FUNCTIONALISED ACRYLIC MICROGELS AS REACTIVE TOUGHNESS MODIFIERS OF EPOXY RESINS

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The effect of glycidyl-functionalised acrylic microgels incorporated into a commercial waterborne dispersion of epoxy resin and a solvent-free low molecular weight epoxy resin, respectively, on mechanical properties of cured materials is described in this paper. The objective of this study was to show the usefulness of prepared reactive microgels as toughness modifiers. It has been found that the incorporation of microgel particles influenced positively both the toughness performance and the other mechanical properties of tested epoxies without affecting significantly their thermal properties.

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Introduction

The present study is devoted to reactive microgels based on methacrylic acid esters. These materials can be defined as submicron intramolecularly cross-linked latex particles with reactive functional groups occurring in the microgel interior and at the surface. The functional groups are being incorporated to the microgel structure mainly as loci for cross-linking and for improving colloid stability of latexes. Microgels of various copolymer composition, particle size, and morphology have been the subject of many studies and have found application in surface coatings industry, optics, magnetism, electronics, colloid chemistry, biochemistry, and medicine. The utilization of microgels in coatings systems provides apart from the reinforcing effect also the advantage in obtaining a higher solid content that would not otherwise be possible without concurrently causing an increase in viscosity compared to the systems without microgels [1].

Microgels are most commonly prepared by standard emulsion polymerisation although other ways of synthesis are also available [2]. Emulsion polymerisation is a versatile technique that yields particles of spherical shape and narrow size distributions. By this technique, microgels can be prepared to meet the requirements of specific applications by varying, for example, the monomer composition, cross-linking density, particle size or nature of the surface charge. Although emulsion polymerisation can be carried out in the absence of added surfactants (i.e., surfactant-free emulsion polymerisation), higher concentrations of microgel particles are generally the result when surfactants are employed (conventional emulsion polymerisation). By adsorbing onto growing polymer particles, surfactants prevent the direct contact between particles, thereby an agglomeration is avoided. Semi-batch emulsion polymerisation is a suitable procedure for synthesis of emulsion microgels comprising monomers with different polarity and variable polymerisation reactivity [3,4].

Epoxy resins are considered as one of the most important classes of thermosetting polymers, having found extensive use in various fields of coating, high-performance adhesives, and other engineering applications. Once cured, they are characterised by a high chemical and corrosion resistance, as well as good mechanical and thermal properties [5]. However, in many applications, they have one major disadvantage — they are very brittle with poor resistance towards crack propagation and low impact strength; i.e., they exhibit low toughness [6]. In this respect, many efforts have been made to improve the toughness of cured epoxies by introducing the rigid particles, reactive rubbers, interpenetrating polymer networks, and engineering thermoplastics within the epoxy matrix [7-12].

The study described in this article relates to glycidyl-functionalised microgels prepared *via* emulsion polymerisation technique. We have aimed to investigate the toughening and reinforcing effects of microgel incorporation into two types of commercially distributed epoxies; namely, a waterborne dispersion

of medium molecular-weight epoxy resin designated particularly for coating purposes and a solvent-free low molecular-weight epoxy resin used mainly in the field of casting and moulding applications.

Experimental

Materials

Monomers: methyl methacrylate (MMA), butyl methacrylate (BMA), allyl methacrylate (AMA), glycidyl methacrylate (GMA), acrylic acid (AA) — technical grade (Roehm, Darmstadt, Germany); emulsifier: Disponil FES 993 IS (Henkel ČR, Prague, the Czech Republic); initiator: ammonium persulphate (Lach-Ner Company, Neratovice, the Czech Republic), epoxies: CHS Epoxy 520 — low molecular weight bisphenol A based epoxy (Spolchemie Company, the Czech Republic), CHS Epoxy 200 V55 — aqueous dispersion of medium molecular weight epoxy resin, solids content of 55 wt. % (Spolchemie Company, the Czech Republic), hardeners: Telalit 180 — aqueous solution of an adduct of epoxy resin with a mixture of amines, and CHS P 11 — diethylene triamine (Spolchemie Company, the Czech Republic); surface active additive: BYK 333 (BYK-Gardner GmbH, Germany).

