CURING BEHAVIOUR OF STRUCTURAL WOOD ADHESIVES – PARALLEL PLATE RHEOMETER RESULTS

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Abstract:
The curing speed of a wood adhesive directly determines the required clamping time. Therefore, the curing time has a considerable influence on the production time and consequently on the efficiency / productivity of wood gluing factories. Conventionally, the curing speed is laboriously determined via lap shear tests according to EN 302-6 and EN 15416-5 for phenolic and aminoplastic and one-component polyurethane (1K-PU) adhesives, respectively. Due to moisture exchange between adhesive systems and wood adherends, only plate rheometers that are equipped with wooden plates offer the possibility to monitor the visco-dynamic curing process of a wooden bond realistically.

This paper compares the results of rheological measurements that were performed during the curing of four different adhesive types with shear strength results. Epoxy and – with limitations – moisture curing 1K-PU adhesives corresponded well with the theoretical curing behaviour, with the occurrence of a gel point at the crossing of the loss modulus G'' and storage modulus G'. In contrast, Polycondensation and EPI adhesives displayed a completely different curing behaviour, most notably that G' was larger than G'' throughout the entire curing time.

The rheological curing data showed a good correlation with regard to the shear strengths for the Epoxy, 1K-PU and MUF adhesives but not for the EPI adhesive. The difference in behaviour of the EPI adhesive could potentially be a result of its special chemistry.

Key words: wood adhesive; rheology; curing time; spruce; MUF; 1K-PUR; EPI; Epoxy.

INTRODUCTION

The curing speed of an adhesive used in glulam production directly determines the clamping time of the glulam beams as well as the time the beams are required to stay in a heated environment after pressing. Both times have a significant effect on the energy consumption of the production process as long as the outdoor temperature is below the standard prescribed curing temperature (typically 20°C), requiring the production hall to be heated. In addition to operating costs due to heating, the operation capacity is limited by the curing speed of the adhesives and thus has a direct impact on investment costs for clamps and heated production halls. Therefore, the curing speed is a major selling point for adhesives.

The European certification rules for adhesives used for structural gluing of solid wood products establishes the required clamping time by lap shear tests according to EN 302-6 and EN 15416-5 for PRF / MUF and 1K-PU, respectively, where an average shear strength of 10 specimens, tested immediately after opening of the clamps, must be greater than 4N/mm².

The rheological measurement of the curing of wood adhesives as presented in this paper can help to determine the required clamping time in a much simpler process than the standard lap shear tests and can therefore to a certain extent be used as a substitution.

OBJECTIVES

The paper correlates shear strength values obtained from single lap specimens according to EN 302-6 with viscoelastic measurements obtained from a rotational rheometer with parallel plate geometry, and discusses the implications for adhesive development, adhesive certification and a better understanding of the curing of bonded wood connections.

EXPERIMENTAL

1. Analysed Adhesives

Polycondensation and polyaddition curing adhesives are the two predominant groups of adhesives used in the production of engineered wood products for structural purposes, comprising the majority of the market. The group of polycondensation type adhesives is composed of phenol-resorcinol-formaldehyde (PRF), urea-formaldehyde (UF), melamine-urea-formaldehyde (MUF) and melamine-formaldehyde (MF) adhesives. From a historical perspective, the PRF adhesives were the only adhesives that fulfilled the requirements of structural bonding for outdoor use. Then UF adhesives were developed in the late 1930ies, which however are not resistant to boil water treatment and not apt for outdoor use. In the 1980's MUF and MF adhesives were invented and approved for structural use. Although the PRF adhesives are capable of delivering excellent bonds, their dark brown colour highlights the glue lines in engineered wood products produced predominantly from light coloured softwoods and hence diminishes the aesthetic appeal of the final products to many customers. PRF adhesives also exhibit disadvantages related to production and environmental concerns due to an intense odour and its toxicity when mixed with water. Subsequently, their use has diminished from a market leader to a niche market. The application of UF adhesives in the production of engineered wood products for structural purposes has been intensely scrutinized throughout Europe since the 2006 Bad Reichenhall ice rink collapse. Their use as structural type adhesives is currently forbidden in Germany. This leaves MUF adhesives as the predominantly used polycondensation curing adhesives for structural purposes. (Note: Currently only one pure MF adhesive with properties very similar to MUF adhesives is approved for structural use in Europe.)

