.J. Kramer, Microscopic and molecular fundamentals of crazing, in: H.H. Kausch
593 (Ed.), *Crazing Polym.*, Springer-Verlag Berlin Heidelberg, 1983: pp. 1–56.
594 doi:10.1295/kobunshi.42.389.
- 595 [27] J. Rottler, M.O. Robbins, Growth, microstructure, and failure of crazes in glassy
596 polymers, *Phys. Rev. E - Stat. Physics, Plasmas, Fluids, Relat. Interdiscip. Top.* 68
597 (2003) 18. doi:10.1103/PhysRevE.68.011801.
- 598 [28] P.A. O'Connell, G.B. McKenna, Yield and crazing in polymers, in: *Encycl. Polym. Sci.*
599 *Technol.*, John Wiley & Sons, Inc, 2004: pp. 627–681.
600 doi:10.1002/0471440264.pst463.
- 601 [29] A. Makke, M. Perez, J. Rottler, O. Lame, J.L. Barrat, Predictors of cavitation in glassy
602 polymers under tensile strain: a coarse-grained molecular dynamics investigation,
603 *Macromol. Theory Simulations*. 20 (2011) 826–836. doi:10.1002/mats.201100006.
- 604 [30] P.A. O'Connell, M.J. Bonner, R.A. Duckett, I.M. Ward, The relationship between Slow
605 crack-propagation and tensile creep-behavior in polyethylene, *Polymer (Guildf)*. 36
606 (1995) 2355–2362. doi: 10.1016/0032-3861(95)97333-B.
- 607 [31] S.K. Bhattacharya, N. Brown, Micromechanisms of crack initiation in thin films and
608 thick sections of polyethylene, *J. Mater. Sci.* 19 (1984) 2519–2532.
609 doi:10.1007/BF00550806.
- 610 [32] R.P. Kambour, A review of crazing and fracture in thermoplastics, *J. Polym. Sci.*
611 *Macromol. Rev.* 7 (1973) 1–154. doi:10.1002/pol.1973.230070101.
- 612 [33] A. Pawlak, A. Galeski, Cavitation during tensile deformation of polypropylene,

613 Macromolecules. 41 (2008) 2839–2851. doi:10.1021/ma0715122.

614 [34] A. Pawlak, A. Galeski, A. Rozanski, Cavitation during deformation of semicrystalline
615 polymers, *Prog. Polym. Sci.* 39 (2014) 921–958, doi:
616 10.1016/j.progpolymsci.2013.10.007.

617 [35] A. Krairi, I. Doghri, A thermodynamically-based constitutive model for thermoplastic
618 polymers coupling viscoelasticity, viscoplasticity and ductile damage, *Int. J. Plast.* 60
619 (2014) 163–181. doi:10.1016/j.ijplas.2014.04.010.

620 [36] R.N. Haward, B.M. Murphy, E.F.T. White, Relationship between compressive yield
621 and tensile behavior in glassy thermoplastics, *J. Polym. Sci. Part A* 9 (1971) 801–814. doi:10.1002/pol.1971.160090503.

623 [37] I.M. Ward, S. J., Mechanical properties of solid polymers, John Wiley & Sons Ltd,
624 2013. doi:10.1016/0032-3861(72)90129-2.

625 [38] A.S. Argon, J.G. Hannoosh, Initiation of crazes in polystyrene, *Philos. Mag.* 36 (1977)
626 1195–1216. doi:10.1080/14786437708239789.

627 [39] E. Riande, R. Díaz-Calleja, M.G. Prolongo, R.M. Masegosa, S. C., Yield crazing and
628 fracture, in: *Polym. Viscoelasticity Stress Strain Pract.*, Marcel Dekker, Inc., 2000: pp.
629 583–652.

630 [40] M. Delucchi, A. Barbucci, T. Temtchenko, T. Poggio, G. Cerisola, Study of the crack-
631 bridging ability of organic coatings for concrete: analysis of the mechanical behaviour
632 of unsupported and supported films, *Prog. Org. Coatings.* 44 (2002) 261–269.
633 doi:10.1016/S0300-9440(02)00054-1.

634 [41] M. Delucchi, A. Barbucci, G. Cerisola, Crack-bridging ability of organic coatings for
635 concrete: Influence of the method of concrete cracking, thickness and nature of the
636 coating, *Prog. Org. Coatings.* 49 (2004) 336–341.

637 doi:10.1016/j.porgcoat.2003.09.016.

