TOUGHENING AND MECHANICAL PROPERTIES OF EPOXY MODIFIED WITH BLOCK CO-POLYMERS AND TITANIUM DIOXIDE NANOPARTICLES

Ankur Bajpai and Bernd Wetzel

Institut für Verbundwerkstoffe GmbH (IVW), Technical University of Kaiserslautern,
67633 Kaiserslautern, Germany
ankur.bajpai@ivw.uni-kl.de, bernd.wetzel@ivw.uni-kl.de,
http://www.ivw.uni-kl.de/

Keywords: Thermosets, Nanocomposites , Block Copolymers, Fracture Toughness

Abstract

The objective of this work is to overcome the disadvantage of epoxy thermosets i.e. brittleness, and to systematically develop and understand novel polymeric hybrid nanocomposites that include innovative in situ block copolymers with tailored morphologies in order to generate high toughness. Further the rigid fillers are added systematically with block copolymers to study the combined effect of rigid nanofillers and soft block copolymers. The resulting matrix will be extensively and carefully characterized by standard methods. This includes thorough characterization of mechanical, fracture mechanical and thermal properties. The resulting formulations led to significant increase in fracture toughness and critical energy release rate.

1. Introduction

Epoxy resin systems are a class of high performance thermosets commonly used as a matrix in a wide range of automotive, electronics, and aerospace applications. Such wide range of applications is achieved by selecting a proper epoxy resin/ hardner system which is further processed in a felicitous curing schedule. Properties like high modulus, high strength, and good thermal and dimensional stabilities make it so popular in composite applications[1]. The mechanical properties of epoxy matrices can further be altered and improved by adjusting the molecular structure and architecture, e.g. by increasing the crosslink density to produce the high stiffness and strength[2].

The incorporation of ductile organic and hard inorganic micro- and nano-particulate fillers is a well-known pathway to improve mechanical properties, and in particular toughness, of brittle thermosetting polymers such as epoxy resins. To overcome brittleness, reactive rubber modifiers, e.g. carboxy-terminated butadiene acrylonitrile (CTBN) can react into the epoxy which increases its toughness but with the sacrifice of strength and thermal properties[3]. Also core-shell particles, typically a PMMA shell surrounding a low Tg rubber core or thermoplastic spheres such as polysulfone (PSU) can increase toughness, but they need to be homogeneously distributed in the matrix to become effective [4, 5]. Especially ceramic fillers with nano-dimension, e.g. alumina and silica have proven their ability to increase fracture toughness, and furthermore to reinforce also mechanical properties such as modulus of elasticity and strength while only marginally restricting polymer ductility at low nanofiller concentrations. Indeed, nanofillers attain a significant improvement in rigidity and reinforcement of epoxy already at rather low filler contents [6-8]. However, one of the main drawbacks is the presence

Excerpt from ISBN 978-3-00-053387-7

of particle agglomerates in commercially available gas phase synthesized ceramic nanoparticle powders. Occurrence of agglomerates in a brittle polymer must be avoided because they act as flaws and generate local stress peaks which reduce strength, ductility, and fracture toughness of the polymer. For manufacturing such nanocomposites costly mechanical dispersion techniques are usually undertaken in order to homogeneously distribute nanoparticles as individuals within the resin.

For avoiding mechanical dispersion efforts an innovative approach creates further potential to realize varying nanostructures with both stiff and ductile building blocks by using a new class of block-copolymers (BCP) [9]. These block-copolymers have the ability to self-assemble on the nanoscale. Various nanophase morphologies can be realized that are well-integrated into the polymer matrix. Available are e.g. functionalized and non-functionalized MAM symmetric copolymers with two poly (methylmethacrylate) blocks surrounding a center block of poly(butyl acrylate) (Fig.1). Also available are SBM copolymers consisting of polystyrene, 1,4-polybutadiene, and syndiotactic poly(methylmeth-acrylate) blocks.

Fig.1: MAM symmetric copolymers. PMMA blocks (red) give compatibility to epoxy, while the PBuA block (grey) provides an immisicible rubber phase for toughening.

Nano-structuration is induced by strong repulsive forces between side and middle blocks, and it is primarily governed by thermodynamics and thus independent of processing conditions. Controlling factors are the polarity of building blocks, miscibility, and concentration which allows to adjust various morphologies, e.g. spherical nanoparticles, vesicles, and micelles with network-like structure [9, 10].

