Influence of the Filler Material on the Thermal Stability of One-Component Moisture-Curing Polyurethane Adhesives

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ABSTRACT: Filler materials are part and parcel for the adjustment of adhesives, in particular, their rheological and mechanical properties. Furthermore, the thermal stability of adhesives can be positively influenced by the addition of an expedient filler, with inorganic types common practice in most cases. In this study, one-component moisture-curing polyurethane adhesives for engineered wood products based on isocyanate prepolymers with different polymer-filled polyether polyols were investigated with regard to the filler's potential to increase the thermal stability of bonded wood joints. The property changes due to the addition of fillers were determined by means of mechanical tests on bonded wood joints and on pure adhesive films at different temperatures up to 200°C. Additional analyses by atomic force and environmental scanning electron microscopy advanced the understanding of the effects of the filler. The tested organic fillers, styrene acrylonitrile, a polyurea dispersion, and polyamide, caused increases in the cohesive strength and stiffness over the whole temperature range. However, the selected filler type was hardly important with regard to the tensile shear strength of the bonded wood joints at high temperatures, although the tensile strength and Young's modulus of the adhesive films differed over a wide range. Prepolymers with a lower initial strength and stiffness resulted in worse cohesion, in particular, at high temperatures. This disadvantage, however, could be compensated by means of the filler material. Ultimately, the addition of filler material resulted in optimized adhesive properties only in a well-balanced combination with the prepolymer used. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3641–3649, 2012

Key words: adhesion; adhesives; fillers; mechanical properties; polyurethanes

INTRODUCTION

Adhesives in modern timber engineering must comply with a set of requirements to ensure accurate and safe processing as well as durable and hard-wearing use of the fabricated wood-construction elements. Given the wide range of requirements, one-component moisture-curing polyurethane (1C PUR) adhesives exhibit certain advantages because their properties can largely be controlled by a variation of the type and molar ratio of their components. The decisive parameters (in particular for thermal stability) are the free isocyanate (NCO) content and the crosslink density of the prepolymer.[1–6] The physical and chemical properties of the adhesives can be further adjusted by additives that are added subsequent to or during prepolymer synthesis.[7] In addition to defoamers, plasticizers, organic solvents, wetting agents, dispersants, rheological agents, and catalysts, filler materials are also commonly used.

Filler materials are generally used for different purposes, with the substitution of a more expensive polymer being only one among many reasons. Furthermore, fillers can improve the mechanical properties, processability, thermal and dimensional stability, and fire retardancy of polymers.[8] A multitude of different filler materials has been used to increase the mechanical properties and thermal stability of adhesives for timber engineering. Inorganic filler materials, such as calcite,[9] silica,[9–11] kaolin,[9] calcium carbonate,[10,12,13] chalk,[14] carbon black,[11,15] nanoclays,[9,11,16] aluminum oxide,[11] and zirconium(III) oxide[11] have, therefore, been investigated in combination with different types of adhesives, such as urea–formaldehyde and phenol–formaldehyde,[17] poly(vinyl acetate),[9,13] 1C PUR,[14] solvent-borne PUR,[10] polyurethane dispersions,[12] thermosetting PUR,[16] and epoxy,[11,15] but organic filler types, such as PUR powder[17] and polyurea dispersions (PHDs),[18] are also described in the literature.

The thermomechanical properties can be modified by reinforcement of the polymer matrix with

expedient fillers. The higher stiffness and strength of the filler are, therefore, used to improve the overall properties of the composite. The improvement of the thermal stability depends on the type, shape, size, and amount of the filler material used. The uniformity of the dispersion is of particular importance and is a disqualifying criterion for many types of fillers because the storage stability over several months must be guaranteed. Furthermore, the aspect ratio and the degree of interaction between the inorganic fillers and the polymer matrix are vitally important.[8,9] Most suitable are fillers of nanoscale dimensions that are uniformly dispersed and interact strongly with the organic matrix.[4]

This investigation was focused on organic filler materials with the potential to improve the thermal stability of 1C PUR adhesives for engineered wood products. Polymer-filled polyether polyols, therefore, came into consideration on the basis of their several advantages over inorganic fillers:

1. Because of the similar density of organic filler materials compared to NCO-terminated prepolymers, filled systems have a better storage stability, even at lower viscosities.
2. Finely dispersed organic particles can increase the interaction by secondary forces, mainly hydrogen bonds, between the filler and the urethane and urea groups of the polyurethane matrix.

