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Cross-linking of cationically polymerised epoxides by nanoparticles

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Abstract

The influence of silica nanoparticles with epoxide groups at the surface on the cationic polymerisation of cycloaliphatic epoxides is shown. When cyclohexene oxide is the monomer the gel content of the polymer increases with increasing amount of the multifunctional particles. The insoluble part of the polymer consists of particles with a silica core and a polymer shell. The core-shell-particles are connected to each other. In the case of a diepoxide as the monomer the storage modulus increases with increasing amount of particles. This is particularly the case for very high loadings. The glass transition temperature of the sample decreases with increasing amount of functional filler and the swelling rate with a solvent goes through a minimum. It is proposed that the particles are surrounded by a softer polymer layer compared to the bulk polymer. This is due to chain transfer reactions with water adsorbed on the particle surface.

Keywords: Epoxide; Cationic polymerisation; Nanoparticles

1. Introduction

The cationic polymerisation of epoxides is widely used for printing inks, adhesives or coatings. Appropriate initiators are diaryliodonium and triarylsulfonium salts with BF_4^-, PF_6^-, AsF_6^- and particularly SbF_6^- as counterions [1,2]. In most cases a photopolymerisation is carried out but during the last few years latent thermal initiators for the cationic polymerisation of epoxides were also developed [2]. The polymerisation of the epoxide is initiated by the super acid or a carbocation formed during the photochemically or thermally induced decomposition of the initiator. The basic reactions for the photochemical decomposition of diaryliodonium [3] and triarylsulfonium salts [4] are described in the literature as well as the initiation, chain growth and chain transfer of the epoxide polymerisation [5].

The influence of nanoparticles on the properties of epoxy resins has been examined during the last years. In many cases the influence of nanoparticles on the mechanical properties of the modified epoxy resins are the focus of the examinations. By the addition of even small amounts of nano-sized aluminium oxide the wear resistance and stiffness of an epoxy resin could be improved significantly and a synergistic effect with micro-sized particles was observed [6]. In order to fix silica nanoparticles covalently in an epoxy resin, polyacrylamide was grafted onto the surface of silica particles; the grafted particles then take part in the curing reaction of the epoxy resin. A strong improvement of the frictional coefficient and the specific wear rate was detected due to the addition of the particles and the materials were superior compared to ones containing microparticles or untreated nanosilica [7]. In other cases the thermal properties of epoxy resins were improved by the addition of silica nanoparticles and a reduction of the glass transition temperature was observed [8]. In order to improve the mixing of nanosized fumed silica with polyethersulphone Jana et al. used an epoxy resin as a reactive solvent. After polymerisation of the epoxy resin a significant improvement in barrier resistance and heat deflection temperature compared to neat polyethersulphone was observed [9]. Fumed silica was also used by Bauer et al. to improve the properties of acrylates; especially abrasion and scratch resistance was examined. A surface modification of the fumed silica using methacryloxypropyl trimethoxysilane was carried out and it was measured that the silane is covalently fixed onto the particle surface. The tridentate silanes also react with each other forming a

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ladder-like structure [10]. In the first step the silanes are hydrolysed by water present in the reaction mixture. Afterwards a condensation of the formed silanols with each other and with the silanol groups present on the particle surface takes place. The curing of epoxy resins by fumed silica grafted with hyperbranched polyamidoamine was recently examined by Okazaki et al. [11]. Most likely the observed curing reaction was a combination of a polyaddition and an anionic polymerisation induced by the amine. Interestingly the amount of gel formed during polymerisation increases with increasing generation of the hyperbranched polyamidoamine grafted onto the silica particles. With γ-amino propyltrimethoxysilane the lowest gel content is formed. This can either be due to the increasing number of amino groups present in the reaction mixture resulting from an increase in the hyperbranched polyamidoamine generation or with an increased mobility or reactivity of the amino groups with increasing distance from the silica core of the particles.

Fumed silica is also used in the work presented here. In order to copolymerise the particles with the cycloaliphatic epoxides used as monomers, the surface was modified by a silane with cycloaliphatic epoxy group. It is of interest whether a copolymerisation between the modified particles and epoxy resins takes place during cationic polymerisation of the epoxy resin. It is known that moisture can increase or decrease the polymerisation rate of epoxides, which depends on whether a cycloaliphatic epoxide or a glycidyl ether is used as the epoxide [12]. In each case the cross-linking density of the polymer is decreased by the chain transfer reaction carried out by water and results in the formation of alcohol groups [13]. As fumed silica always contains traces of water and silanol groups on the surface [14] it is of interest whether the water influences the polymerisation kinetics and the properties of the formed nanocomposites. The cationic polymerisation of monoepoxides leads to linear polymers which are soluble in many organic solvents whereas diepoxides form insoluble highly cross-linked polymers. Unfortunately many analytical techniques are only applicable to soluble polymers but it is only the cross-linked materials which are of technical interest. In order to examine the reactions and properties as detailed as possible the work is carried out with a monoepoxide and a diepoxide.

2. Experimental

2.1. Preparation of the materials

40 g fumed silica (BET surface 200 m^2/g, Aerosil 200, Degussa) dispersed in 650 g butanone was surface treated with 25.2 g (0.102 mol) 3,4-epoxycyclohexylethyl trimethoxysilane (ECHTMO; ABCR) over night. The solvent and the formed methanol were removed with a rotatory evaporator and the powder was vacuum treated at 60 °C for 1 h. The resulting white powder was dispersed into the cyclohexene oxide (Aldrich) in amounts of 10, 20, 25, 30, 40 and 50 wt% using a magnetic stirrer. To avoid the formation of small gel particles and to receive optically clear samples the mixtures were ultrasonicated twice for 30 s (Bandelin UW 2200, 35% power). As soon as the dispersions are transparent the iodonium salt (tolylcumyl) iodonium tetrakis(pentafluorophenyl)borate (Rhodorsil 2074, Rhodia) was added as initiator. To reduce the reaction temperature the initiator was activated with ascorbic acid-6-hexadecanate (Aldrich) [15]. The amount of initiator in the final reaction mixture was 1.5 wt% and that of ascorbic acid-6-hexadecanate 1 wt%. The samples were polymerised at 85 °C for 1 h. Transparent polymers are obtained.