The group of polyaddition curing type adhesives in wood bonding includes polyurethane and epoxy type adhesives. Polyurethane (PUR) adhesives that are used broadly in the engineered wood industry for finger jointing as well as for surface gluing are exclusively moisture-curing, one-component PUR adhesives (1K-PUR). This adhesive type was first approved for structural bonding as a so-called Type I adhesive, apt for outdoor use in the early 1990ies The two-component PUR adhesives are so far only used in the production of glued-in metal parts. Due to their high costs, the use of epoxy adhesives is mainly restricted to the special applications of structural repair and strengthening as well as to gluing-in of rods.

The youngest adhesive family that is certified in Europe for structural use is that of Emulsion Polymer Isocyanate (EPI) Adhesives. EPIs are two-component systems with one component being primarily a Polyvinyl Acetate (PVAc) adhesive and the second component containing Isocyanate.

Upon consideration of the afore mentioned use in structural gluing as well as for differences in curing mechanism and reaction speed, the following adhesives were chosen for the studies:

- **1K-PU**: A certified moisture-curing, one-component Polyurethane adhesive with a rather long minimum clamping time of 180 Minutes as compared to other 1K-PU adhesives was chosen.

Because of limitations on the maximum glue line thickness as related to the approval for the adhesive, the rheometer measurements and the shear strength tests were performed with a glue line thickness of 0.1mm.

▪ **Epoxy:** A two-component Epoxy adhesive that is certified for the repair of glulam as well as for gluing-in of steel rods was chosen, with allowable glue line thicknesses ranging from close gap (<0.1mm) to a maximum of 8mm in case of repair work. A glue line thickness of 0.5mm was chosen for the rheometer measurements and the shear tests for the sake of comparability and practicality. (Note: The larger allowed glue line thickness causes a comparatively long minimum clamping time of 24 hours in the technical data sheets, but is not reflected in the results presented here.)

▪ **MUF:** A two-component Melamine-Urea-Formaldehyde Adhesive was tested. The mixing ratio / weight proportion between adhesive and hardener was 100:100. In this configuration the adhesive is mainly used for finger joints and standard glulam where a glue line thickness of 0.1mm can be guaranteed and a rather short minimum clamping time of 3 hours is desired.

▪ **EPI:** The Emulsion Polymer Isocyanate adhesive chosen for the measurements is restricted to a maximum glue line thickness of 0.2mm for its approval and was therefore tested here with a glue line thickness of 0.1mm. The technical data sheet will presumably contain a minimum clamping time at 20°C of 5 hours 45 minutes.

Table 1

Adhesives used in the current investigations

Abbreviation	Adhesive Family	Clamping Time at 20 °C curing temperature acc. to certification	Investigated glue line thickness (mm)
1K-PU	moisture-curing 1K-PU	3 h	0.1
Epoxy	2K-Epoxy	24 h	0.5
MUF	2K-MUF	3 h	0.1
EPI	2K-EPI	5 h 45 min	0.1

2. Rheology
General

Viscosity measurements are traditionally performed with a rotational spindle viscometer where a cylinder or disk turns inside a cup that is filled with the analysed fluid. The dimensions of the fluid inside the cup have similar magnitudes in all three directions, e.i. it forms a bulk. This is very different to the thin layer of an adhesive bondline with one dimension (the glue line thickness) being much smaller than the other two dimensions.

With regard to the curing process, common to all of the adhesives used in the production of engineered wood products is the strong interaction of the adhesive with the wood surfaces. All polycondensation curing adhesives release water molecules during the hardening reaction. The water transport into the wood adherends speeds up the curing process in comparison to bulk curing. On the other hand, moisture curing 1K-PUR adhesives require water molecules for the polyaddition reaction to materialize. Water from the wood adherends diffuses into the glue line during the bonding process. Moisture curing 1K-PUR adhesives cannot cure properly in bulk volumes or thick glue lines as the outer layers of the adhesive that cure in an initial reaction with the ambient moisture block diffusion into the uncured core of the bulk volume.