2. Experimental

The materials in this study are a standard Bisphenol-F epoxy resin cured by an aromatic diamine curing agent and a functionalized PMMA-*bloc*-PbuA-*bloc*-PMMA copolymer. The MAMs are built up of symmetrically arranged diblock BCPs with one stiff PMMA block which is connected by a more ductile PBuA block (Nanostrength D51N). When MAM block copolymers are dispersed with the DGEBF resin, they self-assemble into the thermosetting network during reaction induced phase separation. Thereby epoxy-miscible PMMA blocks provide affinity to the epoxy monomers, while the PBuA blocks are an epoxy-non-miscible soft rubber phase and precipitate as second phase.

The BCP concentration was varied systematically from 0 to 12 wt-%. For hybrid nanocomposites Titanium dioxide (TiO_2, type Aeroxide P25, Evonik) is used which possesses primary particle diameters of ca. 21nm and a specific surface area of 35-65 m^2/gm. The interfacial area may influence the properties of nanocomposites, so it is necessary to ensure the proper distribution of nano titanium oxide and to avoid agglomerates in the epoxy resin. This was performed by utilizing machines traditionally used for lacquer processing (Dissolver, Bead Mill). A Dissolver provides high shear forces to break up the agglomerates in the liquid epoxy/agglomerate mixture by the rotation of a teeth vested metal disc [11]. A masterbatch was produced containing a high weight fraction of nanofillers (25 wt.%). After dispersing, the masterbatch was thinned down by neat epoxy resin in order to systematically gain nanocomposites with varying nanoparticle content ranging from 3 to 7 wt %.

Preparation of BCP nanocomposites takes less efforts compared to those containing inorganic nanoparticles. Firstly, the required amount of BCP was mixed gently with preheated DGEBF and the mixture was dispersed in a dissolver (Dispermat, Getzmann GmbH) at 90°C until transparent mixture was obtained ensuring complete melting of BCP in the epoxy. After that the modified epoxy was cooled down to 55°C and mixed with a stoichiometric amount of curing agent by stirring for 5-10 min

Excerpt from ISBN 978-3-00-053387-7

at 350 rpm. For preparing hybrid mixtures the masterbatch containing nano TiO_2 (25 wt.%) was thinned down and stirred at 650 rpm for 50 min at 80°C while removing entrapped air by vacuum. Then, the calculated amount of BCP was added and mixed for 30 min at 350 rpm. Finally, the stoichiometric amount of curing agent was added and the mixture was stirred thoroughly for 5-10 min at 350 rpm.The mixture was then cast into glass molds to produce tensile samples and into steel molds for compact tension (CT) specimens, respectively. The samples were cured in two steps at 80°C for 8 hours and at 120°C for 18 hours.

Mechanical properties of the cured nanocomposites were determined by static and dynamic testing methods. Tensile testing was performed using dog bone shaped specimens according to DIN EN ISO 527-1 and a Zwick universal testing machine at room temperature. The testing speed was set to 2 mm/min. For each specimen at least five samples are tested.

Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo equipment (DSC1 Star system) to determine glass transition temperature. The samples were heated from room temperature up to 200 °C and then cooled down to room temperature, and then followed by a second heating cycle to 200 °C at a heating rate of 10 K/min.

Linear elastic fracture mechanics (LEFM) allows measuring the intrinsic fracture toughness of brittle solids [12]. Independent of the specimen geometry the LEFM provides information about the initiation of cracks in epoxy nanocomposites. The static fracture toughness was determined by means of compact tension (CT) tests on at least six specimens according to ISO 13586 standard using a Zwick universal testing machine at room temperature and at low deformation speeds of 0.2 mm/min. The thickness B and the width W of specimens were chosen to be 6 mm and 36 mm, respectively. Prior to testing, a notch was machined and then sharpened by tapping a fresh razor blade into the material, so that a sharp crack was initiated with a length a_0 between $0.45*W$ and $0.55*W$. The fracture toughness K_{1c} was then calculated by Eq. (1), where F is the maximum force observed in the load-displacement curve, and a_0 is the initial crack length for calculating $\alpha = a_0/W$ and $f(a/W)$

$$K_{IC} = \frac{F}{B\sqrt{W}} \,.\, f(a/W) \tag{1}$$

$$f\left(\frac{a}{W}\right) = f(\alpha) = \frac{(2+\alpha)}{(1-\alpha)^{3/2}} \,.\, (0.866 + 4.64\alpha - 13.32\alpha^2 + 14.72\alpha^3 - 5.60\alpha^4) \tag{2}$$