Preparation and Characterisation of Microgel

Two emulsion copolymers M1 and M2 of functionalised microgel particles were synthesised comprising 87 wt. % of methacrylic acid ester comonomer (MMA in the case of M1 microgels and BMA in the case of M2 microgels). A slight cross-linking inside the microgel particles was introduced by a controlled amount (1 wt. %) of AMA. To enable the subsequent cross-linking reaction with an amine hardener and to improve the colloid stability of latexes, glycidyl functionalities were introduced by copolymerisation with 10 wt. % of GMA co-monomer. The microgels were produced in a 2500 ml glass reactor by semi-continuous non-seeded emulsion polymerisation under nitrogen atmosphere at 85 °C. This procedure ensured relatively homogeneous microgel particles of statistical copolymers. The reactor charge was put into the reactor and heated to the polymerisation temperature. Then, the monomer emulsion was fed into the stirred reactor continually (at feeding rate of about 10 ml min^{-1}) during 3 h. Afterwards, during 2 h of hold period, the polymerisation was completed. The aqueous microgel dispersion was cooled to room temperature and filtered to remove any coagulum. The recipe of emulsion polymerisation is shown in Table I.
      Particle sizes of microgels in the water phase were determined from dyna-

Table I   Recipe of emulsion polymerisation

Reactor charge:	
Water, g	400
Disponil FES 993 IS, g	3
Ammonium persulphate, g	4
Monomer emulsion:	
Water, g	700
Disponil FES 993 IS, g	52
Ammonium persulphate, g	4
Monomers, g	800

mic light scattering using a Coulter N4 Plus instrument (Coulter, Corp., UK). All the DLS measurements were conducted at 25 °C. The concentration of the measured microgel dispersion was around 0.05 wt. % of solids. Microgels were isolated from aqueous dispersions diluted to 10 wt. % of solids by drying with the aid of a Mini Spray Dryer B-290 (Büchi, Switzerland) at the spray jet temperature of 60 °C and an air flow of 30 m^3 h^{-1}. After removing the dispersion media, the microgels are defined as xerogels in further text. The glass transition temperatures (T_g) of solid xerogels were determined by means of differential scanning calorimetry using a Pyris 1 DSC instrument (Perkin-Elmer, USA).

The morphology of resulting fine agglomerates formed by spherical xerogel particles was observed by scanning electron microscopy using a LEO Gemini instrument (model DSM 982; Zeiss, Germany). Characteristic properties of the microgels / xerogels are surveyed in Table II.

Table II   Composition and characteristics of relative microgels / xerogels

Sample	Composition of monomer feeds, wt. % MMA/BMA/GMA/KA/AMA	Particle size in water phase nm	T_g °C
M1	88/0/10/2/1	148	105
M2	0/88/10/2/1	153	31

Preparation of Test Sample and Evaluation of the Results

The first series of test samples was based on the waterborne dispersion of epoxy resin CHS Epoxy 200 V55 utilised mainly in coating applications. The microgels

M1 and M2, respectively, in the form of water dispersion (42 wt. % of solids), were stirred into the CHS Epoxy 200 V55. The content of microgels was 15 % by weight of the total amount of solids in the system. After proper mixing with the amine hardener Telalit 180, centrifugation was used to eliminate air bubbles. The coating films were cast on glass panels using a blade applicator; their typical wet thickness being 200 μm. To study tensile performance and glass transition temperatures, the films were also applied at a wet film thickness of 1200 μm onto silicone substrates, which allowed us to cure at ambient temperature for one month.