The aim of this study was to investigate whether the advantages of organic fillers also have an effect on the thermal stability of 1C PUR adhesives. Different variants of filled prepolymers were, therefore, produced, formulated, and subsequently tested with regard to their cohesive strength by means of tensile tests on adhesive films and with regard to their bonding performance by means of tensile shear strength tests on bonded wood joints at elevated temperatures.

EXPERIMENTAL

Prepolymers and adhesives

The adhesives investigated in this study (Table I) were based on two different prepolymers produced by Bayer MaterialScience (Leverkusen, Germany). Mixtures of methylene diphenyl diisocyanate (MDI) isomers consisting mainly of 4,4′- and 2,4′-MDI and polymer MDI with a functionality greater than 2 were used. The NCO content amounted to 16% for prepolymer 1 (P1) and 14.3% for prepolymer 2 (P2). The estimated functionalities totaled 2.8 and 2.4 for P1 and P2, respectively.

TABLE I
Chemical and Physical Properties of the Prepolymers and Adhesives

ID-code	P1	P1SAN5	P1SAN7	P1PHD5	P1PHD7	P1PA5	P2	P2PHD5	P2PHD10
NCO content (%)	16.0	15.5	15.5	15.5	15.5	15.5	14.3	14.3	14.3
Functionality	2.8	2.8	2.8	2.8	2.8	2.8	2.4	2.4	2.4
Crosslink density (mol/kg)	1.09	1.09	1.09	1.09	1.09	1.09	0.55	0.55	0.55
Urethane group content (mol/kg)	0.60	0.60	0.60	0.60	0.60	0.60	0.26	0.26	0.26
Viscosity (20°C; mPa s)	17,000	20,300	31,400	23,450	31,800	24,500	23,900	59,000	67,200
Open time (min)	80.0	84.0	84.5	82.5	83.0	81.0	80.0	68.0	67.5
Filler material	—	SAN	SAN	PHD	PHD	PA	—	PHD	PHD
Filler material content (%)	—	5.0	7.5	5.0	7.5	5.0	—	5.0	10.0
Defoamer	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Pyrogenic silica	—	—	—	—	—	Yes	Yes	Yes	Yes
Amine catalyst	—	—	—	—	—	—	Yes	Yes	Yes

P, prepolymer; PHD, polyurea dispersion; SAN, styrene acrylonitrile; PA, polyamide.

Three types of filler material, styrene acrylonitrile (SAN), PHD, and polyamide (PA) powder, were investigated in this study.

PHD is the branch copolymer product of the poly-addition reaction of a polyisocyanate, a polyamine, and a polyether polyol.[19] When used as a filler material, polyurea particles are finely dispersed in the polyether polyol. The PHD polyols used contained 5% (P1PHD5) and 7.5% (P1PHD7) PHD in combination with P1 and 5% (P2PHD5) and 10% (P2PHD10) PHD solid content in combination with P2. The filler appears as an opaque white dispersion with a median particle diameter of less than 1 μm.[20]

SAN is a random amorphous copolymer of styrene and acrylonitrile monomers that has improved mechanical properties and better chemical resistance than polystyrene.[21] The used SAN contained about 40% acrylonitrile.

Noncrosslinking, free-flowing PA powder characteristically has good mechanical properties, even at elevated temperatures, and good chemical resistance. The used powder had a median particle size of 10 μm and a specific gravity of 1 g/cm^3.

In the case of SAN- and PHD-filled polyols, the fillers were produced and dispersed in a standard polyether by Bayer MaterialScience and, depending on the formulation, mixed with additional polyol components and subsequently reacted with NCO during the prepolymerization process. The appropriate products were provided by Bayer MaterialScience. In contrast to the previous fillers, PA powder was added during the subsequent formulation of the adhesive by Purbond (Sempach-Station, Switzerland). The powder was dispersed in the prepolymer, together with defoamers, rheology modifiers, and catalysts. These additives are commonly used to prepare standard commercial adhesives. An amine catalyst was used to set a similar open time between 60 and 90 min for all of the formulated adhesives.