Therefore, in order to properly quantify the curing process, the properties of the entire curing system consisting of two wood adherends and an adhesive, where the adhesive fills a small gap between the wood adherends, should be investigated. Simple viscosity measurements by a classical Brookfield viscometer are inadequate for this purpose due to the lack of water exchange with the wood adherends as well as to the bulk quantity of adhesive being measured. A rotational type plate rheometer equipped with wooden plates as first described by Witt (2004) provides a measuring environment that satisfies these requirements. Oscillatory measurements with such instruments can provide continuous insight into the curing process under realistic conditions. These measurements can give clear inferences regarding the minimal adhesive curing time.

Oscillatory rheological measurements

Oscillatory measurements with a small amplitude γ_A avoid disturbance of the curing by the deformations that are necessary for the measurements. The imposed deformation $\gamma(t)$ is

$$\gamma(t) = \gamma_A \cdot \sin\omega t \quad \text{[Pa]} \tag{1}$$

t –time, in h
$\gamma(t) = s/d$ –relative deformation, without unit
$s(t)$ –absolute deformation of the upper plate against the lower plate, in mm
d –gap between the upper plate and the lower plate, in mm
$\omega = 2\pi f$ –angular frequency in rad/s
f –frequency, in s^{-1} = Hz

The measured response of the system is a shear stress $\tau(t)$ that is related to the imposed deformation as

$$\tau(t) = \tau_A \cdot \sin(\omega t + \delta) = G^* \cdot \gamma_A \cdot \sin(\omega t + \delta) \quad \text{[Pa]} \tag{2}$$

τ_A –amplitude of the shear stress
$G^* = \tau_A/\gamma_A$ –complex shear modulus, in Pa
δ –loss angle, in ° or rad.

A loss angle $\delta = 0°$ represents an ideally elastic material and $\delta = 90°$ characterizes ideally viscous materials. Viscoelastic materials have a loss angle of $0° < \delta < 90°$.

The absolute value of the complex shear modulus $|G^*|$ is related to its elastic and viscous components, storage modulus G' and loss modulus G'' in a complex number/Pythagorean (see Fig. 1) relationship

$$\left| G^* \right| = \sqrt{(G')^2 + (G'')^2} \quad \text{[Pa]} \tag{3}$$

and thus both moduli can easily be derived by means of

$$G' = (\tau_A/\gamma_A) \cdot \cos\delta \quad \text{[Pa]}; \quad G'' = (\tau_A/\gamma_A) \cdot \sin\delta \quad \text{[Pa]}. \tag{4a,b}$$
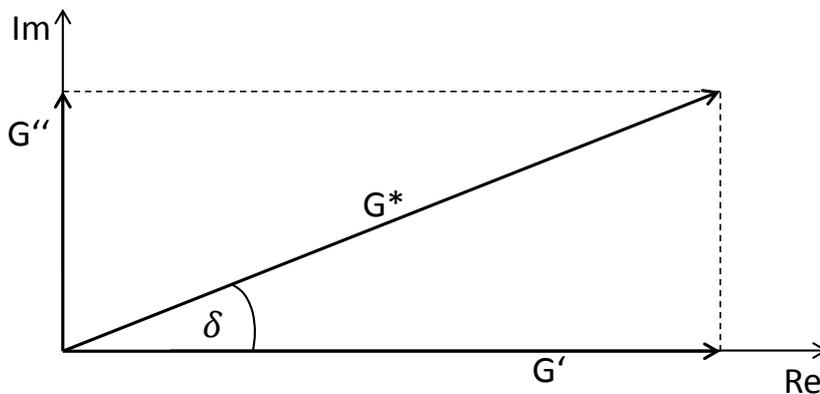

Fig. 1
Vector diagram of the complex viscosity G* with its components – storage modulus G' and loss modulus G'' – as well as the phase angle δ.

