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STSM Applicant: Roland Wetzel, Friedrich Schiller University,
Otto Schott Institute for Material Research,
Fraunhoferstr. 6, 07743 Jena, Germany

STSM topic: Investigation on the working and setting time of novel glass ionomer cements

Introduction:

Glass ionomer cements (GIC) consist of an acid degradable glass and a polymeric acid. The mixture sets due to an acid-base reaction. Because of their possibility to be shaped freely GIC's offer opportunities as void fillers or for the formation of scaffolds. Besides, the cements could be used as adhesives as result of their property to bond to bone. Key characteristic properties of GIC's are their working and setting time. These parameters provide quantitative data about the time during which we can handle the cement and how long it takes to set properly. This has a direct effect on if and how the GIC can be used. Both glass and polymeric acids influence the setting behaviour of such cements.

In commercial GIC only linear polymeric acids were used so far. This study investigated the inclusion of new branched polymeric acids and the results on the workability and setting behaviour of novel GIC's. Rheological properties, such as the storage modulus (G'), loss modulus (G'') and the loss tangent (tan δ), were used to obtain information about the setting process.

The storage modulus characterizes the elastic component whereas the loss modulus provides information about the viscous component of the sample under study. Furthermore, the loss tangent $\tan \delta = G''/G'$ can be used to describe the setting behavior. The point where tan δ crosses a value of $\tan \delta = 1$ the sample reached the gel point. This marks the transition of liquid to solid state of a sample.

Materials and Methods:

Two different glasses (LG26, acid treated LG26), two linear poly(acrylic acids) (PAA, PAA35) and five branched poly(acrylic acids) (OE-2, PE-3, OE-4, OE-5, OE-126) were used to prepare different GIC's. In table 1 you can find detailed information about the different polymeric acids which were utilized in this study. For the preparation of the different GIC's the components were weighed (m_{glass} = 1,000 g, $m_{\text{polymeric acid}}$ = 0,2500 g, $m_{\text{deionized water}}$ = 0,2500 g). These represent a glass powder to polymeric acid ratio of 4:1. First the glass powder and the polymer powder were interblended with a spatula on an acrylic plate. Afterwards the deionized water was added and the powder and liquid was hand-mixed. Simultaneously a stopwatch was started to obtain the time until the rheological measurement began.

table 1: Molecular weight of the different polyacrylic acids used.

	PAA	PAA35	OE-2	OE-3	OE-4	OE-5	OE-126
M_n [g/mol]	18.000		7.000	10.800	13.000	15.500	15.000
M_w [g/mol]			9.500	20.000	26.600	38.300	21.000

To analyze the setting behavior a rheometer AR1500ex (TA Instruments) was used. The samples were run in parallel plate mode. Therefore the cement was placed between two parallel plates (diameter = 20 mm). The bottom stayed stationary and the top oscillated at a specific strain level (%strain = 1,0000). As a result of these investigations the storage modulus (G') the loss modulus (G'') together with the loss tangent (tan δ) were obtained. The measurement for the LG26 containing cements were repeated three times whereas the rheological tests of cements containing the LG26 (acid treated) glasses were rerun two times.

Results:

The rheological investigations for the LG26 containing cements with varying poly(acrylic acids) are shown in figure 1 and **Fehler! Verweisquelle konnte nicht gefunden werden.**. The comparison of the results for the loss tangent of the different cements exhibits that the linear poly(acrylic acid) (PAA35, PAA) reached the gel point (tan δ = 1) first. Whereas the cements containing branched polymeric acids need more time. The transition of the liquid to the solid state enables an approach to get information about the working time of the novel GIC's. The working time ends when tan δ = 1 is reached and is given in table 2 for the different cement formulations. The GIC's containing linear poly(acrylic acid) have shorter working times. Additionally the working times for the cements with branched polymeric acids are almost twice as long.

table 2: Time when tan δ = 1 was reached for the analysis of LG26 containing cements.