Tensile tests on the adhesive films

The adhesive films were produced by application of the liquid adhesive on a plastic sheet; we ensured a constant application thickness with a special applicator. We minimized the typical foaming effect of polyurethanes by applying a film thickness of roughly 0.25 mm and performing the reaction under 50% relative humidity (RH). Once the reaction had progressed sufficiently, the films were removed from the sheet and stored for a minimum of 3 days under standard climatic conditions (20°C and 65% RH). The actual samples were punched with sample shape type 1B according to ISO 527-3.[22]

The tensile properties of the films were obtained according to ISO 527-1.[23] In addition to standard climatic conditions, tests also were performed at 70 and 200°C. The measurements were carried out with a Zwick Z100 universal testing machine with a 500-N load cell with a testing speed of 2 mm/min until failure. Tensile and transverse deformation was recorded optically with a Messphysik (Fürstenfeld, Austria) videoextensometer ME-46. Young's modulus, tensile strength, and strain at maximal load and Poisson's ratio were determined from the load-displacement curves. The mean values were calculated for a series of at least six specimens.

Dynamic mechanical analysis (DMA)

The films for the DMA specimens were prepared as described previously. Samples 20 mm in length and 4 mm in width were cut from them and evaluated in a Seiko (Chiba, Japan) DMS 210 apparatus in the tensile mode over a temperature range of −140 to 250°C at a frequency of 1 Hz and at a ramp rate of 2°C/min. The underlying standard for this test was ISO 6721-4.[24]

Differential scanning calorimetry (DSC)

The thermal properties of the polyurethane prepolymer films were analyzed with a PerkinElmer (Waltham, MA) DSC-7 differential scanning calorimeter. Approximately 10 mg of polyurethane film was placed in a standardized pan with caps at a heating rate of 20°C/min. Two consecutive runs were carried out, with heating from −100 to 100°C followed by cooling down to −100°C (cooling rate = 320°C/min) and nitrogen flushing before the second heating run from −100 to 100°C. The glass-transition temperatures (T_g's) were determined at half height of the glass step.

Viscometry

The viscosity of the prepolymers was determined at 23°C with an Anton Paar (Graz, Austria) MCR 301 cone/plate rheometer (d (cone diameter) = 25 mm, α (cone angle) = 1°) at a shear rate of 150 s^{-1} according to DIN 53019.[25]

Tensile shear testing on the bonded wood joints

The longitudinal tensile shear strength of bonded wood joints was tested according to EN 302-1.[26] The specimens were prepared from beech (*Fagus sylvatica* L.), which is characterized by a low content of extractives (to avoid chemical interactions with the adhesives) and a high strength compared to spruce, which is commonly used in timber engineering in Europe. The raw density of the adherend was 745 ± 50 kg/m^3 at an equilibrium moisture content of about 12 ± 1%. The adhesives were applied to one side by means of a toothed spatula with a spread of 200 g/m^2. The pressing time was at least 3 h at a pressure of about 0.8 MPa.

TABLE II
Results of the Tensile Tests of the Films and Bonded Wood Joints

	Temperature (°C)	P1	P1SAN5	P1SAN7	P1PHD5	P1PHD7	P1PA5	P2	P2PHD5	P2PHD10
τ (MPa)	20	11.06	10.63	9.18	10.23	11.19	13.15	10.87	13.21	13.23
	70	11.28	10.70	11.43	10.46	13.23	13.25	9.79	11.61	12.86
	200	8.41	9.88	10.90	9.71	10.39	10.62	6.96	8.95	10.76
WFP (%)	20	0	0	0	0	20	30	0	20	20
	70	10	0	0	0	50	40	0	0	10
	200	0	0	60	0	100	90	0	0	40
σ (MPa)	20	26.5	37.6	35.5	39.3	39.5	35.1	14.0	16.1	25.0
	70	37.1	47.5	48.1	47.3	49.2	38.1	16.0	19.2	25.4
	200	29.0	37.8	38.9	38.4	41.0	30.3	13.8	17.9	21.0
E (MPa)	20	1360	1965	1899	2016	2019	1716	449	616	945
	70	1199	1646	1867	1763	1823	1251	356	503	798
	200	478	1105	1009	985	1051	464	182	244	387

τ, tensile shear strength; WFP, wood failure percentage; σ, tensile strength; E, Young's modulus; T, temperature; P, prepolymer; PHD, polyurea dispersion; SAN, styrene acrylonitrile; PA, polyamide.

The shear tests were likewise performed at 20, 70, and 200°C. The specimens were randomized to ensure that the wood and processing effects did not introduce bias in the estimation of the tensile shear strength at different temperatures. Sample groups of 15 specimens were tempered at the same time in a drying chamber for 1 h before testing.