For the calculation of the complex viscosity η^* the definition of the strain rate

$$\dot{\gamma}(t) = d\gamma/dt = \gamma_A \cdot \omega \cdot \cos\omega t = \dot{\gamma}_A \sin(\omega t + 90°) \quad \text{[s}^{-1}\text{]} \tag{5}$$

$\dot{\gamma}_A = \gamma_A \cdot \omega$ –strain rate amplitude, in s^{-1}

is needed. Then the complex viscosity η^* which is defined by Newton's viscous law, and its elastic and viscous components η' and η'' can be calculated by means of

$$\eta^* = \tau_A/\dot{\gamma}_A = G^*/\omega \quad \text{[Pas]}; \quad \eta' = G''/\omega \quad \text{[Pas]}; \quad \eta'' = G'/\omega \quad \text{[Pas]} \tag{6a,b,c}$$

Experimental Setup

A rotational rheometer, type Malvern Bohlin CVO 100, equipped with parallel plate geometry was used in routine viscoelastic (oscillation) measurements of the investigated curing systems. Each curing system consisted of a pair of cylindrical wood adherends and the adhesive that was applied in the gap between the two. The diameter of the upper rotating adherend piece was 30mm (PP30). All measurements with the rotational rheometer were performed in a controlled environment with an ambient temperature of 20°C and 65% relative humidity of the air.

European spruce (*Picea abies*) was used as the adherend in all curing systems. Cylindrical specimens were cored from boards that were stored for more than one year in a controlled environment with a temperature of 20°C and 65% relative humidity of the air and exhibited an equilibrium moisture content of about 12%. Prior to coring, the boards were planed with a peripheral milling tool. The clamping set-up of the rheometer and a specimen after the test are shown in Fig. 2. (Note: The trade-off for doing the rheological measurements realistically with spruce wood which is mainly used in production was a lack of comparability with the shear tests that were conducted in this investigation with Beech wood according to the provision of EN 302-6.)
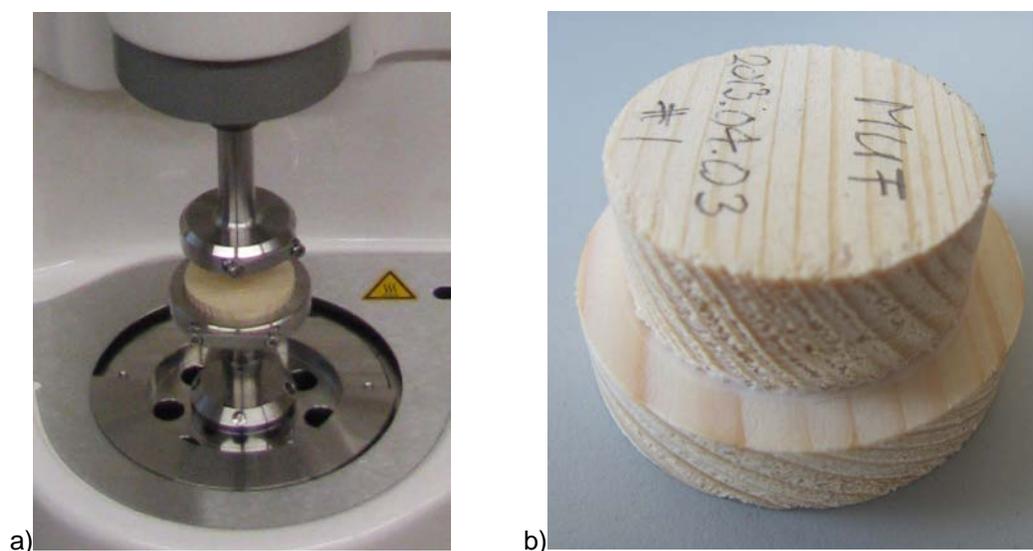

a)   b)

Fig. 2
Clamping set-up for wooden plates in rheometer before test (a) and wooden plates with MUF adhesive after testing (b).

All measurements by the rotational rheometer were performed at a constant frequency of 1Hz. First a quick strain amplitude sweep was conducted for each adhesive type and gap size in order to determine the amplitude range with linear viscoelastic response. From this output, the lowest applicable amplitude was usually selected as an input in the subsequent series of measurements of the curing process. The lowest applicable strain amplitude was selected to minimize the influence of the rotational movement on the curing process and at the same time to minimize the burden on the equipment.