	PAA	PAA35	OE-2	OE-3	OE-4	OE-5	OE-126
$t_{\tan\delta=1}$ [s]	179	153	351	297	296	286	269
$t_{\tan\delta=1}$ [s]	191	152	370	323	262	248	257
$t_{\tan\delta=1}$ [s]	187	151	411	306	264	268	261

mean ± stand. deviation [s]	**186 ± 5**	**152 ± 1**	**377 ± 25**	**309 ± 11**	**274 ± 16**	**267 ± 16**	**262 ± 5**

Furthermore, the results of the loss tangent make it possible to gain knowledge about the setting behavior of the different GIC's. A plateau of tan δ is reached at different times for the different compositions. The faster the curve obtains a plateau, the faster the setting reaction is finished. The cement formulations with the linear poly(acrylic acid) reveal a faster setting by comparison with the branched polymeric acids containing GIC's.

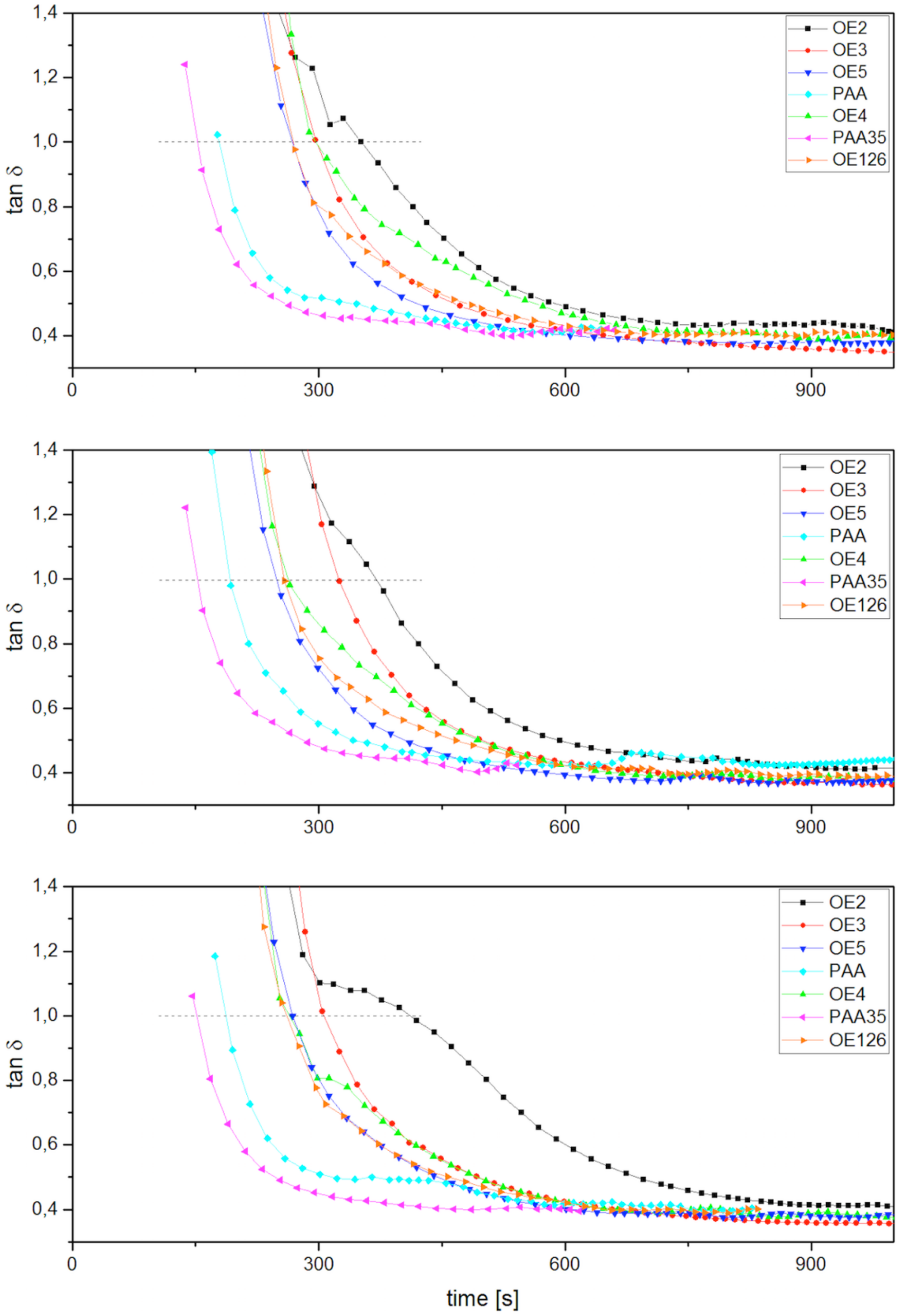

figure 1: Loss tangent (tan δ) as a function of time for repeated measurements on LG26 containing cements. Line serves as guide to the eyes.