The gel content of these samples was determined by Soxhlet extraction with ethyl acetate for 24 h. The residues were dried in a vacuum oven for 24 h at 70 °C and all experiments were carried out in duplicate.

For the preparation of nanocomposites based on a diepoxide, the surface treated fumed silica was dispersed in 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (ERL 4221, Union Carbide) in amounts of 5, 10, 15, 25, 35 and 50 wt% with a dissolver (CA 40-C, VMA Getzmann, Reichshof, Germany). The same initiator system and curing procedure was used as described for the cyclohexene oxide, but an additional postcuring for 30 min at 120 °C was carried out.

2.2. Measurements

DSC measurements were carried out with a DSC 2920 (TA Instruments) with a heating rate of 10 K/min. Photoacoustic infrared spectra were recorded with a Bruker IFS 66 FTIR spectrometer connected with a MTEC 300 PAS unit (resolution 8 cm^{-1}, 150 scans). The particle size distribution was measured by light scattering with 3D cross correlation spectroscopy with a Li.S.A. which is described in detail somewhere else [16,17]. The advantage of this instrument is the possibility to measure turbid samples and to determine the stability of dispersions. Measurements with the torsion pendulum (Myrenne ATM-3) were carried out with a samples size of 80 mm × 10 mm × 1 mm between −100 and +300 °C with a heating rate of 2 K/min and a frequency of 1 Hz. Thermogravimetric measurements were carried out with a TA Instruments TGA 2950 and a heating rate of 5 K/min. The samples for TEM examination were prepared in an epoxy resin and cut into ca. 100 nm thick slices with a Leica Ultracut UCT equipped with a diamond knife. The samples were examined with the TEM TECNAI G^2 from FEI. The SEM examinations were carried out with a LEO 1530 GEMINI after coating the samples with a thin carbon layer. Polymers were characterised using MALDI-TOF MS (Applied Biosystems, Voyager-DE PRO) and 1000 laser pulses were applied to record a spectrum. The samples were dissolved in tetrahydrofuran and dithranol was used as the matrix to which silver trifluoroacetate was added.

3. Results and discussion

3.1. Surface modification of fumed silica

In the first step silica nanoparticles with cyclohexylepoxy groups on the surface were prepared by the surface silanisation of fumed silica with 3,4-epoxycyclohexylethyl trimethoxysilane. The required amount of silane was not estimated via the density of silanol groups on the surface, which is 0.5 mmol per 100 m^2 specific surface of the fumed silica and nearly independent of the history of the fumed silica [14], because this method does not lead to a full coverage of the surface by the silane. By using the surface area of the fumed silica of 200 m^2/g and the specific wetting area of the silane [18] of 7.5 molecules per nm^2 the amount of silane needed to get a monolayer coverage was determined. For the silane used this leads to a silane content which is about 2.5 times that of the amount of silanol groups. As well as the silanol groups adsorbed water (approx. 1 wt%, TGA) is always present on the surface of the fumed silica. The silane is first hydrolysed by this water and the hydrolysis is facilitated by the slightly acidic surface. The silanol formed by hydrolysation of the silane reacts in a condensation reaction with the silanol groups on the silica surface. Additionally a condensation between hydrolysed silanes take place. Due to the excess of silane with respect to the surface silanol, it cannot be fixed completely by a direct reaction with the surface, but the excess can be bound to the particles by the condensation reaction between the hydrolysed silanes. The course of the reaction can be followed by photoacoustic infrared spectroscopy (Fig. 1). The spectrum of the untreated fumed silica shows a broad signal for the adsorbed water with a maximum at 3500 cm^{-1}, which is only slightly influenced by the surface silanisation. The silanol groups lead to a sharp signal at about 3750 cm^{-1}. This signal is very weak in the spectrum of the modified silica showing that the expected condensation reaction of the surface silanol groups as well as the silanol groups formed by the hydrolysis of the silane takes place. Additionally the signals for the organic modification are present in the spectrum of the treated silica. The most prominent signals are caused by the C–H stretching vibrations and are in the range of 2900 cm^{-1}. Furthermore a shoulder is present at 2998 cm^{-1}, which is characteristic for the C–H vibrations of the epoxide ring. The characteristic ring vibrations of the epoxide at 750 and 790 cm^{-1} are overlapped by one of the strong bands of the fumed silica and can, therefore, not be evaluated. The thermogravimetric characterisation of the modified silica between 20 and 600 °C shows that the content of volatile material is 27.8 wt% and the thermal decomposition takes place in two steps. The first decomposition maximum is at 117 °C and corresponds to a weight loss of 4.5 wt%. If the material is washed with butanone and dried again under the same conditions as after the modification, this first weight loss no longer appears in the TGA; the second decomposition step has not changed. The maximum of this main decomposition is at 308 °C and corresponds to a weight loss of 23.3 wt%. The high temperature required to decompose and evaporate the organic content of the modified nanofiller and the fact that it cannot be removed by washing with butanone shows that the silane is strongly bound to the particle surface and one can expect a covalent bond. Nevertheless the weight loss is lower than expected for the amount of silane used for the surface modification. If the silane is physisorbed without any chemical reaction during the surface reaction a loss of 38.6 wt% would be expected. If all three methoxy groups of the silane react during the surface modification and no silicon containing fragments evaporate, the loss should be 25.8 wt%. Assuming a reaction of all methoxy groups the silane must be fixed covalently on the surface of the silica particles. The expected loss of 25.8 wt%, therefore, must be compared with the 23.3% detected for the high temperature decomposition step, which is already close to the theoretical value. From the amount of silane used and the specific surface area of the silica one can estimate the maximum surface density of epoxide groups to be about 7.5 groups per nm^2. Using TGA it was found that the covalently fixed part of the silane is only about 90% of the theoretical value. The amount of epoxy groups can, therefore, be estimated to about 6.8 groups per nm^2. From this coverage of particles and the diameter of the primary particles of the fumed silica (12 nm) one can estimate that each primary particle of the fumed silica bears about 3000 epoxy groups. This means that the modified particles should lead to an enormous cross-linking density of the polymer, much higher than realisable when multifunctional molecules are used as cross-linkers.