The pendulum hardness of coatings was measured by a pendulum hardness tester with Persoz pendulum (model Automatic 500; Tesla, the Czech Republic) in 1, 2, 6, 15, and 21 days after the film casting. Tensile properties were determined using the INSTRON testing machine (model 1122-5500R; Instron, UK) at a crosshead speed of 5 mm min^{-1}. All the tests were carried out according to ČSN EN ISO 527. The sample size used for the tensile tests was 80×5×0.4 mm. All the tensile measurements were carried out at ambient temperature ten times for each coating film to check the reproducibility. T_g was determined by means of the thermal mechanical analysis (TMA) using the TMA CX04R instrument (R.M.I., Pardubice, the Czech Republic) in the range from 0 to 150 °C and the heating/cooling rate of 3 °C min^{-1}.

The second heating curve was used for T_g detection. The cryo-fractures of coating films containing 0 and 15 wt. % of microgels M1 were compared by means of SEM using the LEO Gemini instrument (model DSM 982).

The second series of test samples was prepared from the xerogels M1 and M2, respectively, the solvent-free low molecular weight epoxy CHS Epoxy 520 and the hardener CHS P 11. The content of xerogels was 15 % by weight related to the total amount of solids in the system. For better compatibility, the surface active additive BYK 333 was added in the amount of 0.05 wt. % related to the epoxy resin content. After proper mixing with the hardener using a homogenizer SilentCrusher M (Heidolph Instruments, Germany), centrifugation was used to eliminate air bubbles. Finally, the resultant homogenous mixture was poured into a mould and cured at 25 °C for 24 h, then post-cured at 100 °C for 4 h.

Resulting cured materials were evaluated with respect to their mechanical properties (impact strength, tension, and flexure) and thermal properties (heat resistance and T_g). Impact strength measurements were carried out according to ČSN EN ISO 179, when using the VEB testing machine (model 400/69/40; Werkstoffprüfmaschinen Leipzig, Germany). The sample size used for the test was 50×6×4 mm. Tensile modulus and tensile strength values of test samples were determined using the MTS-4/M universal testing machine (Sintech – MTS Systems Corporation, USA) at a crosshead speed of 5 mm min^{-1}. Tests were carried out according to ČSN EN ISO 527. The sample size used for the tensile tests was 150×10×4 mm. Flexural properties were evaluated using a three-point

bending test according to ČSN EN ISO 178 using the MTS-4/M universal testing machine at a crosshead speed of 2 mm min^{-1}. For the flexure tests, the sample dimension was 80×10×4 mm. All the measurements of mechanical properties were carried out at ambient temperature ten times for each type of test sample to check the reproducibility. The measurements of heat-resistant performance were carried out according to ČSN EN ISO 75 using the INSTRON CEAST HV 500 testing machine (Instron, UK). The sample size used for the test was 115×10×4 mm. The constant heating rate was 120 °C h^{-1}. T_g values of cured materials were determined by means of TMA using the TMA CX04R instrument in the range from 30 to 150 °C and the heating/cooling rate of 3 °C min^{-1}. The second heating curve was used for T_g detection. The cryo-fractures of test samples containing 0 and 15 wt. % of xerogels M1 were compared with the aid of a SEM instrument (model DSM 982; LEO Gemini)

Results and Discussion

Microgel Characterisation

It was shown that after the spray-drying procedure the xerogels were obtained in the form of round-shaped agglomerates of broad size distribution; see Fig. 1. At higher magnification, we could clearly observe the discrete structure of spherical xerogels at the size that corresponded to common emulsion copolymer particles (approx. 100 nm). From the comparison of particle diameters estimated according to SEM and obtained from DLS (see Table II), it can be assumed that the microgels are solvated and swollen by water molecules in accordance with their hydrophilic nature. Their mean particle sizes in water phase (approx. 150 nm) were found to be higher than the corresponding particle sizes in the dry state. Furthermore, it is evident that the microgels M1 have been composed mainly of MMA co-monomer when having the T_g value of 105 °C representing hard and rigid materials without film-forming properties at ambient temperature. In contrast to this, the microgels M2 based on BMA have exhibited the T_g value of 31 °C, which suggests the coalescence and film-forming ability at slightly elevated temperatures.