The test was displacement-controlled with a universal testing machine (Zwick/Roell (Ulm, Germany) Z010). The strain was measured by means of a clip-on displacement transducer. After failure of the specimen, the wood failure percentage (WFP) was estimated visually in steps of 10%.

Microscopic analysis

For a qualitative analysis of the bond line and interphase region, micrographs were taken with a dual-beam scanning electron microscope (FEI (Hillsboro, OR) Quanta 200 3D) in low-vacuum mode. Atomic force microscopy (AFM) imaging was performed in tapping mode Digital Instruments (Tonawanda, NY) D3000 to provide phase-contrast images of the polymer structure.

RESULTS AND DISCUSSION

The investigated film and bonding parameters (Table II) of the cured polyurethane prepolymers and modified adhesives were affected differently by the temperature, prepolymer configuration, and type and the amount of filler material. Furthermore, factorial analysis detected significant interactions between these individual influencing factors. In the following text, the temperature-dependent material behavior of the prepolymers and the formulated adhesives based on them are discussed with consideration of the adhesive parameters varied. The influence of the temperature was clearly revealed by the

Young's modulus (E), which was affected to a much higher degree by the heat treatment than the tensile strength (σ) of the films or the tensile shear strength τ of the bonds. Ultimately, however, the result of the bonded wood assemblies is determining for the use of an adhesive for structural wood bonding.

Influence of the prepolymer configuration

The prepolymer configuration had a clear impact on the temperature-dependent material behavior of the pure adhesive films and the bonded wood joints. Because the material behavior was prescribed primarily by the prepolymer configuration,[6] all tested adhesives revealed linearly decreasing moduli in the observed temperature range. The comparison of the prepolymers revealed that σ and E of P1 at 20°C were about 50 and 30% higher, respectively, compared with the values of P2, with these percentages increasing with rising temperature. The use of branched polyfunctional components ensured a high density of covalent crosslinking with high thermal stability. The crosslinking of the hard segments was supported by hydrogen bonding of the NH groups and carbonyl groups of urea and urethane linkages. As already shown by Clauß et al.,[6] the higher hard-segment content and higher crosslink density were responsible for the stronger polymer network, which is why P1 was found to exhibit better thermal stability with rising temperatures. At higher temperatures, the polymer chain flexibility increased partly because of the disappearance of the secondary hydrogen bonds in the polymer structure. The higher flexibility caused a more ductile material behavior and, thus, a higher strain to failure at a somewhat lower maximal strength. This was confirmed by the stress–strain curves in Figure 1(a) compared with those in Figure 1(c), which show a more ductile behavior and a larger strain at break for P1 and an almost unchanged mechanical behavior for P2.
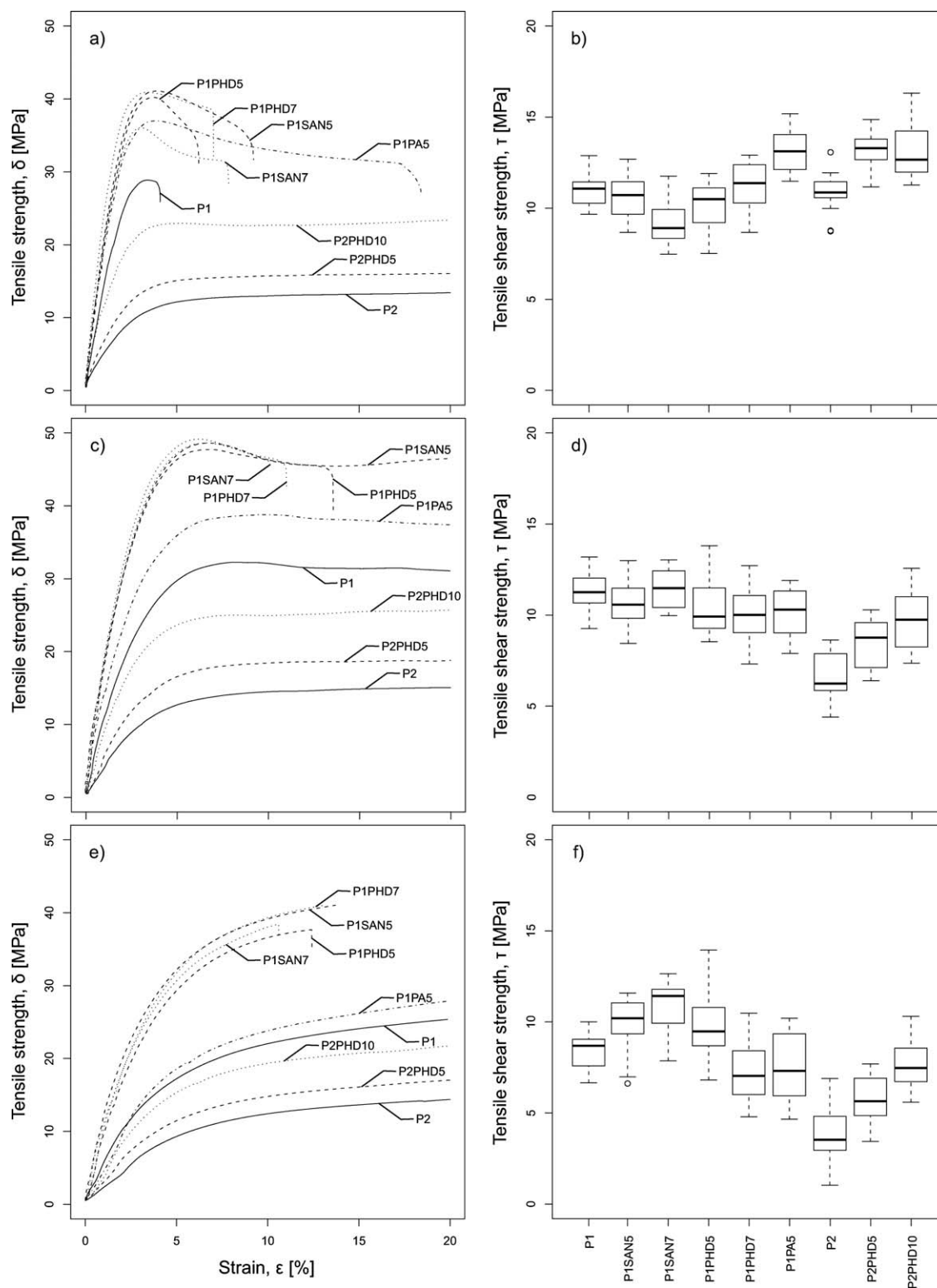
Figure 1 Results of mechanical tests: (a, c, e) stress-strain curves of films tested in tension and (b, d, f) tensile shear strength of bonded wood joints. Prepolymers and adhesives filled with PHD, SAN and PA tested at 20°C (a, b), 70°C (c, d) and 200°C (e, f).

