

Dielectric analysis of light-curing dental restorative materials—a pilot study

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This study tested the potentiality of dielectric analysis (DEA) for determining the reaction performance of light-curing dental resins. The influence of polymerisation conditions and material properties on the ion viscosity were investigated within a current field. The restoratives were light-cured for 20, 40 or 60 s in a layer thickness between 1, 2, or 3 mm with a varying distance between curing light and specimen of 1, 3 or 5 mm. The tests were performed at 25°C/37°C with different polymerisation modes. Nine restoratives (two composites and their derivate flowables, two ormocers, one compomer, one nano-filled composite and one siloran) were investigated. The ion-viscosity-time graph was analysed to characterize reaction velocity and polymerisation conversion. The slope of the ion viscosity decreased with increasing distance between polymerisation light and specimen. The time of exposure affected the affinity and the conversion, with a polymerisation maximum at 40 s. A relation between thickness and reaction time and between polymerisation modus and conversion/velocity was found. The temperature influenced the reaction affinity. Different materials showed an individual curing performance. DEA-monitoring of the ion viscosity gives principal insight in the polymerisation reaction of light curing materials. Further investigations are necessary for identifying the relation between ion viscosity and polymerisation.

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1. Introduction

Polymerisation kinetics and degree of cure of dental materials are of high interest for the processing time or clinical quality of a restorative material. Dental light curing devices and resins were developed to improve the light and chemical polymerisation performance, obtaining optimised resin properties with lowest shrinkage [1, 2], e.g.

Light curing units received lamps which were optimised for the emission spectrum of the light activator champherquinone (400 nm) and the output of light intensity (up to 1000 mW/cm²). For monitoring the performance and the success of the polymerisation, differential thermal analysis (DTA), differential scanning calorimetry (DSC)

[3], Fourier Transform Infrared Spectroscopy (FTIR) [4], rheology, temperature measurements or simple hardness tests [5] are used. Unfortunately, these methods are partly expensive, not precise, have limited data acquisition rates, or may not be performed with monomer liquids or light activatable pastes.

Dielectric analysis is based on measurements where the specimen is in direct contact with a capacitor. A sinusoidal voltage is applied on one electrode, whereas the second electrode serves as a receiver for the resulting current. The dielectric specimen effects the amplitude and phase of the input signal depending on ionic mobility and the alignment of the dipoles in the alternating current field [6, equation].

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$$\sigma = e'' * 2\pi * f * \varepsilon_0 \quad \sigma : \text{ionic conductivity,}$$

$$\varepsilon'' : \text{loss factor, } \varepsilon_0 : \text{dielectric constant, } f : \text{frequency}$$
(1)

In addition, the ion viscosity is depending on the concentration of mobile ions [C] and the ion charge q. It is considered that the ion mobility is reduced during the polymerisation reaction and finally stopped, so the ionic viscosity or the reciprocal frequency dependent ion conductivity is regarded as an indicator for the reaction performance and degree of cure. For most polymers the ion viscosity follows the mechanical changes in viscosity and cure state closely, monitoring the chemical process of the resin from monomeric liquid with different viscosities over gelation to an insoluble polymer [7]. Fitting the results to a mathematical model [8] may help to interpret the kinetic routine. Only a fast frequency (1000 Hz) and a high data acquisition rate (55 ms/digit) make it possible to monitor even fast light or chemical polymerisation reactions. The easy handling may allow to apply the material fast and directly on the sensor, simulating the clinical application. Most of the DEA literature deals with esters and epoxy resins under non-isothermal conditions [9–13] often with conventional parallel plate capacitors, only one paper works on dental materials [7]. DEA relations to DSC, nuclear magnetic resonance (NMR) [14] or FTIR [15] were investigated. DEA analysis allowed the monitoring of thermoplastics and thermosets [16, 17] and is supposed to supplement information concerning environmental influences on the light-curing polymerisation, such as light to restorative-distance, material thickness, influence of the light curing device as well as specific structural polymerisation differences between various types of paints [18] or restorative materials [7].

The aim of this investigation was to test the potentiality of DEA measurements for determining the reaction performance of dental light curing resins. Among others, the influence of light intensity, specimen thickness, polymerisation temperature, and curing time were investigated. A total of eight dental restoratives were investigated to compare their curing performance.