Systems Based on Aqueous Dispersion of Epoxy Resin

The toughening and reinforcing effects of glycidyl-functionalised microgels M1 (comprising predominantly MMA) or M2 (synthesized mainly of BMA) were investigated being incorporated in the form of the latex into the commercial aqueous dispersion of medium molecular weight epoxy resin CHS Epoxy 200
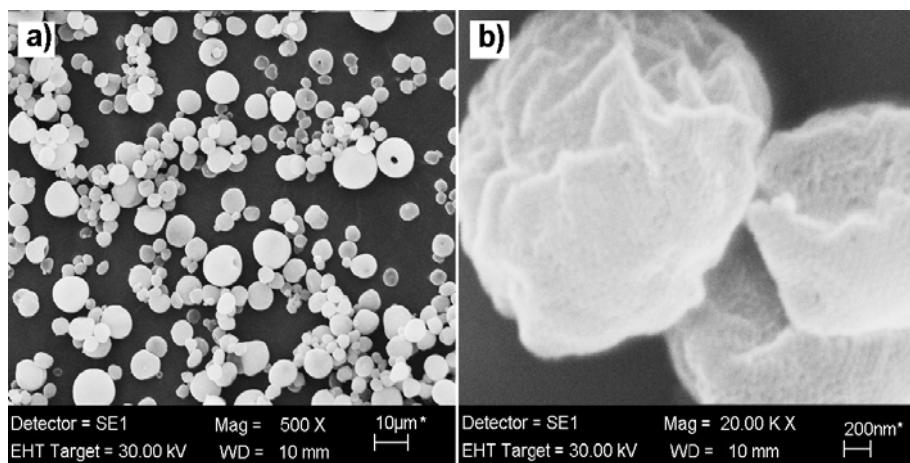
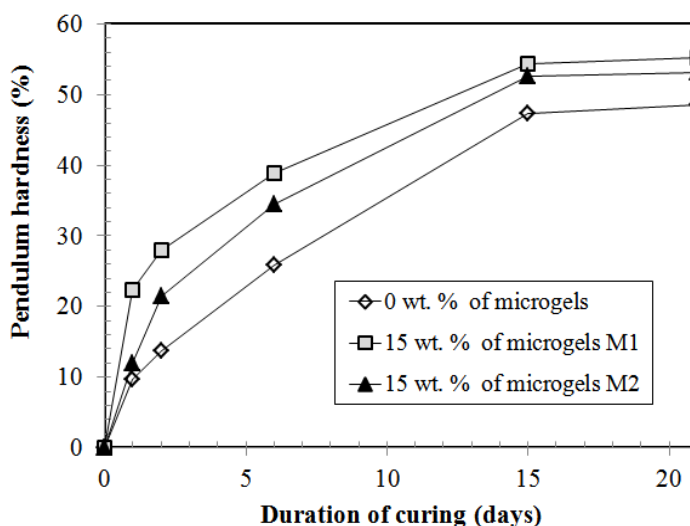Fig. 1 The SEM images of dried xerogels M1: a) magnification 500×, b) magnification 20 000×

Fig. 2 Effect of time and microgel addition on the waterborne dispersion of epoxy resin CHS Epoxy 200 V55 upon the pendulum hardness of coatings. The content of microgels is related to the total amount of solids in the coating