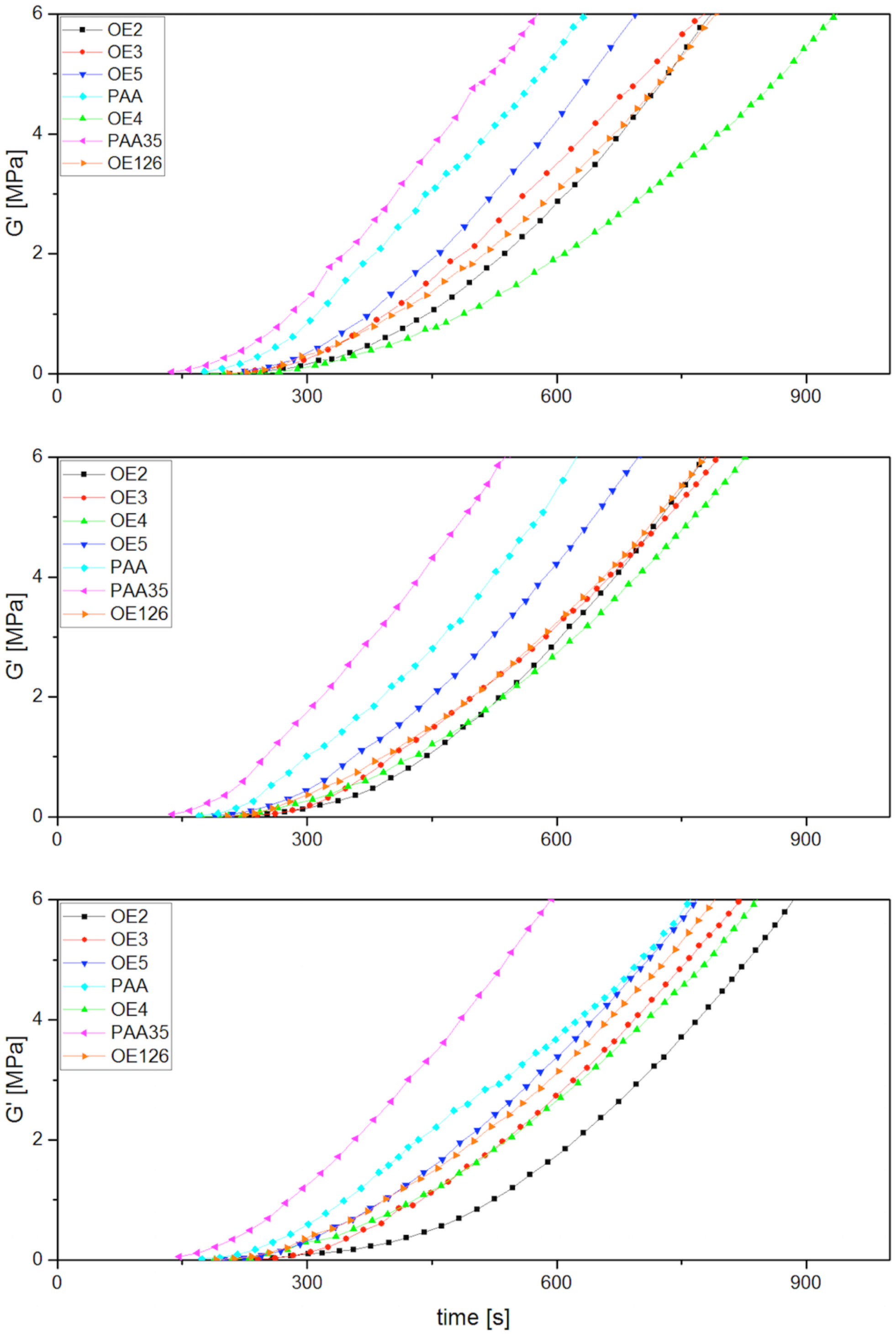

figure 2: Storage modulus (G') for the repeated measurements on LG26 containing cements. Line serves as guide for the eyes.