The comparison of the complex moduli obtained by DMA measurements (Fig. 2) confirmed again significant differences in the temperature-dependent performance of the cured prepolymers. P2 exhibited a very distinct glass transition at about −62°C, which was related to the polyether component. Starting from this temperature, the storage modulus (E') of P2 decreased drastically from about $E' = 4750$ to 1130
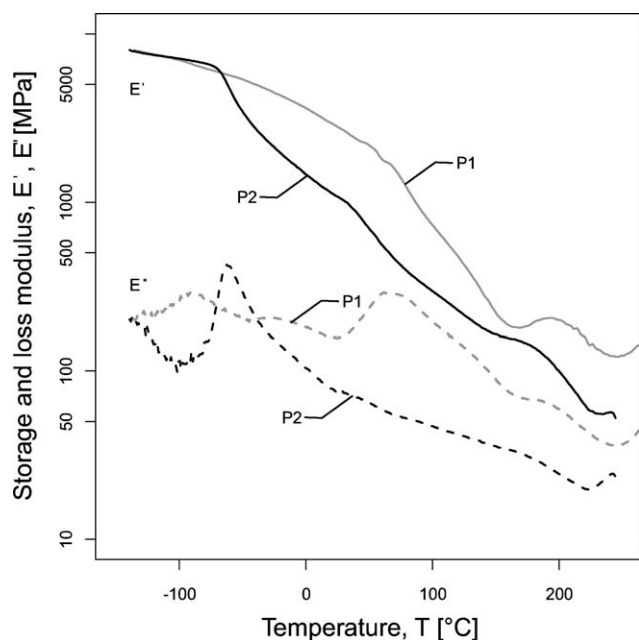
Figure 2 Results of DMA: storage and loss moduli of prepolymers with different hard segment content and cross-link density.