Bond shear strength according to EN 302-6

A universal testing machine equipped with self-aligning grips was used for the tension shear test with single lap specimens as prescribed by EN 302-6 and EN 15416-5 with reference to EN 302-1. Beech wood (Fagus sylvatica) was used as the adherend in all specimens. Plates of dimensions 300mm x 135mm x 5mm were sawn from boards that were stored for over one year in a controlled environment with a temperature of 20°C and 65% relative humidity of the air. The plates were sanded immediately before bonding. The adhesive was then carefully spread over both adherend surfaces and the two plates were overlapped to yield a 10mm thick piece before the required pressure was applied through a mechanical press. The pressure was kept for a set period of time after which 5mm deep notches at 20mm spacing were sawn at the opposite sides in the middle area of the two piece halves. Finally 10 single lap specimens with a length of 150mm and a width of 20mm were sawn from each bonded piece.

RESULTS AND DISCUSSION

1. Bond shear strength according to EN 302-6

The shear strength of wood adhesives during the curing process can be described by a derived exponential growth function $f_v(t)$, where $f_v(t{=}0)$ = 0Mpa at the very beginning of the curing process, and approaches a final strength $f_v(t{=}\infty) = f_{v,final}$ at the end of the curing process. In order to model the speed of curing, a reactivity parameter α is introduced as well as a parameter t_{delay} that shifts the function along the time axis and marks the inflexion point of the function where the change of shear strength per time $f_v/\mathrm{d}t$ is at a maximum. The curing strength equation then is

$$f_v(t) = f_{v,final} \cdot \left(e^{\alpha \cdot \left(-t+t_{delay}\right)}\right)^{-1} \ \text{[MPa]} \tag{7}$$

$f_v(t)$ –lap shear strength of the specimen according to EN 302-6
t –time, in h
$f_{v,final}$ –shear strength at the end of the curing process $f_v(t{=}\infty)$, in MPa
α –reactivity parameter, in h^{-1}
t_{delay} –reaction delay time, in h

The results of the lap shear tests according to EN 302-6 are shown in Figs. 4 to 7 together with the best-fits based on Eq. (7). The fit parameters and the pseudo R² are compiled in Table 2.

Table 2

Summary of fit parameters derived from shear strength test results according to EN 302-6

Adhesive	Final shear strength $f_{v,final}$ MPa	t_{delay} h	pseudo-R² = 1 − RSS/TSS	Reactivity α
1K-PU	14.1	3.92	0.97	1.73
EPI	14.9	3.12	0.97	0.976
epoxi	12.1	6.65	0.91	1.68
MUF fast	13.1	3.61	0.85	1.03
PRF	12.7	14.03	0.98	0.299

2. Rheology

The rheology results are displayed in Figs. 3a–d. Within one adhesive group, the results of the rheology measurements showed that the variability along the time axis was very small, i.e. the moment when the viscosity begins to rise or approaches an asymptote is always at the same time. By contrast, absolute values of viscosity and moduli (*G'* and *G''*) at the end of a measurement showed significant differences when repeating a measurement with the same adhesive.

The progression of viscosity parameters over time was very different for the four adhesive groups.

- The **Epoxy** adhesive clearly formed a gel point as defined by Tung and Dynes (1982) where the loss modulus *G''* is higher than the storage modulus *G'* at the beginning of the measurements and crosses at the gel point. Shortly after the gel point, the loss modulus *G''* reaches its maximum after which it declines before reaching a constant value. *G'* asymptotically approaches its final value slower than *G''* while continuing to rise slightly at the end of the measurements, see Fig. 3a. The phase angle δ has a maximum of about 70° to 80° during the largest inclination of the moduli.

- For **1K-PU** adhesives, the storage modulus *G'* was higher than the loss modulus *G''* at the beginning of the measurements, while intersecting later during the hardening of the adhesive, see Fig. 3b. Further on, *G''* again drops below *G'* (δ = 45°). Quite comparable, but not as clearly as during the curing of the Epoxy adhesive, *G''* reaches a maximum after separating from G' and before dropping to its final value. G' is still rising at the end of the measurements and does not seem to arrive at its asymptote. The phase angle δ reaches its maximum of about 40–60° during the largest inclination of the moduli.