Besides the loss tangent the storage modulus offers an opportunity to obtain further information about the setting reaction of the GIC’s containing LG26. The sooner the slope of the graph of G’ increases the faster is the setting reaction of the cement. The results of G’ of the different LG26 containing cements are shown in figure 2. It becomes apparent that the GIC’s including linear poly(acrylic acids) show a faster setting behaviour in comparison to the cements with branched polymeric acids. Additionally the branched poly(acrylic acid) with the highest molecular weight (OE-5) demonstrates the fastest setting in-between the cements with non-linear polymeric acids.

The measurements on the LG26 (acid treated) glass containing GIC's show a different trend for the comparison of the cements with linear and branched poly(acrylic acid) respectively. In figure 3 the outcomes of the loss tangent for the different compositions are given.

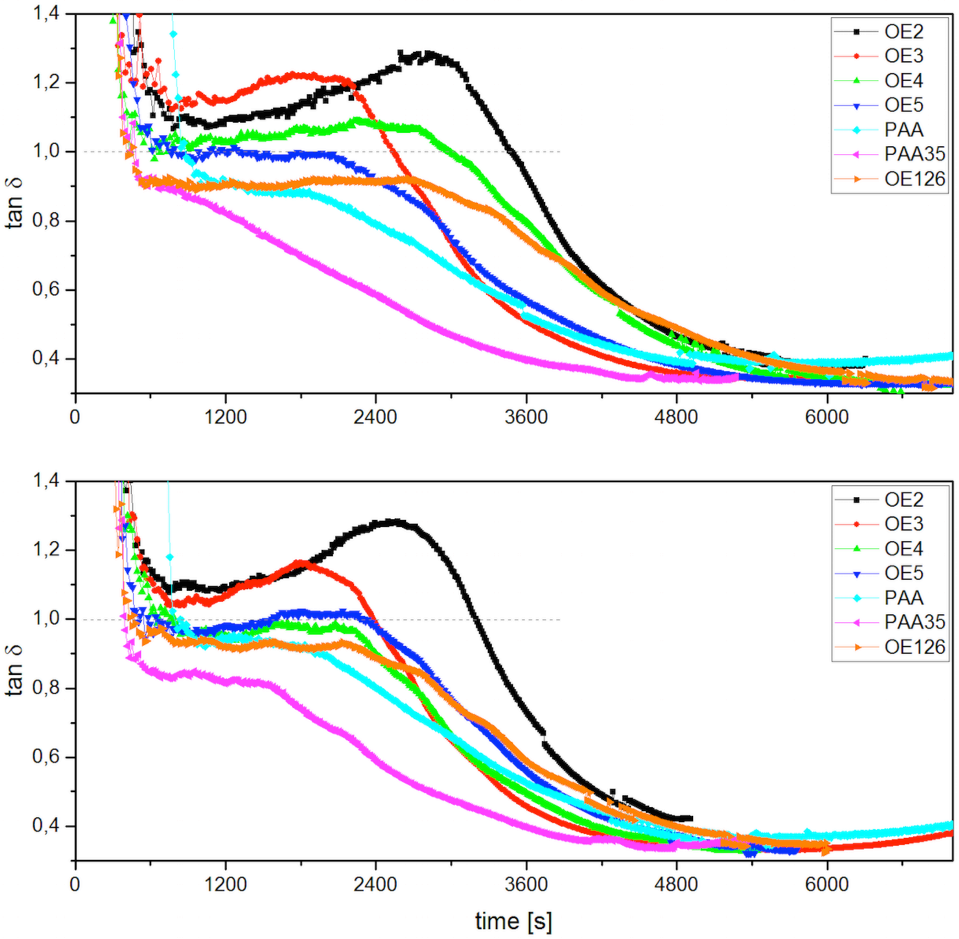

figure 3: Loss tangent (tan δ) as a function of time for repated measurements on LG26(acid treated) containing cements. Line serves as guide to the eyes