MPa at 20°C. The curve of P1, on the other hand, showed a slow and gradual decrease of E' with $E' =$ 1600 MPa at 20°C. Several small maxima in the loss modulus of sample P1, an indication for a very complicated polymer blend morphology, could be seen. At about 63°C, P1 exhibited a somewhat larger transition peak in the loss modulus, probably caused by the T_g of the hard segment. The curves of both prepolymers merged gradually at higher temperatures, up to about 150°C, where they were nearly equal to each other.

Although σ remained almost constant from 20 to 70°C, the ductility of the polymer films increased significantly. At much higher temperatures, σ decreased to the base level at 200°C [Fig. 1(a,c,e)].

The maximum in σ of sample P1 at 70°C was probably caused by the glass transition in that range. Measurements by DSC (not shown) revealed a caloric effect in the temperature range around 70°C, which confirmed the glass transition found in DMA. However, the second heating in DSC measurements did not show a glass-transition temperature, which might have been caused by a change in morphology during the first heating. It was not possible to give a definite explanation at the moment, but investigations into this issue are still in progress.

At 200°C, E decreased by about 60% compared with the values obtained at 20°C [Fig. 1(a,e)]. σ, by comparison, reached values in the range of the values obtained at 20°C. The stress–strain curves showed, for all adhesives, an elastic behavior without a yield point and maximal strains of more than 10%. The differentiability of the adhesives was similar to the results obtained at 20°C. The effect of the temperature, however, had to be interpreted cautiously because the testing itself was carried out at 20°C after heating. Although the samples were taken rapidly from the oven to the testing machine, the temperature decreased significantly because of the low sample mass.

In contrast to the results for the prepolymer films, the results for the bonded joints show no differentiation between the two prepolymers at room temperature [Fig. 1(b)]. Because WFP (Table II) was on a comparatively low level, we assumed that the prepolymers failed and not the adherend. The macroscopic assessment of the fracture surface indicated an adhesive failure of the bond. In the majority, the failure occurred because of an insufficient adhesion between the adhesive and substrate, which is clearly shown in Figure 3(c,d). The use of a UV light source revealed that the adhesive was located at one of the involved adherends. A cohesion failure was, therefore, out of the question.
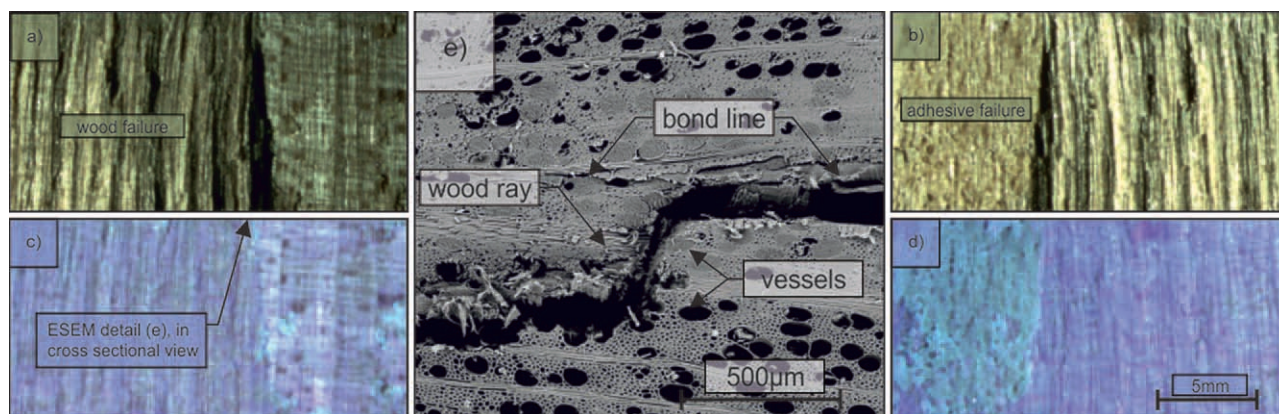