638 [42] A. Volkwein, R. Petri, R. Springenschmid, Oberflächenschutz von Beton mit flexiblen
639 Dichtungsschlämmen, Betonw. + Fert. 9 (1988) 72–78.

640 [43] H. Zhao, W. Li, Y.M. Zhang, Study on crack bridging ability of polymer-modified
641 cement based compounds for waterproofing material, Adv. Mater. Res. 1129 (2015)
642 217–221. doi:10.4028/www.scientific.net/AMR.1129.217.

643 [44] A. Dubey, P.B. Groza, United States Patent Patent No .: US 9,302,448 B2, 2016.

644 [45] M. Waldvogel, R. Zurbruggen, A. Berger, M. Herwegh, Evidences for strain localisation
645 on surfaces of waterproofing membranes - a link between structures and mechanics,
646 in: H.B. Fischer, A. Volke (Eds.), 20. Int. Baustofftagung, Tagungsbericht, Band 2,
647 F.A. Finger-Institut für Baustoffkunde, Weimar, 2018: pp. 17–24.

648 [46] M. Waldvogel, R. Zurbruggen, A. Berger, M. Herwegh, Combined methods to
649 investigate the crack-bridging ability of waterproofing membranes, in: M.M.R. Taha
650 (Ed.), Int. Congr. Polym. Concr. (ICPIC 2018), Springer International Publishing,
651 2018: pp. 249–254. doi:10.1007/978-3-319-78175-4.

652 [47] EuropeanCommittee for Standardization, FprEN 14891 Liquid-applied water
653 impermeable products for use beneath ceramic tiling bonded with adhesives -
654 requirements, test methods, evaluation of conformity, classification and designation,
655 2011.

656 [48] European Committee for Standardization, DIN EN ISO 527 1-3 Plastics -
657 determination of tensile properties, 1996.

658 [49] J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S.
659 Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J.Y. Tinevez, D.J. White, V.
660 Hartenstein, K. Eliceiri, P. Tomancak, A. Cardona, Fiji: an open-source platform for

661 biological-image analysis, *Nat. Methods*. 9 (2012) 676–682. doi:10.1038/nmeth.2019.

662 [50] T. Wagner, H. Lipinski, IJBlob : an imagej library for connected component analysis
 663 and shape analysis, *J. Open Res. Softw.* 1 (2013) 6–8.
 664 doi:http://dx.doi.org/10.5334.jors.ae

665 [51] E.J. Kramer, Microscopic and molecular fundamentals of crazing, in: H.. Kausch (Ed.),
 666 Crazing Polym., Springer-Verlag Berlin Heidelberg, 1983: pp. 1–56.
 667 doi:10.1295/kobunshi.42.389.

668 [52] A.J. Kinloch, R.J. Young, Fracture behaviour of polymers, Springer Netherlands,
 669 1995. doi:10.1007/978-94-017-1594-2.

670 [53] R.N. Haward, B.M. Murphy, E.F.T. White, Relationship between compressive yield
 671 and tensile behavior in glassy thermoplastics, *J. Polym. Sci. Part A-2 Polym. Phys.* 9
 672 (1971) 801–814. doi:10.1002/pol.1971.160090503.

673 [54] L.L. Berger, E.J. Kramer, Chain disentanglement during high-temperature crazing of
 674 polystyrene, *Macromolecules*. 20 (1987) 1980–1985. doi:10.1021/ma00174a049.

675 [55] R.A.C. Deblieck, D.J.M. Van Beek, K. Remerie, I.M. Ward, Failure mechanisms in
 676 polyolefines: the role of crazing, shear yielding and the entanglement network,
 677 *Polymer (Guildf)*. 52 (2011) 2979–2990. doi:10.1016/j.polymer.2011.03.055.

678 [56] A.M. Donald, The effect of temperature on the deformation and fracture of
 679 polystyrene, *J. Mater. Sci.* 20 (1985) 2630–2638.

680 [57] H.H. Kausch, R. Gensler, C. Grein, C.J.G. Plummer, P. Scaramuzzino, Physics
 681 crazing in semicrystalline thermoplastics, *J. Macromol. Sci. , Part B Phys.* 38 (1999)
 682 803–815.

683 [58] A.B. Thompson, Strain-induced crystallization in polyethylene terephthalate, *J. Polym.*
 684 *Sci.* 34 (1959) 741–760. doi:10.1002/pol.1959.1203412749.