The knowledge of the critical stress intensity factor K_{Ic}, the elastic modulus E_t and Poisson's ratio ν (~0.35) allows calculating the critical energy release rate G_{Ic}:

$$G_{Ic} = \frac{K_{Ic}^2(1 - \upsilon^2)}{E_t} \tag{3}$$

Information about toughening mechanisms in the nanocomposites were studied with the help of a field emission scanning electron microscope (SEM SUPRA™ 40 VP, Carl Zeiss NTS GmbH, Germany). Before scanning, the surfaces of the samples were sputtered with a thin layer of gold and platinum for 70 sec using a sputtering device (SCD-050, Balzers, Liechtenstein).

Excerpt from ISBN 978-3-00-053387-7

3. Results and Discussions

3.1 Glass Transition Temperature

The *Tg* of the unmodified epoxy was measured to be 141 °C. The values of *Tg* were reduced by the addition of the MAM block copolymers, see Table 1, although the reduction of *Tg* was small . The PMMA fraction and the better compatibility of the PMMA with epoxy is expected to lead to a plasticisation effect in the D51N modified epoxies, since more PMMA with low *Tg* (about 100 °C) [13, 14] remains dissolved in the epoxy matrix. This explains the lower *Tg* measured for the D51N modified epoxies. Due to lower amount of titanium dioxide nanoparticles the *Tg* of the TiO_2 modified epoxies remain similar or is even higher than for the unmodified one.

3.2 Tensile Behavior of the Composites

The values of the elastic modulus, the tensile strength and the strain a maximum stress of the MAM modified epoxy polymers are shown in the Table 1. A tensile modulus of 2950 MPa and a tensile strength of 84 MPa were measured for the unmodified epoxy. The addition of MAM led to a decrease in the tensile modulus and strength , which was expected because the D51N block copolymers are softer than the epoxy and more over it contain the softer phase content in medium range [10]. This is clearly demonstrated for 12 wt% of D51N where modulus and strength are reduced to 2670 MPa and 76.2 MPa, respectively.

D51N *wt% (vol. %)*	E_t **(MPa)**	σ_m **(MPa)**	ε_m **(%)**	K_{1c} **(MPa.m$^{0.5}$)**	G_{1c} **(KJ/m²)**	T_g **(°C)**
0%	2950(±75.8)	84(±0.7)	6.3(±0.4)	0.57(±0.04)	0.096(±0.03)	141.0
2% (1.7%)	2920(±18.7)	86(±0.3)	6.8(±0.4)	1.34(±0.09)	0.540(±0.07)	139.39
4% (3.5%)	2890(±19.6)	84.5(±0.3)	6.6(±0.3)	1.54(±0.14)	0.720(±0.13)	140.16
6% (5.2%)	2850(±14.8)	82(±0.2)	6.2(±0.5)	1.76(±0.11)	0.960(±0.12)	135.52
8% (7%)	2750(±25.3)	79.6(±0.6)	6.2(±0.6)	1.94(±0.15)	1.210(±0.19)	136.55
10% (8.6%)	2690(±47.5)	78.4(±0.7)	6.1(±0.5)	2.01(±0.13)	1.320(±0.16)	134.73
12% (10.4%)	2670(±15.6)	76.2(±1)	5.8(±0.6)	2.10(±0.26)	1.460(±0.40)	137.38
TiO_2 *wt% (vol. %)*	E_t **(MPa)**	σ_m **(MPa)**	ε_m **(%)**	K_{1c} **(MPa.m$^{0.5}$)**	G_{1c} **(KJ/m²)**	T_g **(°C)**
3% (0.75%)	3060(±13.8)	89.9(±0.6)	6.3(±0.5)	0.89(±0.06)	0.230(±0.12)	141.20
5% (1.25%)	3160(±26.2)	91.3(±0.3)	6.5(±0.1)	0.99(±0.08)	0.240(±0.16)	140.84
7% (1.75%)	3210(±17.6)	91.3(±0.2)	6.5(±0.1)	1.10(±0.05)	0.330(±0.03)	142.87
D51N+TiO_2	E_t **(MPa)**	σ_m **(MPa)**	ε_m **(%)**	K_{1c} **(MPa.m$^{0.5}$)**	G_{1c} **(KJ/m²)**	T_g **(°C)**
4%+3% (3.5% + 0.75%)	3020(±28.8)	84.6(±0.8)	6(±0.7)	1.27(±0.07)	0.470(±0.05)	140.17
6%+3% (5.2% + 0.75%)	2970(±16.7)	82.5(±0.2)	6(±0.5)	1.50(±0.04)	0.670(±0.04)	138.45
8%+3% (7 % + 0.75%)	2880(±14.7)	80.4(±0.3)	6.4(±0.04)	1.72(±0.17)	0.900(±0.17)	139.08