Figure 3 AFM phase images: (a) prepolymer without additives, (b) formulated prepolymer (incl. defoamer, rheology modifier and catalyst), (c) adhesive filled with PHD and (d) adhesive filled with SAN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
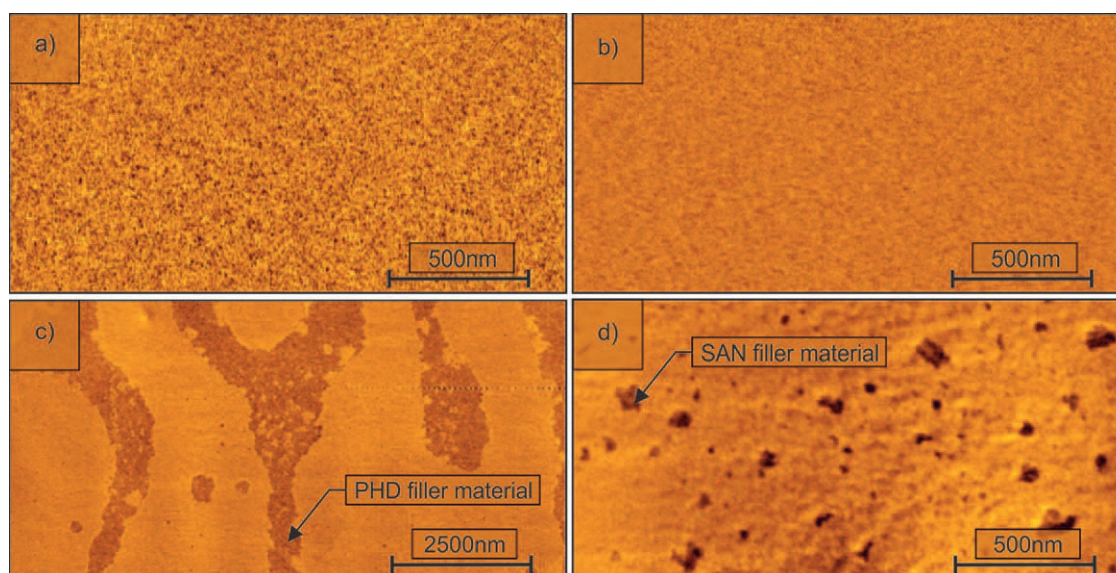
Figure 4 Light microscopy (LM) and environmental scanning electron microscope (ESEM) micrographs of a bonded wood joint after tensile shear test: (a-d) stereo light microscopic images of the fracture surface (top (a, c), bottom (b, d)) with visible light (a, b) and UV light source (c, d). (e) ESEM micrograph (mag 100×) of the cross section showing a change in crack propagation from adherend (wood failure) into bondline (adhesive failure). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

At 70°C, the same differentiation as for the film properties was found for the bondings, with P1 exhibiting a significantly higher τ than P2 [Fig. 1(d)]. The increase in the temperature to 200°C resulted in decreases in τ by about 30% for P1 and 55% for P2. Finally, the bonded joints also reflected the differences in the prepolymer composition, albeit not at 20°C.

Influence of the filler material type

Three types of filler materials were used with the intention of increasing the thermal stability of the prepolymers. A comparison of the adhesives with 5% filler content showed that SAN and PHD exhibited nearly the same results for the film and bonding properties. Both adhesives achieved significantly higher strengths and stiffnesses compared with the unfilled prepolymer at all of the tested temperatures. The tensile shear strength, however, was positively affected only at 200°C [Fig. 1(f)].

Compared with P1, P1PA5 also exhibited increased values for E and σ, but the values were much closer to those of the prepolymer compared to P1SAN5 or P1PHD5, in particular, at 70 and 200°C. The stress–strain curves of P1 and P1PA5 revealed a more elastic behavior at 70°C, whereas the adhesives filled with SAN and PHD exhibited a rather ductile behavior. The tensile shear strength and WFP, however, significantly increased for P1PA5 at all of the tested temperatures.

The results led us to the conclusion that an improvement of the cohesion did not necessarily cause an improvement in the bonding performance. The higher stiffness of the adhesives filled with PHD or SAN may have possibly been disadvantageous with respect to the bonding strength at room temperature. Because the reactivity and viscosity of the adhesives with 5% filler material ranged on the same level (Table I), the influence of these factors could virtually be neglected.

The AFM phase-contrast images (Fig. 4) showed that the fillers differentiated clearly from the prepolymer structure, which revealed no obvious difference between the pure prepolymer [Fig. 4(a)] and the formulated prepolymer without filler material [Fig. 4(b)]. The presence of a phase-segregated system became visible as bright, hard-segment-rich phases and dark, soft-segment-rich phases within the polymer structure. The filler materials, PHD [Fig. 4(c)] and SAN [Fig. 4(d)], differed significantly with respect to their size and dispersion. PHD exhibited larger and agglomerated structures, whereas SAN was homogeneously dispersed, with particle diameters up to 100 nm.