- 685 [59] J. Richeton, S. Ahzi, K.S. Vecchio, F.C. Jiang, A. Makradi, Modeling and validation of
686 the large deformation inelastic response of amorphous polymers over a wide range of
687 temperatures and strain rates, *Int. J. Solids Struct.* 44 (2007) 7938–7954.
688 doi:10.1016/j.ijsolstr.2007.05.018.
- 689 [60] S. Jabbari-Farouji, J. Rottler, O. Lame, A. Makke, M. Perez, J.L. Barrat, Plastic
690 deformation mechanisms of semicrystalline and amorphous polymers, *ACS Macro*
691 *Lett.* 4 (2015) 147–150. doi:10.1021/mz500754b.
- 692 [61] L.A. Felton, P.B. O'Donnell, J.W. McGinity, Mechanical properties of polymeric films
693 prepared from aqueous dispersions, in: L.A. Felton (Ed.), *Aqueous Polym. Coatings*
694 *Pharm. Dos. Forms*, CRC Press, 2017: p. 400.
- 695 [62] B.W. Cherry, T.S. Hin, Stress whitening in polyethylene, *Polymer (Guildf)*. 22 (1981)
696 1610–1612.
- 697 [63] T. Juska, I.R. Harrison, A criterion for craze formation, *Polym. Eng. Sci.* 22 (1982)
698 766–776. doi:10.1002/pen.760221207.
- 699 [64] R.J. Oxborough, P.B. Bowden, A general critical-strain criterion for crazing in
700 amorphous glassy polymers, *Philos. Mag.* 28 (1973) 547–559.
701 doi:10.1080/14786437308221002.
- 702 [65] T.T. Wang, M. Matsuo, T.K. Kwei, Criteria of craze initiation in glassy polymers, *J.*
703 *Appl. Phys.* 42 (1971) 4188–4196. doi:10.1063/1.1659752.
- 704 [66] E.G. Kirsch, Die Theorie der Elastizität und die Bedürfnisse der Festigkeitslehre,
705 *Zeitschrift Des Vereines Dtsch. Ingenieure.* 42 (1898) 797–802.
- 706 [67] G.P. Tandon, G.J. Weng, Stress distribution in and around spheroidal inclusions and
707 voids at finite concentration, *J. Appl. Mech.* 53 (1986) 511-518.
708 doi:10.1115/1.3171804.

- 709 [68] W.D. Pilkey, D.F. Pilkey, Peterson's stress concentration factors, John Wiley & Sons,
710 2008. doi:10.1002/9780470211106.ch3.
- 711 [69] M. Matsuo, T.T. Wang, T. Kwei, Crazing of polystyrene containing two rubber balls: A
712 model for ABS plastics, *J. Polym. Sci. Part A-2 Polym. Phys.* 10 (1972) 1085–1095.
713 <http://onlinelibrary.wiley.com/doi/10.1002/pol.1972.160100610/abstract>.
- 714 [70] G. Michler, Kriterien für den Größeneinfluß der Kautschukteilchen in schlagzähen
715 kautschukmodifizierten Polymeren, *Plaste Und Kautschuk*. 35 (1988) 347–350.
- 716 [71] A.A. Griffith, The phenomena of rupture and flow in solids, *Philos. Trans. Ser. A*. 221
717 (1920) 163–198.
- 718 [72] H.M. Westergaard, Bearing pressures and cracks, *J. Appl. Mech.* 6 (1939) 49–53.
- 719 [73] G.R. Irwin, Analysis of stresses and strains near the end of a crack traversing a plate,
720 *J. Appl. Mech.* 24 (1957) 361–364.
- 721 [74] Z.Y. Deng, J. She, Y. Inagaki, J.F. Yang, T. Ohji, Y. Tanaka, Reinforcement by crack-
722 tip blunting in porous ceramics, *J. Eur. Ceram. Soc.* 24 (2004) 2055–2059.
723 doi:10.1016/S0955-2219(03)00365-0.
- 724 [75] P. Wang, I.M. Hutchings, S.J. Duncan, L. Jenkins, E. Woo, Strain whitening of a
725 thermoplastic olefin material, *J. Mater. Sci.* 41 (2006) 4847–4859.
726 doi:10.1007/s10853-006-0066-z.
- 727 [76] Y. Lu, Y. Men, Cavitation-Induced Stress whitening in semi-crystalline polymers,
728 *Macromol. Mater. Eng.* 303 (2018) 1–31. doi:10.1002/mame.201800203.
- 729 [77] L. Farge, S. André, F. Meneau, J. Dillet, C. Cunat, A common multiscale feature of the
730 deformation mechanisms of a semicrystalline polymer, *Macromolecules*. 46 (2013)
731 9659–9668. doi:10.1021/ma4019747.
- 732 [78] P.M. Vitvitskii, V. V. Panasyuk, S.Y. Yarema, Plastic deformation around crack and

733 fracture criteria. A review, *Eng. Fract. Mech.* 7 (1975) 305–319. doi:10.1016/0013-
734 7944(75)90012-0.