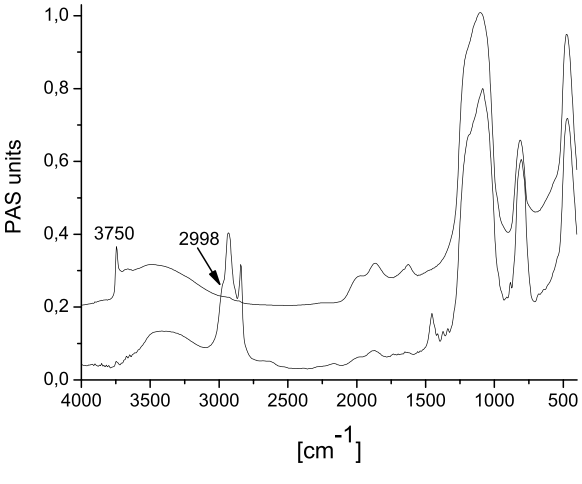


Fig. 1. Photoacoustic infrared spectrum of the fumed silica before (top) and after treatment (bottom) with the silane ECHTMO.

As with every solid with a large surface area the modified silica adsorbs water from the atmosphere. For the unmodified fumed silica the content is in the range of 1 wt% (TGA) and the amount should be in the same order of magnitude for the modified material. It is well known from the cationic polymerisation of epoxides that water traces strongly influence the reaction and for cycloaliphatic epoxides the polymerisation reaction is accelerated [12]. Since the water is located close to the epoxy groups of the surface, side reactions and a different polymerisation kinetics at the surface must be considered in the following discussion of the polymerisation of the modified particles with the cycloaliphatic epoxides.

3.2. Polymerisation and properties of nanocomposites based on cyclohexene oxide

The modified fumed silica was dispersed in the monoepoxide cyclohexene oxide. Since monomer and particles contain the same reactive groups, a statistic copolymerisation should take place. To obtain a homogeneous mixture without any gel particles a combination of stirring and ultrasonication was used for the dispersion of the particles. Samples which contained between 10 and 50 wt% of the organically modified filler were prepared. All samples are completely transparent liquids with low viscosity. Even low amounts of unmodified fumed silica strongly influence the viscosity of organic liquids, due to a strong interaction between the particles. From the low viscosity one can, therefore, conclude that the interaction between the particles is strongly decreased by the organic modification. The particle size distribution and the interaction between the particles were examined in more detail via light scattering with 3D cross correlation spectroscopy. This will be discussed for the sample with 25 wt% modified fumed silica. At the original concentration no determination of particle size was possible, due to a strong deviation of the correlation function from the theoretical form. This indicates that the particles are interacting with each other and that no independent diffusion of the particles is possible. This diffusion is the requirement for a correct measurement and the particle interaction is most likely due to the high particle concentration. The samples were, therefore, diluted with either cyclohexene oxide or ethyl acetate. From concentrations of about 4 wt% correct measurements were possible and resulted in mean particle diameters in the range of 180 nm and a distribution width of 60 nm. With further dilution of the samples a slight decrease in the mean particle diameter as well as the width of the distribution is observed. This might be an indication for the decomposition of agglomerates. Nevertheless the results show that not single particles, but small aggregates and agglomerates are present in both solvents.

The cationic polymerisation of cyclohexene oxide was carried out with the iodonium salt (tolylcumyl) iodonium tetrakis(pentafluorophenyl)borate as the initiator. Iodonium salts are usually used as photoinitiators for the cationic polymerisation of epoxides. To obtain a significant polymerisation rate at the polymerisation temperature of 85 °C a redox activation with ascorbic acid-6-hexadecanate was required [15]. The polymerisation of the cyclohexene oxide without nanoparticles leads to a brittle polymer which is completely soluble in solvents like tetrahydrofuran or ethyl acetate. The prepared polymers were examined by IR spectroscopy with photoacoustic detection. The C–H stretching band of the respective bonds next to the epoxide ring (2998 cm^{-1}) and the vibrations for the epoxide ring (750, 790 and 1260 $\mathrm{cm}-^{2}$) were below the detection limit in any spectrum of the polymers. As the band at 2998 cm^{-1} is not superimposed by other signals evaluation was mainly carried out with that band. If the polymerisation is carried out in the presence of nanoparticles covered with epoxy groups and the same polymerisation conditions (temperature, time) were used, the amount of residual epoxy groups was below the detection limit for all samples. As the amount of epoxy groups fixed on the particle surface is clearly above the detection limit for the samples with higher filler content (30–50 wt%), one can conclude that the epoxy groups fixed at the particle surface react at least partially under the chosen conditions. This should lead to a cross-linked polymer, which is confirmed by the partial insolubility of the polymers containing the modified particles. This behaviour indicates that the epoxy groups fixed at the particle surface have a similar reactivity as the epoxy groups of the cyclohexene oxide.

The DSC evaluation of the samples shows that partially crystalline polymers are formed but the melting peak is asymmetrical. Occasionally in the second heating run not the asymmetric melting peak is present in the DSC diagram but a glass transition is observed at very similar temperatures. This shows that the poly(cyclohexene oxide) has a melting point as well as a glass transition around 55 °C. The melting enthalpy is in the range of 8 J/g for the pure polymer and 4 J/g for the nanocomposites. The reduction in melting enthalpy is only partially caused by the reduced amount of polymer. The lower melting enthalpy indicates that the reactive nanoparticles present in the nanocomposites interfere with crystallisation. The multiple measurement of some samples shows that the melting enthalpy deviates by about 30%. This is most likely caused by the similarity of the glass transition and melting temperature. Therefore, a proper quantification is not possible and a dependence of the degree of crystallisation on the amount of particles could not be verified.