- The **Polycondensation** adhesive behaved very differently from the Polyaddition adhesives: the storage modulus *G'* was considerably higher than the loss modulus *G''* during the entire curing process – the relative distance between the two moduli increased only gradually. Consequently, the phase angle started at a comparatively low value, at under 20°, and decreased slowly and inconsistently to a value of around 10°, see Fig. 3c.

- The **EPI** adhesive shows an evolution of the viscosity during the curing process very similarly to the Polycondensation adhesive, however with the separation between G' and G'' being clearer and thus the behaviour of the phase angle δ being more stable, see Fig. 3d.

The predominantly elastic behaviour at the beginning of the gluing process of MUF, EPI and partially 1K-PUR adhesives are a desired feature, especially in the production of finger joints where the adhesives are usually applied to the vertically aligned fingers. If the adhesive were to be too fluid in this application, the adhesives would follow gravity and flow from their intended destination.

In contrast, the main use of the Epoxy adhesive analysed in this paper consists of the injection into cracks during the repair of glulam and into drilled holes for the gluing-in of steel rods. For this purpose, fluid behaviour is necessary. The steepness of the change in phase angle during the curing process is due to heat production of the exothermic polyaddition reaction which can indirectly be observed during production when the adhesive sometimes starts to flow into thin cracks hours after the application.

The comparatively large phase angle of the 1K-PU adhesive during parts of the curing process is most likely due to foaming of the adhesive because of CO_2-production. Whether this behaviour also occurs in a full size production or is only amplified by the small size of the specimen will be part of further investigations.
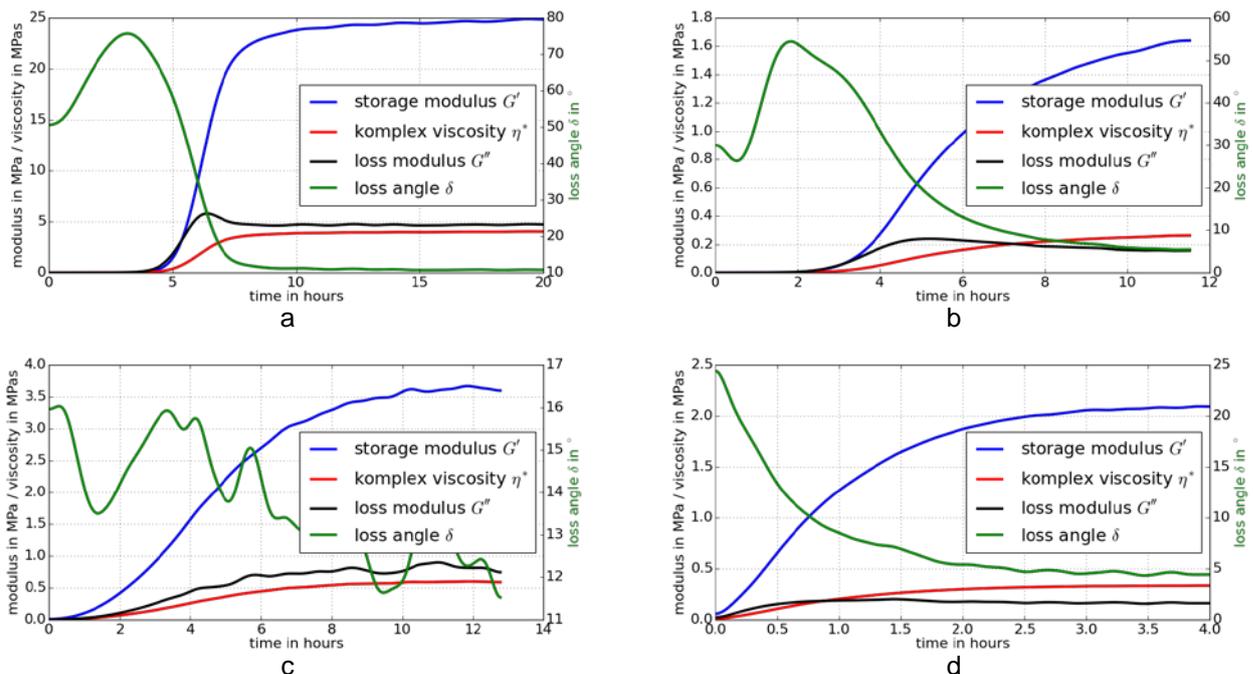