Obviously, the behaviour varies for the different cements. Compared to the results of the LG26 containing cements the GIC's reveal a first plateau around tan δ = 1. As a result, the interpretation of data regarding to the working time of each LG26 (acid treated) containing cement is complicated. The times where tan δ reaches a value of 1 are shown in table 3.

table 3: Timewhen tan δ = 1 was reached for the analysis of LG26 (acid treated) containing cements.

	PAA	PAA35	OE-2	OE-3	OE-4	OE-5	OE-126
$t_{\tan\delta=1}$ [s]	877	479	3476	2535	2982	1308	462
$t_{\tan\delta=1}$ [s]	836	391	3195	2378	790	2305	472
mean ± stand. deviation [s]	**856 ± 20**	**435 ± 44**	**3335 ± 140**	**2456 ± 78**	**1886 ± 1096**	**1806 ± 498**	**467 ± 5**

Apparent from figure 3 the courses of the curve of the loss tangent have a first plateau between tan δ = 1.2 and tan δ = 0.8 depending on the composition. The times after the values drop to the second plateau are given in table 4.

table 4: Time after tan d drops of the first plateau of the loss tangent for the LG26 (acid treated) containing cements.

	PAA	PAA35	OE-2	OE-3	OE-4	OE-5	OE-126
$t_{plateau}$ [s]	1931	750	3011	2188	2762	2087	2794
$t_{plateau}$ [s]	1870	1575	2686	1931	2228	2258	2188
mean ± stand. deviation [s]	**1900 ± 30**	**1162 ± 412**	**2848 ± 162**	**2059 ± 128**	**2495 ± 267**	**2127 ± 85**	**2490 ± 303**

A further source for information about the setting behaviour of the cements made with LG26 (acid treated) glass are the plots of G'. In contrast to the results for the GIC's made with the LG26 glass a statement about the setting behaviour of the LG26 (acid treated) containing cements is not easy to make. In figure 4 the storage modulus for the different GIC's are shown. The linear PAA35 shows the fastest setting behaviour as in the LG26 glass containing cements. Surprisingly, the linear polymeric acid PAA do not show a faster setting than the cements with the branched poly(acrylic acids). Besides that the branched polymeric acid with the highest molecular weight does not show the fastest setting in-between the cement compositions with the branched poly(acrylic acids). A relation between the molecular weight of the branched polymers can not be noted. This opposes the result of the GIC's made with LG26.