Ethyl acetate is a good solvent for pure poly(cyclohexene oxide). Therefore, ethyl acetate was selected as solvent for the Soxhlet extraction to determine the gel content of the nanocomposites prepared by the copolymerisation of the multifunctional particles and cyclohexene oxide. The dependence of the gel content on the amount of functionalised fumed silica is shown in Fig. 2. At particle contents up to about 40 wt% a more or less linear increase of the gel content is observed, which is about twice that of the particle content. At higher particle amounts the gel content becomes

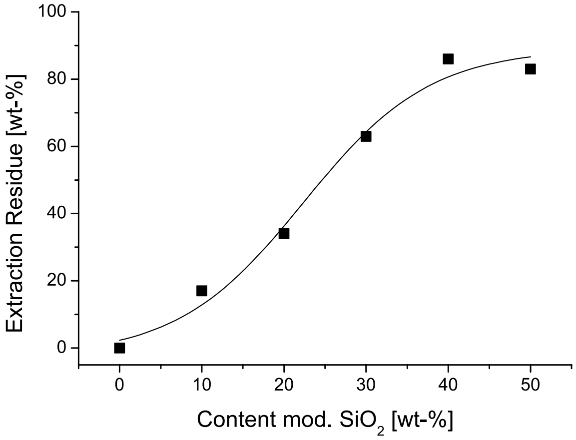


Fig. 2. Extraction residue of samples prepared by the copolymerisation of cyclohexene oxide with different amounts of fumed silica with a primary particle size of 12 nm and surface treatment with ECHTMO after Soxhlet extraction with ethyl acetate for 24 h.

saturated at about 80%. Although the number of reactive groups fixed at the particles is very high, the gel content is surprisingly low. Numerous experiments were carried out to examine the formation of the cross-linked part of the polymer in more detail. This is shown for the sample with 25 wt% modified silica as an example. First the extract was examined to show that the gel content values are not underestimated due to the transfer of a part of the particles into the extract. This can be expected if one assumes that the particles are still in the nanometre range. No particles could be detected by light scattering of the solution showing that the insoluble part of the polymer is completely retained in the solid residue of the extraction. This result is supported by the infrared spectrum of the dried extract, which is characteristic for poly(cyclohexene oxide) and no additional signals are present, especially not in the range of 1200 cm^{-1} where silicon dioxide shows an intense signal. On the other hand the spectrum of the residue shows in addition to the signals of the poly(cyclohexene oxide) a strong Si–O vibration. The DSC diagram of the residue shows a reduced melting enthalpy (2 J/g instead of 4 J/g for the not extracted nanocomposite) and a higher temperature (82 °C instead of 55 °C) for the combined melting point/glass transition. The reduced melting enthalpy is mainly caused by the reduced amount of polymer. The higher transition temperature is in agreement with a lower chain segment mobility of the polymer and is an indication for the proposed cross-linking. The SEM examination of the residue shows that it consists of particles. In the case of the sample with 25 wt% modified fumed silica the diameter of the particles is about 30 nm (Fig. 3) which is about 2.5 times that of the size of the primary particles of the fumed silica. This diameter shows that the polymer shell has a thickness of about 9 nm. The image of the particles shows that only a few individual particles can be observed and that the majority of the particles are connected to each other. In an attempt to destroy the agglomerates at least partially by ultrasonication a small amount of residue ($\leq 1\%$) in ethyl acetate and tetrahydrofuran was used. Although both solvents are good solvents for the polymer, a quick sedimentation of the particles takes place, indicating that micro- but not nanoparticles are present in the dispersion. The qualitative observation was supported by light scattering: no particles could be observed in the liquid phase. Furthermore the SEM images of these particles show no changes when compared to the not ultrasonicated material. TEM examination of the samples was possible at the edges of the agglomerates. Fig. 4 shows that the particles consist of a dark core which is silicon dioxide and a brighter shell which is the polymer.

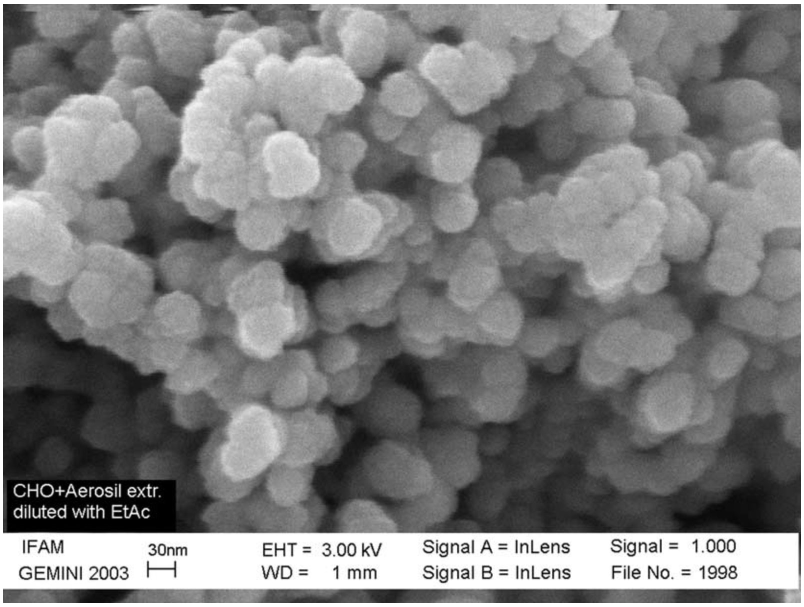


Fig. 3. SEM image of the extraction residue of the copolymer of cyclohexene oxide and 25 wt% surface treated fumed silica.