Fig. 3
Results of plate rheometer measurements with different adhesives. A) 2K Epoxy adhesive, b) moisture curing 1K-PU adhesive, c) MUF adhesive and d) EPI adhesive.

3. Comparison of Rheology Measurements with shear strength

The Figs. 4 to 7 display the shear strengths together with the rheology results for the four tested adhesives. All values were normalized to 1 to guarantee comparability. Due to their strictly increasing nature, normalized storage modulus *G'*, complex viscosity *η** and shear strain *τ* can be regarded as a rate of curing. To gain a monotonic function from the loss modulus *G''*, the modified loss modulus G''_{mod} was derived by integrating the absolute value of the derivation of *G''*.

$$G''_{mod}(t) = \int |G''/dt| \cdot dt \, [MPa] \tag{8}$$

For the studied Epoxy, 1K-PU and MUF adhesives, the normalized strength fits lie in the vicinity of the normalized rheological values G', G'' and η^*, see Figs. 4 to 6. Contrarily, the strength, i.e. the evolution of shear strength depending on curing time of the EPI adhesive, increases considerably slower as compared to the rheological values. This different behaviour is likely due to the hybrid curing mechanism of EPI adhesives that is characterized by a combination of a faster physical curing of the PVAc component and a slower chemical reaction of Isocyanate with the active hydrogen molecules from the water and with PVAc molecules.

The rheological shear stress τ is close to the lap shear strength value for 1K-PU adhesive but occurs about 20% earlier for the tested Epoxy adhesive and provides no hint as to the curing speed of MUF and EPI adhesives.

The phase angle δ drops to a constant value when the final strength is reached for the Epoxy adhesive but is almost constant for MUF adhesives and coincides only vaguely with strength values of 1K-PU and EPI adhesives.

For the Epoxy and the 1K-PU adhesive, where the loss modulus G'' drops clearly after rising to an early maximum, the modified loss modulus is a better approximation of strength values than the unmodified loss modulus G''.

The storage modulus G' was a good approximation for the strength fit of the Epoxy and the MUF systems where it asymptotically converged to a final value. For the 1K-PU adhesive, where the storage modulus didn't converge within five hours of G'' reaching its maximum value, the storage modulus rose approximately 30% later than the strength fit.
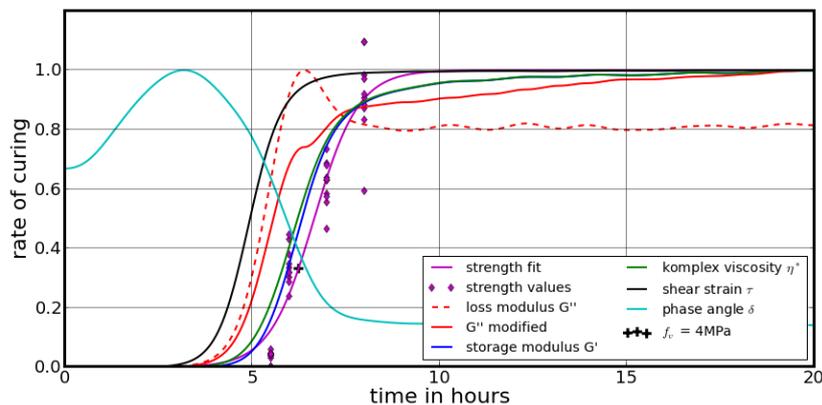