2. Material and methods

The light curing performance of dental resins (Table I) was investigated with a dielectric analyser (DEA 231/1 Epsilon, Netzsch-Gerätebau, Selb, Germany). All measurements were performed with an interdigitated electrode IDEX sensor (frequency 1000 Hz, data acquisition rate 0.2 s). The electrodes of the sensor were arranged in a fringed design with comb electrodes (65S, A/D Ratio: 80, distance between electrodes: 115 μm , sensing area: 1.2 \times 2.5 mm²). The mode of action is described in detail by Zahouily *et al.* [19]. A perforated ($d=5$ mm) 1 mm thick polyethylene mask film was fixed on the sensor and the resins were applied with a dental spatula and pressed

with an object slide. The glass slide prevented the material from oxygen inhibition and allowed to light-cure the resin. A retaining jig was used to assemble the light curing device (Elipar Triligh, 3M Espe, Germany) directly above the material. Light polymerisation was started manually after 20 s to guarantee basic starting conditions. Sensor and material were fixed on a tempered plate (isothermal 25°C or 37°C) for keeping a constant temperature. Temperature was controlled with a thermocouple on a second input of the DEA electronics. With one composite (Tetric Ceram, Ivoclar-Vivadent, FL), different settings were investigated (Table II) to test the influence of specimen position, distance between light curing unit and sensor, thickness of the specimen, time and temperature of polymerisation and polymerisation modus. All other restoratives were investigated with 40 s polymerisation time at 37°C, standard and exponential modus, 1 mm thickness, 0 mm distance between slide and lamp, and with the sample at a central sensor position. All measurements were repeated three times. Control measurements with mask film, but without composite and with composite but without light activation were performed. A logarithmical ionic viscosity/time graph (Fig. 1) was recorded and for the ion viscosity the minimum, maximum, difference max-min, inflection point and maximum slope were calculated. The difference between maximum and minimum ion viscosity is supposed to represent the progress of the polymerisation and network density, whereas the slope provides information about the reaction velocity (conversion rate). Mean and standard deviations were calculated and the results were statistically analysed using t-test ($\alpha = 0.05$).

3. Results

The results are displayed showing the influence of the varying parameters and finally the differences between the tested materials (Figs 2 and 3 and Tables III and IV).

3.1. Sample thickness

Inversion point and slope of the ion viscosity decreased with increasing sample thickness. Minimum, maximum and amount of ion viscosity showed no significant differences between 1, 2 and 3 mm thickness.

3.2. Sample position

Approaching the sample position to the cable connector increased slope (0.2–0.3–0.5) and amount of log ion viscosity (0.46–0.64–1.14 Ωcm). Minimum ion viscosity and inversion point were higher in position #1 compared to the positions #2 and #3. The significantly highest maximum was found at position #3, whereas no differences were established for the maximum results at the positions #1 and #2.

TABLE I Materials and manufacturers

Name	Manufacturer	Batch	Type
Dyract AP	Dentsply DeTrey (D)	0209Z06024	Compomer
Enamel Plus HFO	GDF/Micerium (D)	2002001107	Microhybrid
Enamel Plus HFO	GDF/Micerium (D)	2002001107	Flowable Microhybrid
Experimental material	3M Espe (D)		Siloran
Filetek supreme	3M Espe (D)	2AA	Nanofilled composit
Ceram X	Dentsply DeTrey (D)	AFA 01-125-01	Ormocer
Tetric ceram	Ivoclar-Vivadent (FL)	D 51531	Hybrid
Tetric flow	Ivoclar-Vivadent (FL)		Flowable Hybrid

TABLE II Experimental settings and variations

Sample position	Light curing unit	Specimen	Polymerisation	Polymerisation	Temperature
Distance [cm] from cable connector: 1, 2, 3	Distance [mm] from specimen to curing unit: 0, 3, 10	Thickness [mm]: 1, 2, 3	Time [s]: 20, 40, 60	Modus: Standard (800 mW/cm ²), exponential (soft start from 100 mW/cm ² to 800 mW/cm ²), medium (500 mW/cm ²)	Isothermal 25°C, 37°C