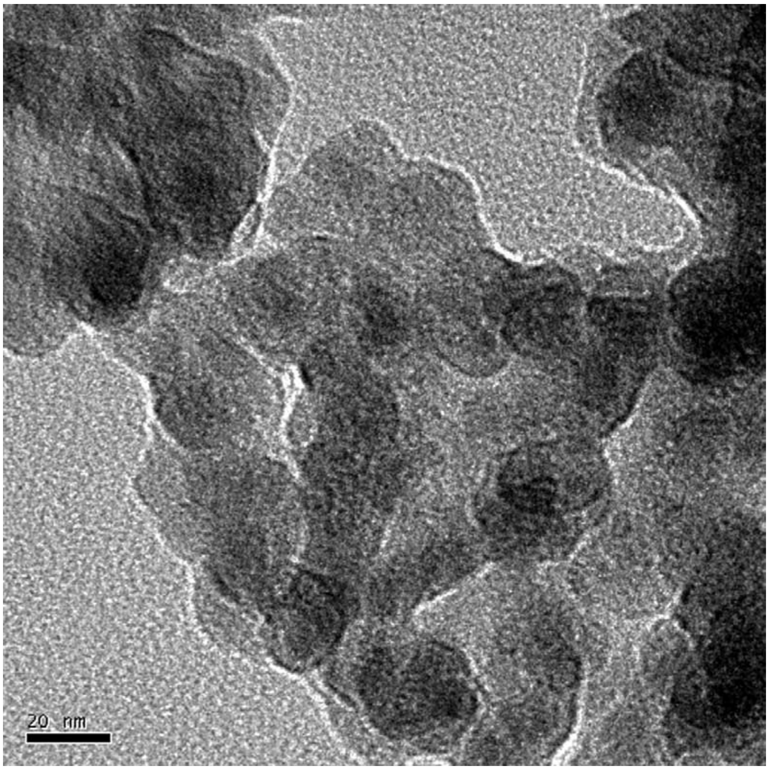


Fig. 4. TEM image of the extraction residue of the copolymer of cyclohexene oxide and 25 wt% surface treated fumed silica.

The image indicates that the particles of the fumed silica are mainly separated and covered by the polymer.

The poly(cyclohexene oxide) containing no particles and the soluble part of the polymer prepared in the presence of 40 wt% of the modified silica were analysed by MALDI-TOF mass spectrometry. In order to detect an influence of the modified silica on the formation of the soluble part of the polymer, a sample with a high content of silica was selected for these examinations. Dithranol was used as the MALDI matrix to which silver trifluoroacetate was added and masses were detected between 350 and 2500 Dalton. No difference between the two samples could be detected; especially no molecules containing silicon were present which would indicate that a part of the silane from the particle surface is present in the soluble part of the polymer formed by the copolymerisation of the modified particles with the cyclohexene oxide. The main peaks represent oligomers of the formula $H–(O–C_6H_{10})_n–OH$ and the base peaks are 410 and 508 g/mol corresponding to $n=4$ and $n=5$. The intensity of the signal decreases with increasing n and the corresponding masses could be detected over the whole detection range. The presence of hydroxyl groups at both ends of the polymer chain shows that the chain growth was terminated by the reaction with water traces. In earlier publications it could be shown that the cationic polymerisation of cycloaliphatic epoxy resins is mainly driven by chain transfer reactions initiated by water traces present in the epoxy resin [12]. For each of the oligomer chains a signal with a mass of 18 Dalton was detected, which shows that rings are present. It is unlikely that these rings are formed by a condensation reaction due to a split off of water. Most likely the chain growth was terminated by the reaction of the positively charged chain end with the other chain end carrying the hydroxyl group formed by the initiation. This is similar to the reaction shown in Scheme 2 for the formation of a ring at the surface of a particle. Since the sensitivity of the method for the different polymers is not known, it cannot be concluded if cyclic or linear oligomers are the main components of the materials.

The results lead to the following model for the copolymerisation of modified silica particles and cyclohexene oxide:

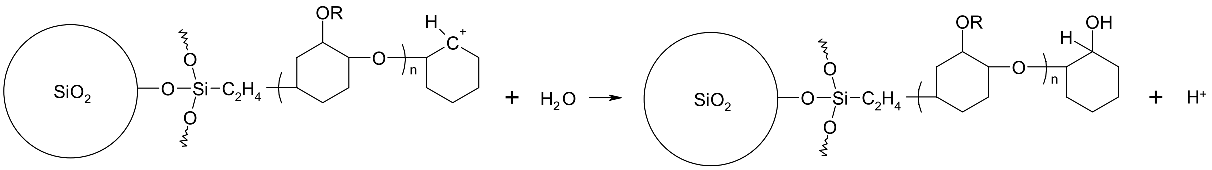
- A copolymerisation takes place and the reactivity of the ‘bound’ epoxide groups seems to be similar to that of the ‘free’ ones.
- The formed particles have a core-shell-structure and are covalently connected to each other by polymer bridges.
- The silica particles interact with each other in the monomer and are, therefore, close enough to be connected by the polymer. At the same time soluble polymer is formed in the ‘monomer rich domains’ of the reactive mixture. The formation of this polymer is not influenced by the presence of the nanoparticles. Due to the very low molecular weight of the soluble part of the polymer of up to only some thousand grams per mole, the growing polymer chains do not reach a particle and are,

therefore, not fixed in the polymer network. This could be the reason for the surprisingly low gel content.

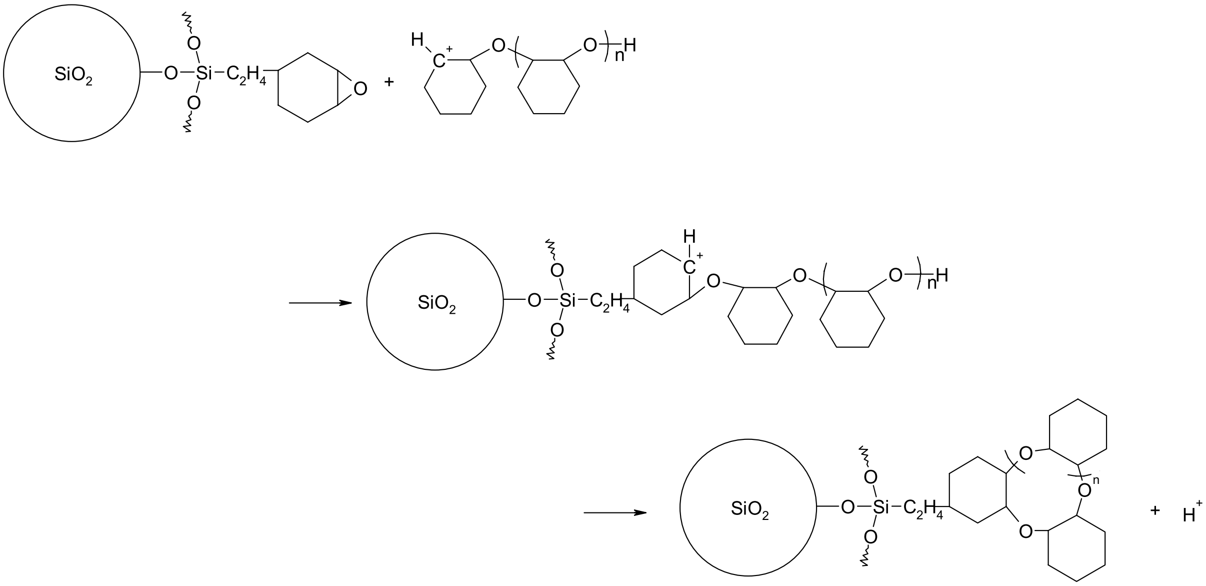
- The fixation of the polymer on the particles, is most likely strongly influenced by chain transfer reactions carried out with water traces present on the particle surfaces and by alcohols formed due to the reaction with water. Scheme 1 shows an example for the reaction of the growing polymer chain fixed on a particle surface with water. The formed proton can initiate the next chain by reacting either with the epoxide group of a monomer or one fixed at the particle surface. The formed alcohol can carry out a second chain transfer reaction, in which an ether bridge is formed (see Scheme 2 for an example). In earlier studies it was found that water accelerates the cationic polymerisation of cycloaliphatic epoxides and that the polymerisation rate is extremely low under absolute dry conditions [12]. One can, therefore, conclude that this is also the case in the present study.
- The epoxide groups fixed at the particle surface can react with a growing polymer chain, as is shown in Scheme 2. The chain can grow further and possibly react with the epoxide group bound to another particle. This results in a bridge being formed between particles. But due to the initiation of the chain by the acid all chains are cycles or are terminated with hydroxyl groups which are also able to carry out chain transfer reactions. Scheme 2 illustrates the intramolecular case forming a ring as an example. But the group can also react with the positively charged chain end fixed on the same or another particle. All three reactions lead to a cross-linked polymer surrounding the particles, like the isolated extraction residue. Furthermore a reaction with a free polymer chain is possible, in which the chain is simply extended.