735 [79] K. Arakawa, K. Takahashi, Displacement fields around a crack tip in polymers, *Int. J.*
736 *Fract.* 86 (1997) 289–300. doi:10.1023/A:1007321906116.

737 [80] Y. Ju, H. Xie, X. Zhao, L. Mao, Z. Ren, J. Zheng, F.P. Chiang, Y. Wang, F. Gao,
738 Visualization method for stress-field evolution during rapid crack propagation using 3D
739 printing and photoelastic testing techniques, *Sci. Rep.* 8 (2018) 1–10.
740 doi:10.1038/s41598-018-22773-0.

741 [81] P.J. Withers, A. Soc, Fracture mechanics by synchrotron X-ray microscopy, *Philos.*
742 *Trans. R. Soc. A Math. Phys. Eng. Sci.* 373 (2015) 1–26.

743

744

Fig.1: Sketch of the evolution of the crack-bridging ability (CBA) with time. At t_0 , the membrane is in a relaxed state and a flaw is present in the substrate. With time, the flaw develops into a crack, the membrane becomes stretched and the CBA of the waterproofing membrane inhibits a cracking of the membrane (t_1 and t_2). At t_3 , the CBA of the membrane is reached and the membrane ruptures. This allows water to infiltrate along a continuous crack and starts degradation of the substrate.

753

754 Fig. 2: Sample preparation: (a): Crack-bridging samples: Application of the freshly mixed
 755 slurry on the substrate (steps 1–3). The cured membrane is represented by a darker shade
 756 of grey. Step 4 shows the preparation of the samples for subsequent crack-bridging tests.
 757 (b): Dog bone samples: The fresh slurry is spread out and cured (step 1). Dog bone samples
 758 are punched out of the cured membrane (step 2).

760

761 Fig. 3: (a): Photograph of the universal tensile rig used for crack-bridging tests and dog bone
 762 tests with a crack-bridging sample placed in the machine. (b): Technical drawing of the
 763 crack-bridging test, the time-lapse photography as well as the geometry of later thin section
 764 plane. (c): Photograph of a thin-section of a sample being deformed up to a displacement of
 765 220 μm (TS-1 in d). Top and bottom layer represent waterproofing membranes which
 766 sandwich the two fibre board plates (dark grey). (d): Stress-displacement curve of a crack-
 767 bridging test showing the different displacement positions of the manufactured thin-sections.

768

Fig. 4: (a1-d1) and (a2-d2) show the photos and segmented binary images, respectively, of the sample's surface as a function of progressive displacement for four main deformation stages: (a1) and (a2): Discontinuous-Strain-Whitening; (b1) and (b2): Continuous-Strain-Whitening; (c1) and (c2): First Failure (spots of loss of sealing capacity are magnified in the orange and blue rectangles in c1); (d1) and (d2): Final Failure. The white arrows in (a1) show the tensile load direction. The green dashed lines in (a2)-(d2) represent lines along which the number of the strain whitening spots and their widths were measured. The respective displacement of images (a1)-(d1) is noted on the right. See text for explanations.

Fig. 5: Close-up photos of the surface of the waterproofing membrane for different deformation stages. (a): The surface of the waterproofing membrane shows quartz grains, air pores and the polymer-cement matrix. (b): Appearance of first elliptical holes with their long axes parallel to the tensile load direction (red arrows). Strain whitening lines bend around the quartz grains (orange rectangle) and run perpendicular to the pore rim (blue rectangle). (c): Several individual elliptical holes formed (red rectangle) and started to connect, i.e. form cracks. Cracking often nucleates at air pore rims (pink arrow). (d): Crack propagates into the cement-polymer matrix (green arrow). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Strain Whitening Width, number and width of Strain Whitening spots

Fig.6: Diagrams show the evolution of microstructural features as a function of displacement. The vertical lines represent important moments during the crack-bridging. (a): The evolution of the Strain Whitening Width (SWW). (b): Average number of strain whitening spots along a profile (Fig. 4) (c): Average width of the individual white spots along a profile (Fig. 4).