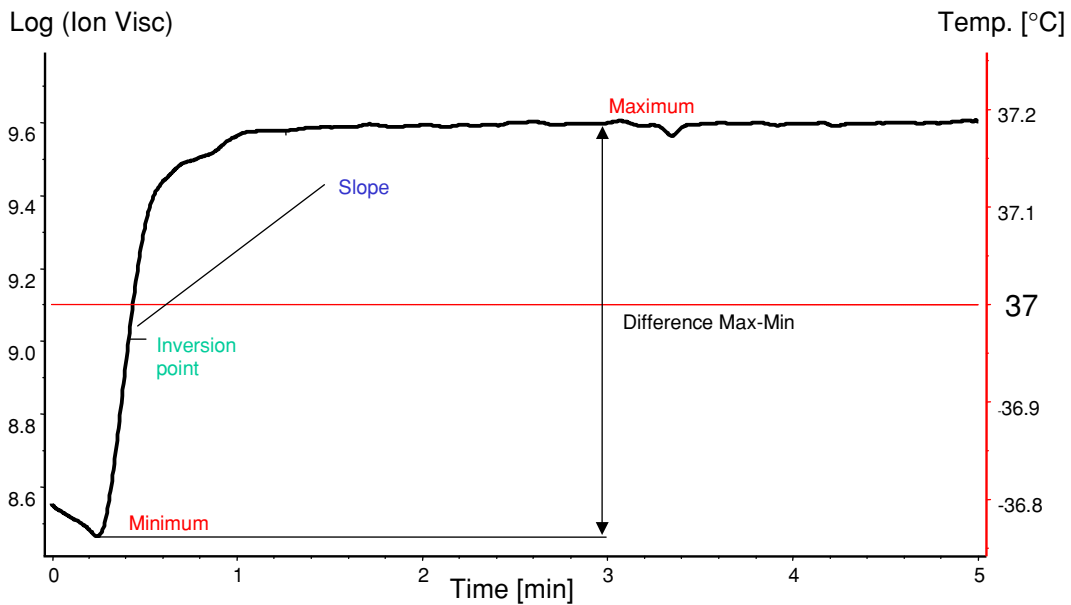


Figure 1 graph log (Ω m) ion viscosity versus temperature (example).

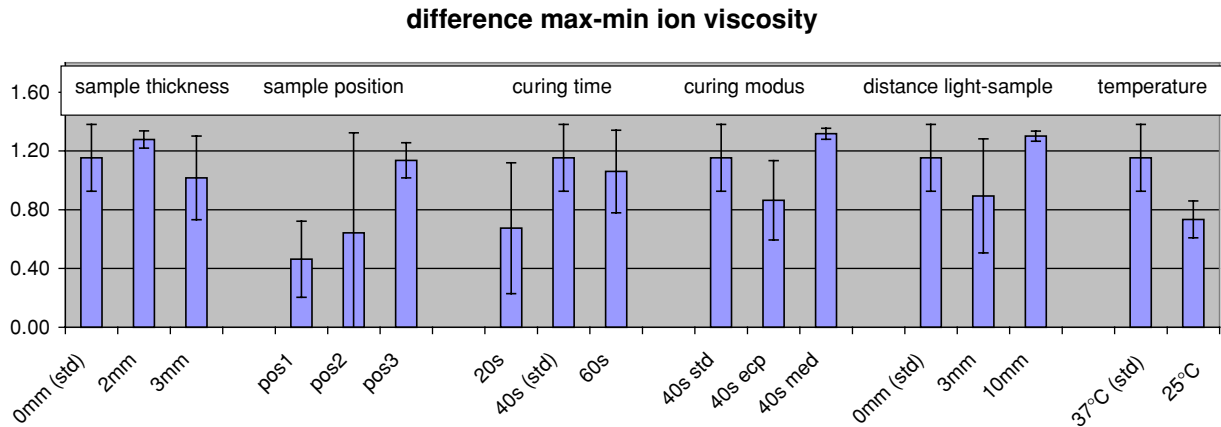


Figure 2 difference between maximum and minimum log ion viscosity (Ω m) for Tetric Ceram; varying settings.

TABLE III DEA log ion viscosity (Ωcm) results (mean, standard deviation (std)); (Standard: sample thickness 1 mm, std curing modus, curing time 40s, distance light-sample: 1 mm, 37°C)

	Minimum		Maximum		Inversion point	
	Mean	Std	Mean	Std	Mean	Std
Standard	8,44	0,14	9,60	0,14	8,80	0,12
Sample thickness 2 mm	8,32	0,04	9,60	0,08	8,63	0,06
Sample thickness 3 mm	8,32	0,04	9,34	0,32	8,53	0,08
40 s ecp curing modus	8,47	0,11	9,33	0,25	8,79	0,13
40 s med curing modus	8,31	0,02	9,63	0,04	8,59	0,05
Position 1 (3 cm)	8,67	0,13	9,13	0,13	8,74	0,13
Position 2 (2 cm)	8,35	0,05	8,99	0,73	8,53	0,14
Position 3 (1 cm)	8,37	0,08	9,51	0,20	8,46	0,12
Curing time: 20 s	8,53	0,06	9,20	0,38	8,78	0,11
Curing time: 60 s	8,48	0,13	9,54	0,15	8,86	0,03
Distance light-sample: 3 mm	8,40	0,20	9,30	0,55	8,68	0,36
Distance light-sample: 10 mm	8,40	0,04	9,71	0,05	8,75	0,06
Isothermal 25°C	8,96	0,10	9,70	0,04	9,18	0,05

TABLE IV DEA log ion viscosity ($\Omega\text{ cm}$) results (mean, standard deviation (std))