3.3. Polymerisation and properties of nanocomposites based on a diepoxide

The previously examined poly(cyclohexenoxide) is not of practical interest, but the described examinations can be used as a model for the work with the diepoxide described in the following. Due to the high cross-linking density examinations of the interaction between particles and polymer are difficult if not impossible without the knowledge gained with the monoepoxide used as model. To examine the influence of modified silica particles on the properties of a polymer which is already cross-linked in the absence of reactive particles, experiments with the surface modified fumed silica with a primary particle size of 12 nm were also carried out. The cycloaliphatic diepoxide 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate was used as the resin and a thermally induced cationic polymerisation was carried out. In this case (tolylcumyl) iodonium tetrakis(pentafluorophenyl)borate was used as the initiator. A redox activation of the initiator with ascorbic acid-6-hexadecanate was carried out to ensure a polymerisation below 100 °C. In contrast to the monoepoxide cyclohexene oxide postcuring at 130 °C was necessary to ensure a complete polymerisation of the samples. This is due to the high cross-linking density of the polymer based on the diepoxide and, therefore, restricted molecular mobility. Samples without filler and with 5, 10, 15, 25, 35 and 50 wt% of the organically modified fumed silica were prepared. To verify a mostly complete polymerisation of the samples, they were controlled by photoacoustic infrared spectroscopy (absence of the epoxide bands) and dynamic DSC (absence of exothermic peaks). The respective signals were below the detection limit for both methods. The TEM examination of the samples (Fig. 5 for 25 wt%) shows that the large agglomerates typical for fumed silica are decomposed to a large extent resulting in small aggregates and occasionally even single particles. This shows that due to the similarity between the monomer and the surface composition of the particles the affinity between the resin and the particle surface is at least as large as the affinity between the particles. The thermo-mechanical properties of the polymers were examined by torsion pendulum measurements. The glass transition temperature (maximum of tan δ) decreases linearly with increasing amount of modified filler (Fig. 6). This indicates a lower cross-linking density. Changes of the peak form of tan δ are discussed later. On the other hand the storage modulus at 25 °C (below T_G) and 200 °C (above T_G) of the samples increases exponentially with increasing amount of filler (Fig. 7). The increase is characteristic for the reinforcement of a polymer by fillers, but the effect is surprisingly low especially at lower contents and might be connected with the decreasing glass transition temperature. But at higher particle concentrations they interact with each other leading to a higher reinforcement similar to microparticles. Next the polymerisation enthalpy was examined by DSC. The onset temperature, the temperature for the peak maximum and the peak form are the same for all samples, but the polymerisation enthalpy decreases linearly with increasing amount of modified filler. For the reaction enthalpy of the pure resin 538 J/g was measured and for the composite with 50 wt% modified filler 259 J/g. If one considers that the filler consists of only



Scheme 1. Termination of the growing chain by reaction with water. The circle illustrates the silicon dioxide particle.



Scheme 2. Reaction of the growing polymer chain with the reactive particle and intramolecular chain transfer reaction with the hydroxyl functionalised chain end.

64 wt% inorganic and 36 wt% organic material with a similar epoxide equivalent than the resin, the measured enthalpy is much too low. This can either indicate that the epoxide groups on the surface are not reactive, which would be in strong contrast to the results found for the copolymerisation of the particles with cyclohexene oxide, or that the reaction is incomplete for example by a sterical hindrance, which can be disproved by the absence of epoxy bands in the IR spectra and an exothermic peak in DSC diagrams of the samples. The third possibility is that all epoxide groups react, but in the presence of the particles a second reaction with lower reaction enthalpy takes place. It could be shown earlier [19] that the epoxide consumption by a chain transfer reaction with proton donors (water, alcohol) is less exothermic than the cationic polymerisation of the pure epoxide. The IR spectrum of the modified fumed silica shows that the material still contains a distinct amount of water or alcohol (Fig. 1, broad band at 3400 cm^{-1}). If alcohol contributes to the broad hydroxyl band in the IR-spectrum then it might result from the hydrolysis of a small