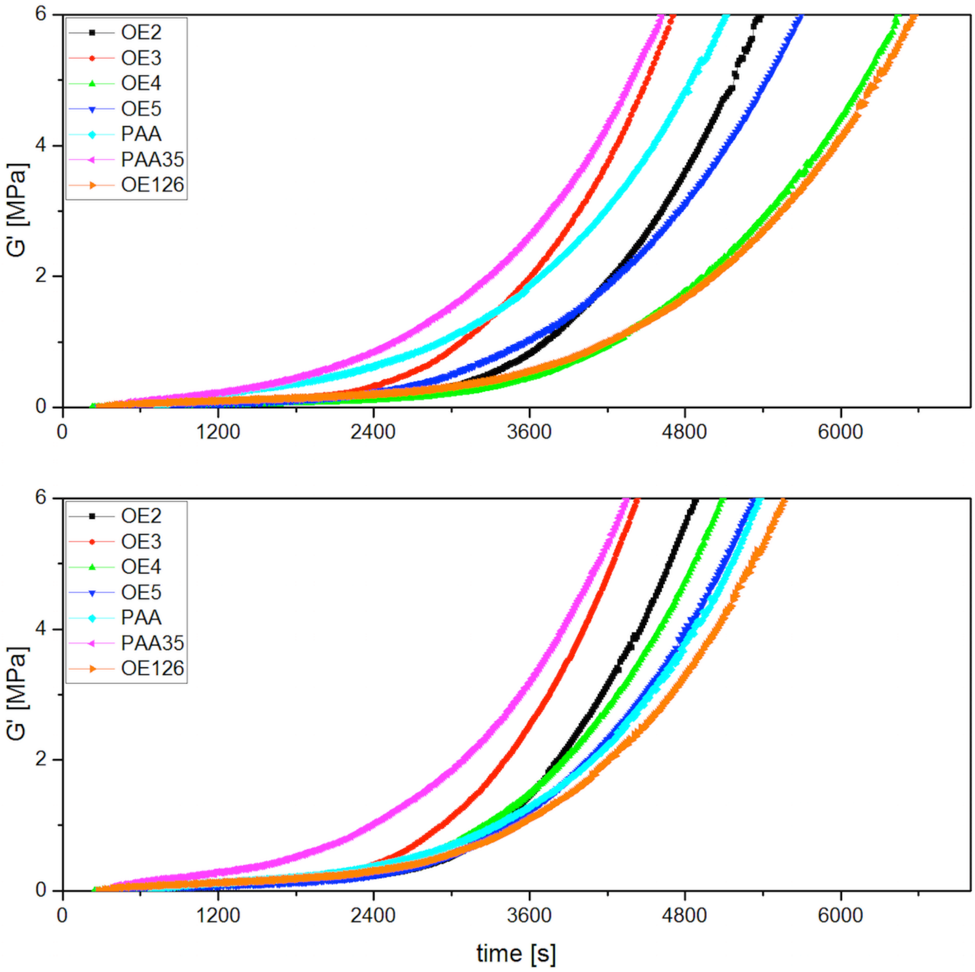

figure 4: Storage modulus (G') for the repated measurements on LG26 (acid treated) containing cements. Line serves as guide for the eyes.

Conclusion:

The analysis of the results for the loss tangent and the storage modulus of the cement compositions reveals differences regarding the working time and setting behaviour depending on the cement components. The glass component has a huge influence on the working and setting properties. The use of the LG26 shows shorter working times and a faster setting reaction compared to the GIC's which contain the acid treated glass. A possible explanation could be the manufacturing process. The acid treatment leads to the solution of ions out of the glass network. Furthermore, a dissolution of smaller particle of the LG26 glass powder can occur. As a result, the amount of ions and more reactive particles which can be part of the setting reaction decrease and the working and setting time rise.

An interesting point in the plots of the loss tangent of the LG26 (acid treated) containing cements are the formations of a first plateau between a value of tan δ = 1.2 and tan δ = 0.8. It can be assumed that the working time does not end until the value drops and the end of the plateau is reached.

Also the choice of the polymeric structure of the poly(acrylic acid), e.g. linear or branched, has an influence of the workability and setting characteristics of the GIC's. This effect is noticeable by comparing the cements containing PAA and OE-3. The molecular weight of linear and branched poly(acrylic acid) are alike. The results show that the LG26 cements which contain linear polymeric acid posses a shorter working time and a faster setting reaction. In addition, the mixtures made of the acid treated glass and the linear polymeric acid show a comparable behaviour regarding the working time. However, the properties concerning the setting reaction of the LG26 containing cements are completely different. The novel GIC's which contain the acid treated LG26 and the branched polymer exhibit a faster setting. The setting reaction of GIC made of branched polymers is currently not investigated and it seems that the reaction proceeds more complex than the setting with linear polymeric acids.

Also the impact of the molecular weight of the branched polymeric acids was investigated. For the glass ionomer cements which include the glass LG26 a relation between the molecular weight and the working time can be assumed. It seems that the increase in molecular weight leads to a decrease in the working time. Furthermore, the setting reaction is faster due to the higher molecular weight. However, this requires further investigation due to the discussed deviation. The correlation between the molecular weight and the working and setting properties is indistinguishable in the outcome of the rheological measurements for the novel cements which include the acid treated glass.

Taking all the rheological measurements into account the results indicate that besides the glass component also the structure of the polymeric acid (e.g. linear, branched) as well as the molecular weight have an influence on the working and setting properties of the investigated glass ionomer cements.