796

797 Fig. 7. Optical microscopy reveals the presence of deformed polymer film in the membrane
 798 represented as stretched polymer fibrils (red arrows) and elliptical voids (blue arrows) in front
 799 of a crack tip. The fibrils and voids are oriented subparallel to the tensile load direction. (For
 800 interpretation of the references to colour in this figure legend, the reader is referred to the
 801 Web version of this article.)

802

803

804

805

806

807

808

809

810

Fig. 8. (a)-(d): Photos of thin-sections (cut through the crack-bridging sample). At given displacement, every first and second image represent the upper and lower membrane, respectively, of the crack bridging sample (see Fig. 3c). (e)-(h): Corresponding maps show FVM deformation structures and associated heterogeneities in between which the FVMs initiate and propagate. The red dashed rectangle is a close up image in Fig. 9. Images were acquired from the entire thin-section. After the image acquisition, all images were cropped to show the membrane only and rotated with the substrate to bottom prior to mapping.

Fig. 9. (a): Close up view of a part of a thin-section (red dashed square in Fig. 8c) with probable former air pores (yellow) incorporated in the crack in pink dashed ellipses. (b) and (c): Crazing microstructures are deflected in close vicinity of quartz grains and follow the quartz-polymer matrix interface (black arrows). (d) and (e): Straight crazing trail in the polymer matrix perpendicularly oriented to the air pore boundary (white arrows).

818

819 Fig. 10. Formation of fibril-void microstructures (surface view): The arrows, top left in all
 820 images, indicate the tensile load direction. All elliptical voids show an orientation of their long
 821 axis parallel to the tensile load direction. (a): Top view on a stretched waterproofing
 822 membrane under reflected light. Strained areas (arrows) bend around quartz grains. The red
 823 dot indicates the position of the profile along the thickness of the membrane in Fig. 11. (b)-
 824 (g) SEM investigation. (b): Overview of the area. The strained parts bend around quartz
 825 grains and cause a flat topography. (c): Non-strained polymer with topography caused by a
 826 quartz grain. Inside the polymer film many remnant structures of primary latex particles exist.
 827 (d): SEM view of a low strain part. Present cement grains cause minor topography found
 828 inside the polymer film. Small elliptical voids and few non-redispersed latex particles are
 829 found. (e): SEM view of a low strain area. The polymer film contains cement particles, small
 830 round to slightly elliptical voids and occasional non-redispersed latex particles. The red
 831 dashed line marks the transition to a high strain part. (f): SEM view of a high strain zone. The
 832 polymer film is strongly stretched, shows no topography and is free of cement particles. The
 833 flattened polymer film bends around cement particles. The voids are enlarged compared to
 834 (d) and (e). (g): Close up SEM view of a cement grain in strained polymer film. Voids initiate,
 835 grow and terminate at the cement grain. (For interpretation of the references to colour in this
 836 figure legend, the reader is referred to the Web version of this article.)

Fig. 11. (a): Cross view through the thickness of a waterproofing membrane: SEM profile along the red dot in Fig. 10a. The red dot in Fig. 10a corresponds to the top of the image. The tensile load direction is indicated by the black arrows. (b): An air pore in the polymer film with strained polymer film around. (c) The elliptical holes with strings of polymer film in between run from the rim of the pore into the matrix. Both features are oriented parallel to the tensile load direction.

Fig. 12. Fibril-void microstructures: The double arrow in the bottom right of each picture indicates the tensile load direction. (a): Inside the white ellipse a FVM is present. A white rim forms around the fibrils and voids. Inside the white rim, no cement particles, which are ubiquitous in the unstrained membrane, are present. (b): In the centre of an FVM, the polymer fibrils are strongly strained and contain nearly no cement grains. Inside these fibrils, dark areas are found (black arrows). Less strained polymers containing cement particles surround this highly strained centre (white arrows). The entire FVM is encapsulated in non-strained polymer film, which contains several cement grains.

Fig. 13. Sketch of the 3D geometry of the fibril void microstructure (FVM): Sketched are only the voids. FVM initiates at cracks, hard inclusions (cement grains and quartz grains), and air pores. They can grow vertically through the membrane's thickness and laterally, e.g. on the membrane's surface. The type of inclusion governs the propagation orientation of the FVM.