V55. Figure 2 demonstrates that the pendulum hardness of all the prepared coating films has been rising with time due to the simultaneously progressing processes. The first one represents the crosslinking reaction between the amine groups of the hardener and glycidyl functionalities of the epoxy resin and microgels connected with the increase in T_g of the coating system. The second one is the process of water evaporation followed by deformation and coalescence of polymer or pre-polymer particles. It is worthy to mention that the presence of reactive microgels has accelerated the curing process because of the film formation in early stages of the coatings with microgels exhibiting higher values of hardness at the same duration of curing in comparison with coatings without microgels. It is believed that the initial elevated values of coating hardness have been caused just by the

addition of cross-linked microgel particles. In later stages of film-formation, however, the coating hardness was governed also by the formed crosslinked polymeric structure of the epoxy binder. It was found as well that coatings containing microgels exhibited had increased the final hardness values in contrast to the coatings composed of the cured neat epoxy binder. This phenomenon was probably caused by the presence of cross-linked domains represented by microgel particles inside the epoxy matrix. Microgels M1 composed predominantly from MMA co-monomer and having a higher T_g than microgels M2 (see Table II) were found to affect the hardness elevation more significantly.

Table III Properties of test samples based on the waterborne epoxy resin CHS Epoxy 200 V55 and microgels M1 and M2, respectively. The content of mocrogels is related to the total amount of solids in the system

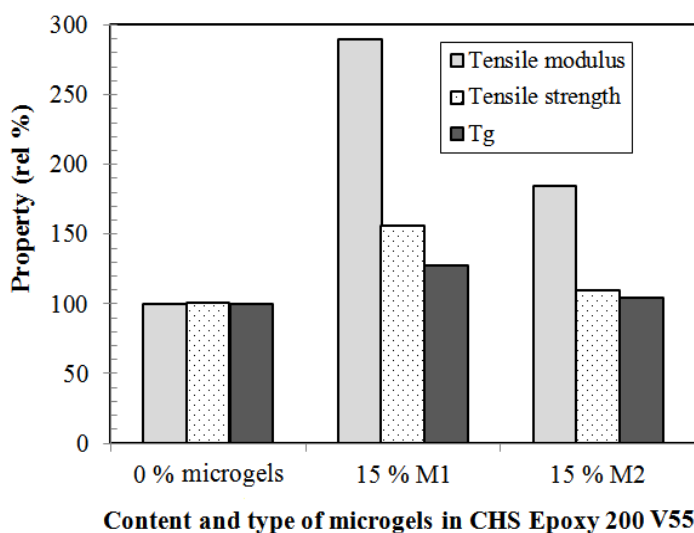| Property	Content and type of microgels		
	0 wt. %	15 wt. %	15 wt. % M2
Tensile modulus, MPa	292	845	538
Tensile strength, MPa	17.9	27.1	19.6
T_g, °C	54	68	56

Fig. 3 Properties of test samples based on the waterborne dispersion of epoxy resin CHS Epoxy 200 V55 and microgels M1 and M2, respectively. Properties expressed in rel. % are related to the corresponding properties of the neat cured CHS Epoxy 200 V55. The content of microgels is related to the total amount of solids in the system
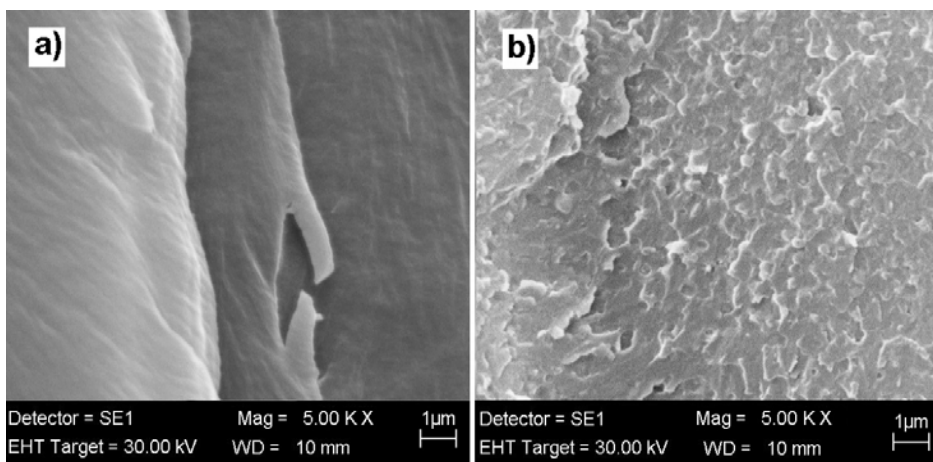
Fig. 4 SEM images of the cryo-fracture surface of the coating film based on the on the waterborne dispersion of epoxy resin CHS Epoxy 200 V55 a) without the addition of microgels, b) containing 15 wt. % of microgels M1