Table 1: Mechanical, fracture mechanical and thermal properties of different nanocomposites

Excerpt from ISBN 978-3-00-053387-7

The addition of the MAM particles reduced the modulus nearly linearly with increasing content, but up to a content of 4 wt.% the tensile strength even slightly increased or remained at the level of the neat epoxy. By adding TiO_2 nanoparticles the modulus and strength increased linearly with TiO_2 content by up to 9% in case of nanocomposites containing 7 wt.% TiO_2, while strain at maximum stress remains at ca. 6.5% without any reduction.

In case of hybrid nanocomposites (D51N+ TiO_2) modulus and strength decrease and strain at maximum stress remains same with MAM particle concentration. For hybrid nanocomposites the elastic modulus is comparatively high as compared to corresponding MAM modified nanocomposites which shows that titanium oxide nanoparticles imparting stiffness in the nanocomposites.

3.3 Fracture Properties

The fracture toughness, K_{Ic}, and fracture energy, G_{Ic}, for the unmodified epoxy, MAM and TiO_2 modified epoxy samples are summarized in Table 1. The values of K_{Ic} and G_{Ic} for the unmodified epoxy were measured as 0.57 MPa.$m^{1/2}$ and 0.0960 KJ/m², respectively. The addition of MAM led to a significant improvement in the toughness. For D51N modified epoxy, the values of K_{Ic} and G_{Ic} increased strongly with increasing concentration of MAM. The maximum fracture toughness, K_{Ic} of 2.1 MPa.$m^{½}$ and G_{Ic} of 1.46 KJ/m² was measured for 12% D51N.The results are in good agreement with the work of Klingler et al [15]. The fracture toughness of epoxy resin nanocomposites is slightly increasing with the addition of TiO_2. For manufacturing hybrid nanocomposites a constant amount of 3 wt % TiO_2 was selected, and the content of D51N was systematically varied. For hybrid nanocomposites, an increase in fracture toughness K_{Ic} was detected . For the material containing 8 wt % D51N and 3 wt % TiO_2 the K_{Ic} is 1.72 MPa.$m^{1/2}$ and the G_{Ic} is 0.9 KJ/m^2. The titanium dioxide nanoparticles enhanced the toughness of epoxy less efficiently than the D51N.

3.4 Toughening Mechanisms

Visual analysis of the fracture surface under the electron microscope gives an insight on the cause and location of failure as well as the dispersion state of the particles within the epoxy matrix. The fracture surface of the unmodified epoxy resin exhibits a brittle behavior characterized by the smooth surface area, only small scale riverlines are observed at the crack tip, which was caused by the presence of local mixed mode I/III stresses [16].

The addition of D51N did not notably change the macroscopic emergence of the fracture surface of the epoxy structure as shown in Figure 2b. In high magnification FEG- SEM micrographs the epoxies containing D51N showsmall cavities in the dimension of ca. 50 nm as shown in Figure 2b and 2d. It should be noted that the cavities and nodule like projections were not artefacts of the coating process used prior to the SEM imaging, because they were not observed on the coated unmodified epoxy, and the presence of the cavities and protrusions were independent of the coating material used. Furthermore, small scale matrix tearing was observed on the fracture surfaces of the D51N modified epoxies with all morphologies. These features indicate the enhanced plastic deformation of the epoxies. Based on the observations of the fracture surfaces in Figure 2b, the toughening mechanisms of the modified epoxies with different morphologies are proposed to be the cavitation of the spherical micelles and the enhanced plastic deformation of the epoxy matrix due to the localised plasticisation effect of the epoxy/PMMA interface or mixing region. Numerous nano-scale cavities, as well as considerably enhanced matrix tearing and multi-planar features on the fracture surfaces of the D51N modified epoxies with spherical micelles were observed.