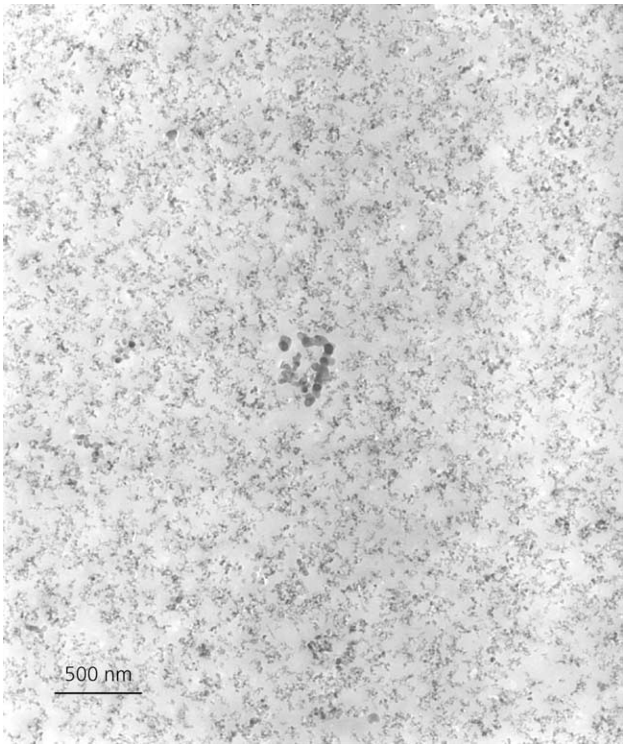


Fig. 5. TEM image of the cycloaliphatic epoxy resin with 25 wt% of fumed silica with a primary particle size of 12 nm and surface treatment with ECHTMO.

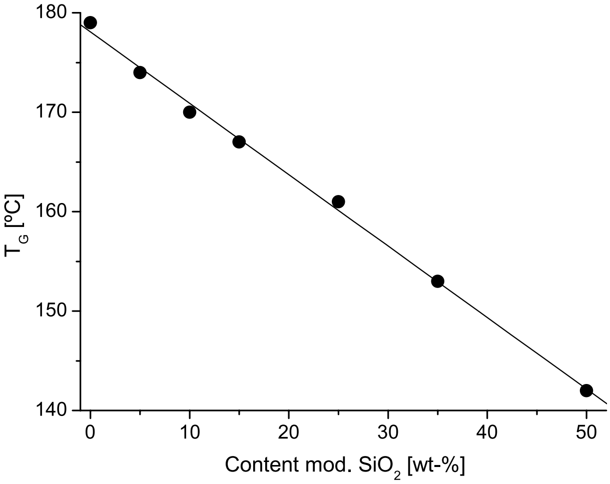


Fig. 6. Glass transition temperature of the diepoxide copolymerised with different amounts of modified fumed silica.

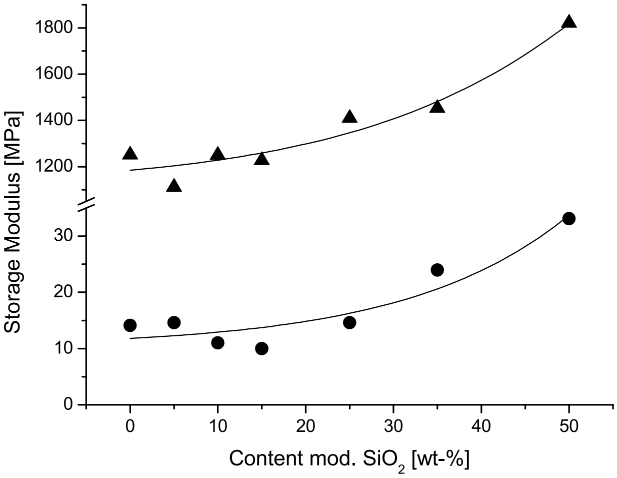


Fig. 7. Storage modulus at 25 °C (▲) and 200 °C (●) of samples received after polymerisation of the cycloaliphatic diepoxide with different amounts of modified fumed silica.

amount of the epoxide groups or the alcohol are residual methanol traces from the modification reaction with trimethoxysilane. If the water or alcohol leads to chain transfer reactions, the reaction enthalpy and glass transition temperature should decrease, as was observed. Furthermore the surprisingly low increase of the storage modulus can be explained by softening of the polymer due to the chain transfer reactions with the proton donors present on the particle surfaces. Due to the higher affinity of water to the oxidic surface compared to the organic resin, one can assume that the water is preferably located on the surface of the particles. This leads to a non homogeneous polymerisation, close to the surface of the particles the epoxide is preferably consumed by a chain transfer reaction leading to a softer polymer but in a distinct distance from the particle surface the epoxide is mainly consumed by the chain growth of the cationic polymerisation giving a highly rigid polymer. This means that a gradient structure of the material is assumed. The particles are surrounded by a soft polymer shell and the strength of the polymer increases with increasing distance from the surface. For the core-shell-particles formed by the copolymerisation of the same particles with a monoepoxide of identical base structure, a shell thickness in the range of 9 nm was observed (Section 3.2). At this distance the influence of the particle surface on the polymerisation seems to be negligible. Otherwise a thicker shell should be formed by the copolymerisation between the particle surface and the monoepoxide. Therefore, one can conclude that the cross-linked diepoxide has the bulk properties at distances from the surface of about 9 nm and higher. The formation of a heterogeneous polymer network is confirmed by the torsion pendulum measurements. Not only is a decreasing glass transition temperature (maximum of tan δ) with increasing filler content observed, but the temperature range in which the glass transition temperature takes place becomes broader and the peak of tan δ is not as pronounced. The dependence of tan δ on the temperature of the samples without modified silica, with 25 wt% and 50 wt% modified silica is shown in Fig. 8. In context of the discussion of the formation of a heterogeneous polymer structure due to a chain transfer reaction localised close to the particle surfaces, it must be mentioned that the ascorbic acid hexadecanate used as redox catalyst for the acceleration of the reaction is also able to carry out chain transfer reactions during the cationic polymerisation of an epoxide. The same is true for traces of moisture always present in resins. But in both cases the possibility of a reaction does not depend on the filler content and there is no reason why these reactions should lead to a heterogenity of the polymer network.