The effect of microgels M1 or M2 addition upon the tensile properties and glass transition temperature of coating systems (based on CHS Epoxy 200 V55) is demonstrated by the data in Table III and in Fig. 3. It is obvious that the tensile properties, especially the tensile modulus, were influenced positively by the presence of reactive microgel particles. The results of tensile properties measurements indicate the existence of cohesive polymeric materials possessing microgel particles that are chemically bonded inside the epoxy matrix. Also, it can be seen that the thermal properties, represented by the value of T_g, had not been affected significantly by incorporation of microgels. The cryo-fracture SEM image of a coating without any microgels was compared with that containing 15 wt. % of microgels M1 (see Fig. 4). Separated spherical microgel particles of the size around 200 nm were observed distinctly in the case of the coating containing microgels. It can be noticed as well that microgels are distributed regularly inside the coating film.

Systems Based on Solvent-free Epoxy Resin

Table IV summarises mechanical and thermal properties of cured materials based on the solvent-free low molecular weight epoxy resin CHS-EPOXY 520 and spray-dried reactive xerogels M1 or M2. When comparing with the neat epoxy matrix, the systems containing 15 wt. % of xerogels had exhibited the improved mechanical properties, only a slight drop in tensile modulus and flexural properties was noticed in the case of materials containing M2 xerogels. Nevertheless, the addition of xerogels was found to be beneficial with respect to the toughness performance of the resulting epoxy-based materials considerably, which is demon-

Table IV Properties of test samples based on the solvent-free epoxy resin CHS-EPOXY 520 and xerogels M1 and M2, respectively. The content of xerogels is related to the total amount of solids in the system

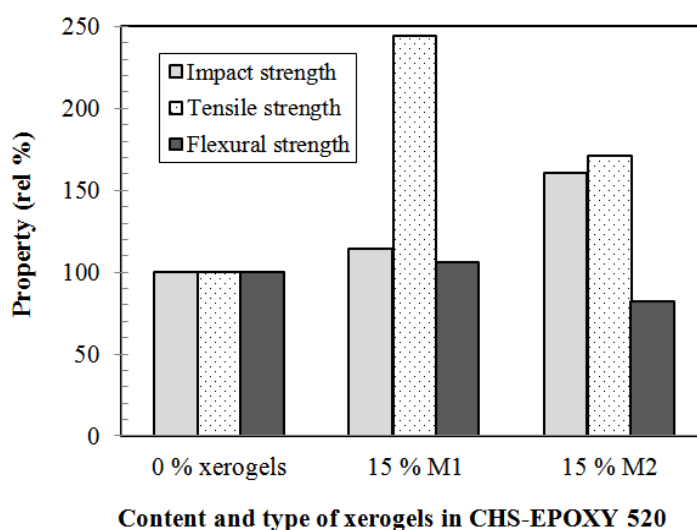| Property	Content and type of microgels		
	0 wt. %	15 wt. % M1	15 wt. % M2
Impact strength, kJ m^{-2}	58.1	66.6	93.2
Tensile modulus, MPa	2635	2711	2017
Tensile strength, MPa	26.6	65	45.5
Flexural modulus, MPa	2965	3023	2389
Flexural strength, MPa	110.9	117.5	81
T_g, °C	109.8	104.1	105.1
T (ČSN EN ISO 75)	100.3	96.3	93.7