TiO2-nanoparticles occur to be well bonded to the matrix, and they induce a crack pinning effect. The fracture surfaces and fracture toughness of the hybrid D51N/titanium dioxide nanoparticle modified epoxies were almost the same as the epoxies modified with D51N alone. It can be concluded that the addition of the titanium dioxide nanoparticles has little effect on the toughening mechanisms. The toughening mechanisms in hybrid modified epoxies are dominated by D51N, which is the cavitation of the D51N spherical micelles and the enhanced plastic deformation of the epoxy matrix due to the localised plasticisation of the epoxy/PMMA interface.

Excerpt from ISBN 978-3-00-053387-7

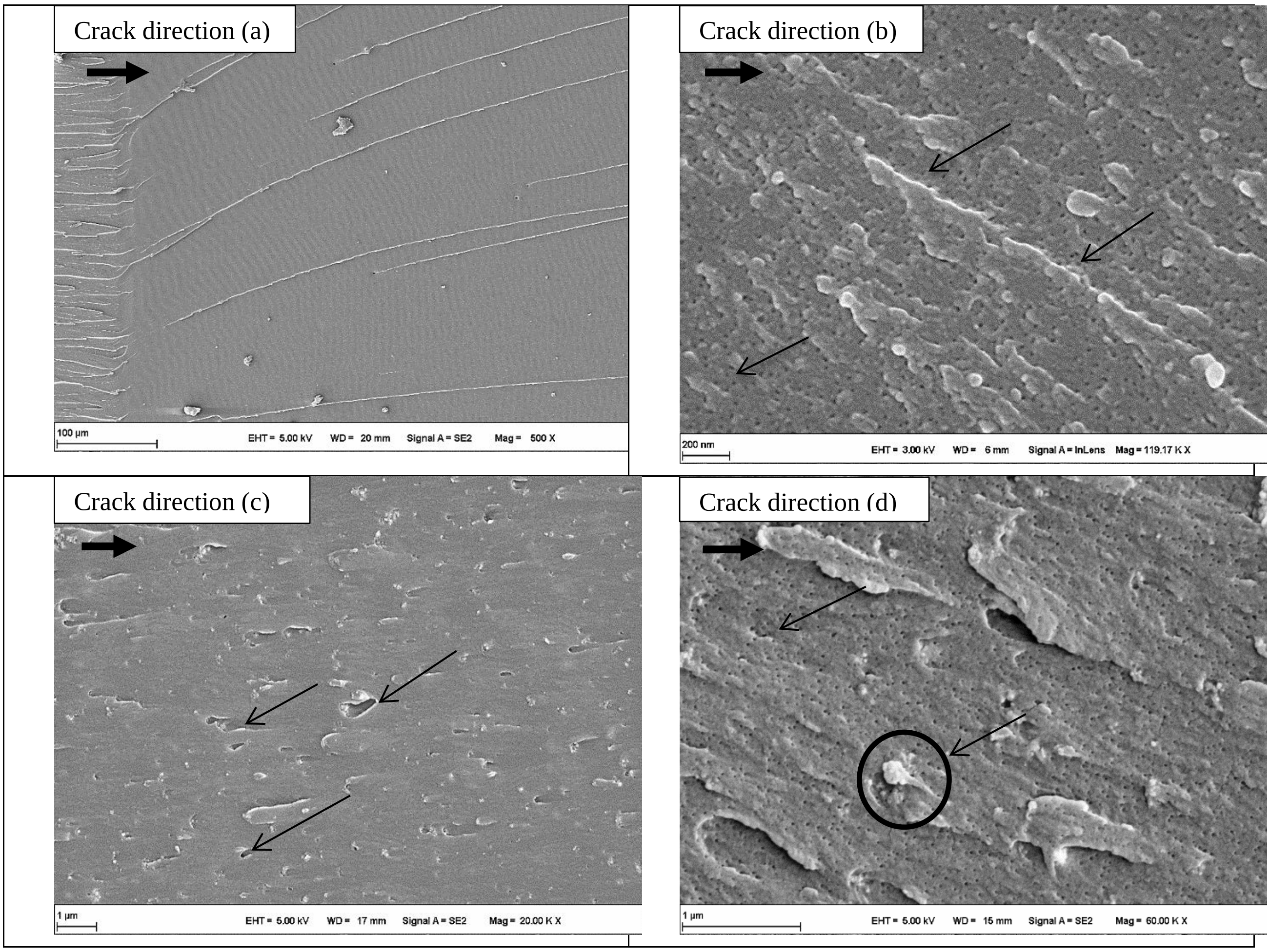

Figure 2: showing SEM images of fractured surfaces. The crack propagation direction is from left to right. (a) Unmodified epoxy (b) 8 wt % D51N (c) 3 wt % TiO_2 (d) 4wt. % D51N+3wt. % TiO_2