To examine the formed network in more detail the swelling behaviour of the nanocomposites with different solvents were examined. First butanone was used as a solvent, but even after storage of the samples for 768 h in the solvent, the weight increase of all samples was less than 1%. Therefore, chloroform was used in the following experiments and a noticeable swelling of all samples was observed for this solvent. The results are presented for a swelling time of 72 h in Fig. 9, which shows that the degree of swelling decreases with increasing amount of filler. This leads to the idea that swelling of the composites is mainly determined by the polymer content of the nanocomposites. But the second curve in Fig. 9 illustrates the weight increase of the samples by swelling normalised to the polymer content of the samples. This shows clearly that the normalised swelling goes through a minimum for samples with filler contents in the range of 20 wt%. This corresponds quite well with the stability of the samples in the solvent. During swelling all samples disintegrate into small pieces after a distinct time. For the samples without and with only 5 wt% filler this was already the case at the first control after 72 h. The samples with 10 and 50 wt% filler were destroyed

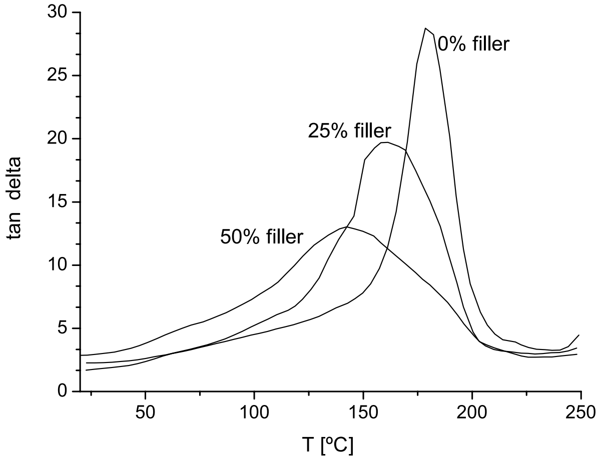


Fig. 8. Dependence of tan δ on the temperature of the samples containing 0 wt%, 25 wt% and 50 wt% of the modified silica.

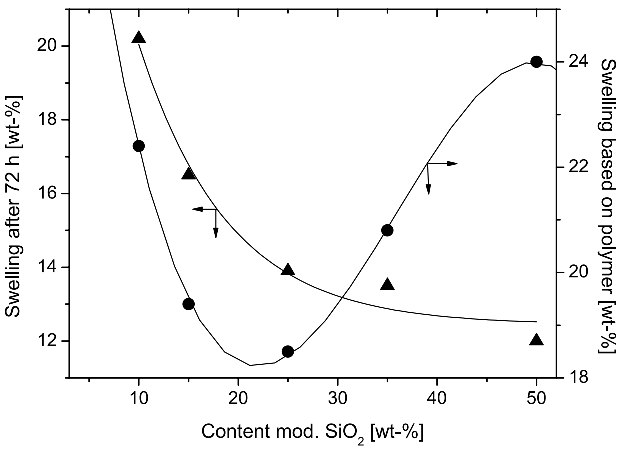


Fig. 9. Dependence of the degree of swelling (72 h in chloroform) of the nanocomposites on the filler content based on the composite (▲) and normalised to the polymer content of the composite (●).

after 144 h and the sample with 35 wt% filler after 196 h. The samples with 15 and 25 wt% filler were the most stable ones and destruction was observed after 220 h. This behaviour indicates that all samples are destroyed as soon as the polymer is swollen with a distinct amount of solvent and that the function of the filler is a reduction of the swelling rate but the final degree of swelling is not influenced. On the other hand it was found that the glass transition temperature decreases with increasing amount of filler and it was proposed from the reaction mechanisms that the polymer surrounding the particles is softer and less cross-linked. Both effects should lead to an increase in the diffusion rate which was only observed for high filler contents if the solvent uptake is normalised to the polymer content. At lower filler contents the opposite is true; the normalised swelling rate decreases with increasing filler content. This leads to the conclusion that the presence of fillers decrease stresses in the sample which typically form crazes in the presence of solvents. The reduction of stresses might either be caused by the reduction of the curing shrinkage or the presence of the soft shell around the silica particles discussed earlier. Most likely both points apply. Therefore, the minimum of the normalised swelling rate in Fig. 9 is explained by an increase of the swelling rate due to softening of the polymer with increasing amount of filler on the one side and a decrease of the swelling rate by a reduction of stresses on the other side.

4. Conclusions

It could be shown that a copolymerisation between silica nanoparticles covered with epoxide groups and cycloaliphatic epoxides takes place but the formed materials are heterogeneous. Due to the nanometric size of the cross-linking centres the copolymerisation is not statistically in the common sense. Although the distance between the cross-linking centres can be bridged, a high amount of monomer molecules are not close enough to the cross-linking centres to be fixed within the polymer network. In the case of the monoepoxide cyclohexene oxide core shell particles are formed with a silica core and an insoluble shell of poly(cyclohexene oxide). These particles are embedded in a matrix of soluble poly(cyclohexene oxide). The dispersion of the core-shell-particles in organic solvents is not possible. One can, therefore, conclude that the particles are connected to each other by polymer bridges. This means that a polymer network is formed in which the particles are embedded as cross-linking centres. If the distance between the growing polymer chain and the particles is too large, a reaction is not possible, because the molecular weight of the soluble polymer is only up to some thousand grams per mole. Most likely the polymerisation close to the particles is accelerated by water fixed at the particle surface, because it is known from the cationic polymerisation of cycloaliphatic epoxides that the polymerisation rate increases with increasing humidity. However, on the other hand it is known that the chain transfer reactions by water lead to a lower network density and a softer polymer. This is the reason why it is proposed that the silica particles in the highly cross-linked polymer based on the diepoxide are surrounded by a polymer which is softer than the bulk polymer. Apart from the presence of the nanoparticles this is a second heterogeneity in the polymer and is not only proposed by the reaction mechanism of the polymerisation, but also on some experimental indications. These are the decreasing glass transition temperature together with an increase of the temperature range in which the glass transition takes place as well as the surprisingly low increase of the storage modulus with increasing filler content. But also the solvent uptake and the stability of the polymers in the solvent give indications on a heterogeneous structure. If the solvent uptake is normalised to the polymer content of the samples, it goes through a minimum for filler contents in the range of 20 wt% and the samples with such amounts of filler are stable in the solvent for the longest time. The minimum is explained by a reduction of the permeability due to fewer stresses with increasing amount of filler on the one side but a softening of the polymer on the other side.

Acknowledgements

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