Fig. 5 Mechanical properties of test samples based on the solvent-free epoxy resin CHS Epoxy 520 and xerogels M1 and M2, respectively. Properties expressed in rel. % are related to the corresponding properties of the neat cured CHS Epoxy 520. The content of xerogels is related to of the total amount of solids in the system

strated clearly in Fig. 5. The tensile strength of the test sample with M1 xerogels had increased more than twice and only slightly less improvement was achieved for the impact strength of the material comprising M2 xerogels. Thus, the microgels are supposed to be chemically linked to the final epoxy network thus apparently serving as loci of the impact energy dissipation inside the brittle epoxy matrix. Similarly to water-based systems, the addition of xerogels in the solvent-free epoxy resin did not affect substantially thermal characteristics of the resulting cured materials (see Table IV). Finally, Fig. 6 represents the distribution of

xerogels inside the epoxy matrix, where xerogel particles of around 20 nm can be distinguished on the cryo-fracture surface under monitoring. Last but not least, it can be seen that the xerogels were distributed regularly without any formation of domain-like structure of xerogel-rich and xerogel-pure binder areas.
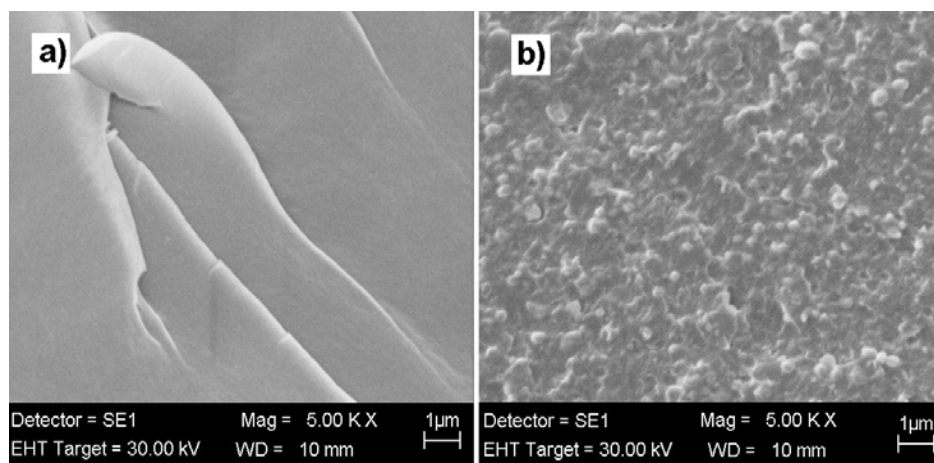

Fig. 6 SEM images of the cryo-fracture surface of the coating film based on the solvent-free epoxy resin CHS-EPOXY 520. a) without addition of xerogels, b) containing 15 wt. % of xerogels M1

Conclusion

Cross-linked reactive microgels consisting predominantly of glycidyl-methacrylate, methylmethacrylate, or butylmethacrylate were prepared as the particles in aqueous emulsion *via* the semi-batch emulsion copolymerisation. It has been shown that the addition of aqueous dispersion of glycidylyl-functionalised microgel particles into a film-forming waterborne dispersion of epoxy resin causes an increase in the coating hardness. This effect was apparently caused by the presence of microgels having a high value of T_g. Further, as found out as well, the presence of reactive microgel particles in the water-borne epoxy binder influences positively toughness characteristics of the cured materials; especially, the tensile modulus. Finally, the effect of the addition of spray-dried xerogels on the mechanical properties of the solvent-free low molecular weight epoxy resin has been investigated as well revealing that the xerogels are distributed regularly inside the epoxy binder where they are able to improve considerably the toughness of the resulting epoxy-based materials.

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