Considering the interaction between the prepolymer type and the filler material, it can be stated that the presence of PHD caused, in the case of P1, a significant increase in the film properties at all tested temperatures but, aside from 200°C, no significant difference in τ. The combination of P2 with the same filler, however, revealed moderate increases in E and σ but a large increase in τ of up to 30% at 200°C. Surprisingly, P1PHD5 also exhibited an increase in τ at this temperature of about 15% so that, in the end, this combination achieved the best

thermal stability of the bondings as a result of the higher initial strength of P1.

Influence of the filler material content

The effect of the filler material content on the film properties was completely different for the two prepolymers investigated. In case of P1, SAN and PHD resulted in almost similar values of E between 1.9 and 2.0 GPa and σ's between 37.6 and 39.5 MPa with both contents, with the only significant differences being in σ ($\sigma = 35.5$ MPa) in the case of P1SAN7. P2, in combination with PHD, however, revealed statistically significant increases in σ and E of about 25 and 35%, respectively. Because the difference between the two filler material contents was only 2.5% in the case of P1, it may be possible that an influence was not detected for this reason in view of the statistical spread.

In the case of P1, statistically significant effects of the filler material content on τ were shown at 20 and 70°C. In the case of P2, an increase in the filler material content from 5 to 10% PHD revealed significant effects at 70 and 200°C. Increasing the filler material led, in both cases, to an increase in τ of about 15%, and the higher filler material content was further accompanied by an increase in WFP. One reason for this behavior could be found in a delayed penetration and, consequently, a higher concentration of the adhesive in the bond line.[14] Another aspect could have been the fact that liquid prepolymer penetrated into the wood and resulted in a bond line with a higher filler content, which increased the modulus.

SAN showed no improvement of the bonding when the filler material content was increased from 5 to 7.5%. A significant difference between the different contents was found only at 20°C. Surprisingly, τ decreased in this case.

Influence of the substrate

Because WFP increased with increasing temperature, the drop in bonding strength was caused, on the one hand, by the decreasing polymer strength and, on the other hand, by the wooden adherend. The stereo light micrographs in Figure 3(a,b) show the two fracture surfaces of the same sample with about 60% wood failure. The crack followed the lowest resistance, which partly occurred within the substrate and partly between the substrate and adhesive [Fig. 3(e)]. Wood rays and areas with changing wood density strongly influenced the fracture behavior of the individual samples.

The resulting wood failure at higher temperatures was the consequence of greater substrate degradation compared with the adhesive. An increasing temperature at a constant or decreasing RH caused a decrease in the wood moisture content due to the hygroscopic behavior of the material. Besides drying stresses, additional internal stresses developed as a consequence of the fixation of the adherends by the adhesive. The drying process, furthermore, reduced the elasticity and tensile shear strength of the wood. A linear correlation between τ and the temperature of different wood species was shown in a previous study by Clauß et al.[6] The reasons for the strength reduction from about 65°C are depolymerization reactions within the wood structure that occur without significant weight loss. The chemical bonds of wood start breaking at temperatures higher than 100°C.[27] A pyrolysis of the wood components was not to be expected in the temperature range we investigated.

Consequently, we assumed that all filled adhesives based on P1 and P2 filled with 7.5 and 10% PHD, respectively, exhibited higher τ than the adherend. Values obtained for beech under similar conditions lay at about 8.42 MPa,[6] compared with values over 9.5 MPa obtained for the adhesives mentioned.

CONCLUSIONS

- Adhesives based on prepolymers with higher initial strengths and stiffnesses reveal better cohesion over the entire temperature range, which was why the filler material had a greater impact for more elastic polymers.
- The addition of the filler material caused an increase in the cohesive strength and stiffness over the entire temperature range. However, no substantial difference between PHD and SAN was found.
- PA powder revealed a lower strength and stiffness but better bonding performance at low temperatures compared with SAN or PHD.
- At high temperatures (200°C), the type of filler material was hardly important with respect to τ of the bonded wood joints, although σ and E of the adhesive films differed over a wide range.
- The filler materials ensured an adequate bond line between the adherends, although because of the porosity of the substrate, low-viscosity adhesive fractions tend to penetrate into it. If penetration occurred, the stiffness of the bond line was increased by the relative increase in filler material content; this could be considered as an advantage.
- Organic filler materials have, compared to, for example, chalk, the special advantage of a very similar specific density, which results in improved storage stability for even low-viscosity adhesives because segregation is virtually precluded.

• PHD fillers ensure very good cohesion to an adhesive matrix because of hydrogen bonding.

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