4. Conclusions

An amine-cured bisphenol-F based epoxy polymer was modified using functionalized poly (methylmethacrylate) block joined with poly (butyl acrylate) MAM diblock copolymers supplied by Arkema, France. The microstructure, fracture properties and toughening mechanisms were identified. The D51N micro-phase separated into spherical micelles, which became increasingly interconnected into a network as the concentration of modifier was increased. The glass transition temperature of unmodified epoxy was affected by the addition of D51N MAM, and the tensile modulus decreased, as expected when incorporating a relatively softer material into epoxy. The fracture energy, G_{Ic}, was increased linearly to a maximum of 1.46 KJ/m^2 by the addition of 12 wt% D51N MAM. Fracture toughness value are less affected by the addition of titanium dioxide nanoparticles.

Acknowledgments

The authors gratefully acknowledge the provision of the materials by Arkema.

References

[1] Petrie EM. *Epoxy Adhesive Formulations,* 1st ed. New York: McGraw-Hill, 2006

Excerpt from ISBN 978-3-00-053387-7

[2] Sue H-J, Puckett PM, Bertram JL, Walker LL. The network structure of epoxy systems and its relationship to toughness and toughenability. In: Pearson, Sue, Yee, editors. Toughening of plastics: Advances in modelling and experiments. ACS Symposium Series 2000. p. 759.

[3] Y.L. Liang, R.A. Pearson The toughening mechanism in hybrid epoxy-silica-rubber nanocomposites. Polymer 51 (2010) 4880-4890

[4] Jorg Frohlich, Holger Kautz, Ralf Thomann, Holger Frey, Rolf Mulhaupt. Reactive core/shell type hyper branched block copolyethers as new liquid rubbers for epoxy toughening. Polymer 45 (2004) 2155–2164

[5] Raymond A Pearson, Albert F. Yee Toughening mechanisms in thermoplastics-modified epoxies. Polymer, 1993, Volume 34,Number 17

[6] Wetzel B., Haupert F., Friedrich K., Zhang M. Q., Rong M. Z., Impact and Wear Resistance of Polymer Nanocomposites at Low Filler Content, Polym. Eng. Sci. 2002, 42 (9): 1919-1927.

[7] Wetzel B., Haupert F., Zhang M. Q., Epoxy nanocomposites with high mechanical and tribological performance, Compos. Sci. Technol. 2003, 63: 2055-2067

[8] Wetzel B., Rosso P., Haupert F., Friedrich K., Epoxy nanocomposites – fracture and toughening mechanisms, Engineering Fracture Mechanics. 2006, 73: 2375-2398

[9] Barsotti R. et al., Paper presented at a meeting of the Thermoset Resin Formulators Association at the Hilton Suites Chicago Magnificent Mile in Chicago, Illinois, September 15 through 16, 2008.

[10] Technical Data Sheet - Nanostrength® for Epoxies, Arkema Inc., Paris, France, 2011.

[11] Carballeira P. Mechanical and electrical properties of carbon nanofiber–ceramic nanoparticle polymer composites. PhD Thesis Technische Universität Kaiserslautern (2010).

[12] Sautereau H. The application of fracture mechanics to the fatigue crack propagation of toughened thermosets. In: Moore, editor. The application of fracture mechanics to polymers, adhesives and composites. ESIS, 33. Oxford: Elsevier; 2004.

[13] Biron M. *Thermoplastics and Thermoplastic Composites*. Oxford: Elsevier Science Publishers Ltd, 2007.

[14] Fried JR. *Polymer Science and Technology*, 2nd ed. Upper saddle river: Pearson Education, Inc, 2003.

[15] Klingler A. Ermüdungsrissausbreitung in duroplastischen Nanoverbundwerkstoffen, Institut für Verbundwerkstoffe GmbH, Studienarbeit, 2013

[16] Pritchard G and Rhoades GV. *The fracture of highly crosslinked resins. An invited review*, Materials Science and Engineering, 1976. 26(1): pp. 1-11.

Excerpt from ISBN 978-3-00-053387-7