Fig. 14. Dog-bone tests of the waterproofing membrane: Stress-strain data from dog bones of the waterproofing membrane showing the elastic yield (red arrow), the peak stress (blue arrow) and the moment of failure of the entire dog bone (green arrow). The Discontinuous Strain Whitening on the surface of the dog bones appears after the elastic yield and is therefore a structure of permanent deformation. The First Failure (black spot) appears shortly after peak stress. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 15. Sketch of permanent deformation structures forming in pure polymer films. Crazes are expressed by fibrils and voids oriented parallel to the tensile load direction. Crack propagation is due to fibril rupture. Figure modified from Ref. [30].

Fig. 16. Orientation of craze initiation positions as a function of the type of heterogeneity. (a): Mapping of air pores, quartz fillers and crazes at a displacement of 440 μm (Fig. 8f). (b1): In a soft inclusion in polystyrene crazes initiate at the equator and run (sub)perpendicular relative to the tensile load direction. (b2): In a rigid inclusion crazes initiate with an angle θ to the polar axis of the inclusion and run out with an angle β relative to the equator of the inclusion. Figures (b1) and (b2) are modified from Ref. [65]. (c): Sketch of orientation of the inclusion, its polar axis and equator with respect to the tensile load direction.

$$\tan(\alpha) = (SWW/2 - gap/2) / thickness = (SWW - gap) / (2 \times thickness)$$

Fig. 17. Sketch of the relationship between the Strain Whitening Width (SWW) and the geometry of the zone in which deformation occurs. The activation angle α is the crucial parameter which defines the area of trapezoidal deformation zone.

889

890 Fig. 18. Plot of the evolution of the opening angle α calculated from the SWW (Fig. 6a) with
 891 displacement. The opening angle starts to evolve with the Continuous Strain Whitening. The
 892 evolution of α shows a steep increase to ca. 33° at $950 \mu\text{m}$. This growth behaviour is
 893 followed by a constant value of α .

894

Fig. 19. Connection between mechanical behaviour of the waterproofing membrane and deformation structures: The initiation of strain whitening spots on the membrane's surface coincides with the Discontinuous-Strain-Whitening and starts during plastic deformation of the membrane (see Fig. 14). During this stage, the crack-bridging sample is in a stress-increasing part. With the onset of the Continuous-Strain-Whitening (red line), the individual spots connect to white lines on the membrane's surface. Mechanically, the crack-bridging sample changes from the stress-increasing part to the stress decreasing part. The evolution of the Strain Whitening Width subdivides in an active accumulation (purple shaded), during which new white lines form, and a passive growth part (green shaded), during which existing white lines stretch. The match of the evolution of the Strain Whitening Width with the rig speed indicates that the rig speed is the dominant mechanism driving the passive stretching.

Fig. 20. Generalised sketch of the deformation evolution of waterproofing membranes during crack-bridging. (a): Evolution of (micro)structures (FVM) and deformation mechanisms inside the membrane's volume with increasing displacement and time during a crack-bridging test. During a specific displacement (e.g. 0.6 mm), the membrane shows several different mechanical stages (red parts of stress-strain curves from dog bone tests). Yellow lines represent slices through the membrane at fixed displacements and time (see c). (b): Stress–displacement diagram of corresponding crack-bridging test. The peak stress correlates to the crack initiation at the membrane-substrate interface. From peak stress onwards, cracks propagate from substrate-membrane interface to the surface. The First Failure (first connected crack through entire thickness of the membrane) does not influence the stress–displacement curve. (c): Slices through the membrane's volume at fixed displacements and time. The crack front forms lobes due to heterogeneities such as air voids and sand grains, which are not shown in this graphic. Their influence is shown in detail in Figs. 8 and 9. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

924 Tab. 1: Weight percentage of the respective components in the waterproofing membrane.

Component	Quartz sand	OPC 52.5 N	RPP	Water
Wt. %	56	19	25	19

925

926 Tab. 2: Composition in weight fraction of the dry mix and volume fraction of the hardened
 927 waterproofing membrane after all water is consumed and air is entrained during the mixing
 928 process.

Component	Quartz sand	OPC 52.5 N	RPP	Air
Wt. %	56	19	25	-
Density kg/m ³	2650	3100	938	-
Vol. %	37	11	40	12*

929

930 * Air pore content is based on point counting of air pores in thin sections

931

932 Tab. 3: Displacements of the prepared thin-sections and the position of sampling on the
 933 stress-displacement curve (Fig. 3d).

Thin-section	Displacement [μm]	Position at stress-displacement curve
TS-1	220	After elastic part in stress increasing regime
TS-2	440	Shortly after peak stress, begin of stress decreasing
TS-3	800	Mature stress decreasing
TS-4	1040	First vertically continuous hole present

934