Fig. 4
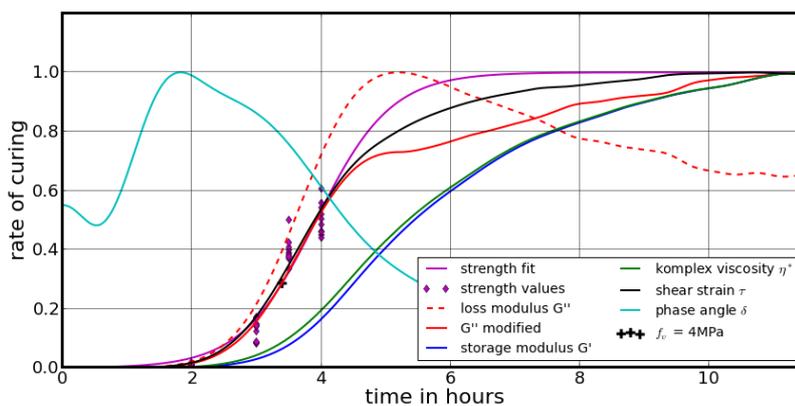*Comparison of plate rheometer measurements and shear strength values of a 2K Epoxy adhesive.*

Fig. 5
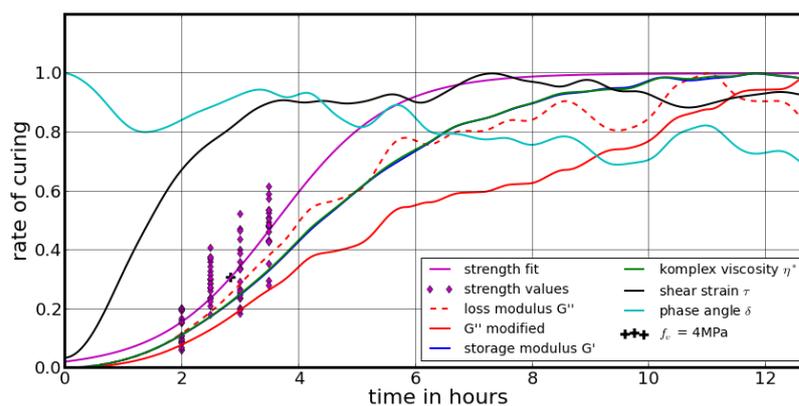*Comparison of plate rheometer measurements and shear strength values of a moisture curing 1K-PU adhesive.*

Fig. 6
Comparison of plate rheometer measurements and shear strength values of a MUF adhesive.
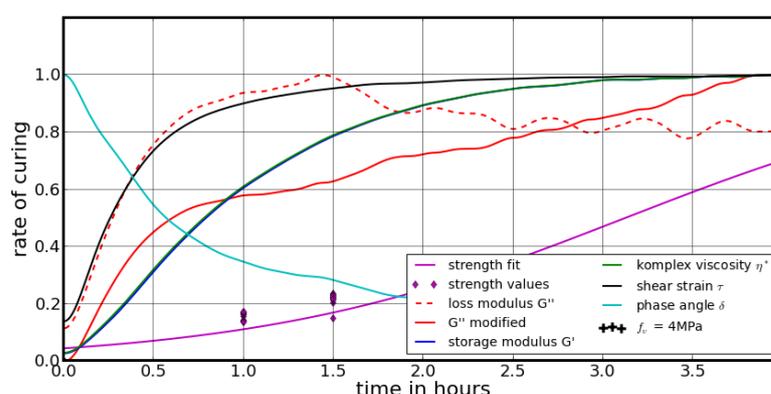

Fig. 7
Comparison of plate rheometer measurements and shear strength values of an EPI adhesive d).

4. Conclusions

Rheological measurements can provide a quick insight into the curing behaviour of wood adhesives. The evolution of the loss modulus G'' and the storage modulus G', which are time dependent, coincided sufficiently well with the strength of the measured Epoxy, 1K-PU and MUF wood adhesives during their curing. However, the strength behaviour of the tested EPI adhesive was in discordance with the rheological values due to its complex curing mechanism. The discrepant behaviour of EPI adhesives as well as the influence of foam formation during the curing of 1K-PU adhesives will be examined in further investigations. Furthermore, the influence of the adherend substrate beech vs. spruce will be studied in greater detail.

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