Material	Type	Minimum		Maximum		Difference maximum-minimum		Inversion point		Slope	
		Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
Ceram X	Ormocer	9,40	0,11	9,95	0,01	0,55	0,01	9,58	0,06	0,06	0,01
Dyract AP	Kompomer	9,10	0,11	9,78	0,07	0,67	0,18	9,33	0,02	0,05	0,04
Enamel Plus HFO	Composite	8,11	0,03	9,67	0,07	1,55	0,05	8,61	0,08	0,12	0,01
Enamel Plus HFO flow	Flow	7,97	0,15	9,09	0,31	1,12	0,16	8,14	0,18	0,03	0,01
Tetric ceram	Composite	8,44	0,14	9,60	0,14	1,15	0,23	8,80	0,12	0,08	0,03
Tetric flow	Flow	8,03	0,06	8,52	0,39	0,49	0,33	8,12	0,10	0,01	0,01
Filtek Supreme	Nano	8,44	0,09	9,65	0,07	1,21	0,13	8,77	0,09	0,08	0,01
exp. Material	Siloran	7,83	0,09	9,45	0,08	1,62	0,15	8,28	0,35	0,11	0,02

3.3. Time of polymerisation

No differences were found between the minimum and inversion point results after 20, 40 and 60 s. The lowest minimum, amount and slope were found after a 20 s-polymerisation. A maximum for these results could be determined after 40 s curing time.

3.4. Polymerisation modus

Starting with comparable minimum results, standard (std) and medical (med) polymerisation resulted in comparable amount and maximum values. Exponential (Ecp) and medical modus resulted in comparable slope results. The inversion point was lowest for the medical polymerisation modus.

3.5. Distance between polymerisation light and sample

Minimum and inversion point showed no differences between the three distances. At the distances 0 mm and 10 mm no differences were found for the amount and maximum of the ion viscosity. In tendency smaller values were found, when the light was positioned 3 mm from the sample. The slope in tendency decreased with increasing distance between light and sample.

3.6. Surrounding temperature

Minimum, maximum and inversion point of the ion viscosity were higher at room temperature, whereas amount of ion viscosity and slope of the graph were lower at room temperature.

3.7. Log ion viscosity

The composites had higher results for all tested variables than their flowable derivatives.

The different materials showed varying results: The highest slope and amount of log ion viscosity was found for the siloran and Enamel Plus HFO, whereas the ormocer CeramX and the compomer Dyract AP provided the lowest slope and lowest differences between minimum and maximum log ion viscosity. The minimum results varied between 7.83 Ωcm (Siloran) and 9.40 Ωcm (Ormocer), whereas the maximum values were higher than 9.45 Ωcm with the only exception Tetric flow (8.52 Ωcm).

4. Discussion

Principally, DEA allows the *in-situ* monitoring of a polymerisation reaction. The tested materials already showed different basic ion viscosity (min). The change of ion viscosity was about one order of magnitude from light

slope ion viscosity

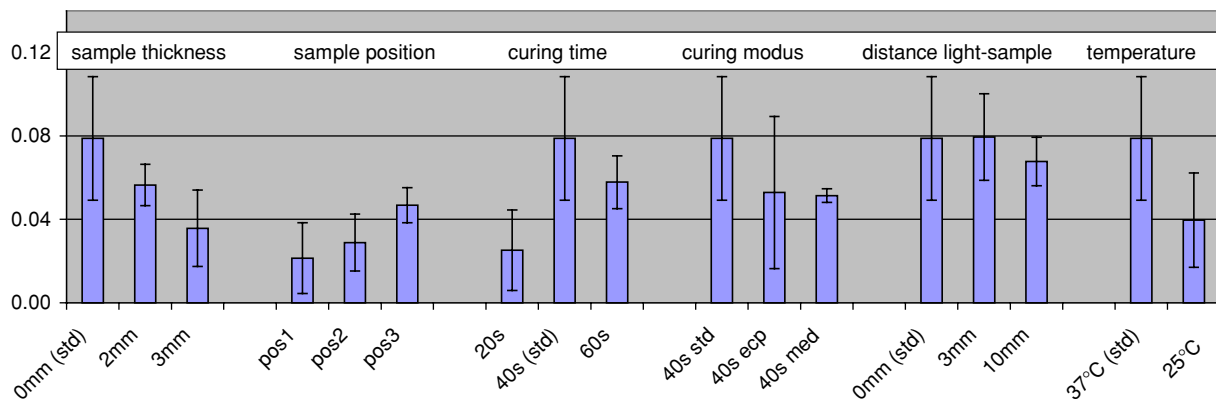


Figure 3 slope log (Ωm) ion viscosity for Tetric Ceram; varying settings.

activating until the end of the reaction. Higher ion changes may not be achieved because of the low percentage of reactive monomer compared to the high composite inorganic filler content of about 80 weight percent. It was obvious, that the polymerisation endured longer than the light exposure, indicating a proceeding polymerisation reaction perhaps combined with a chemical activated reaction. The reaction finally culminated in a maximum horizontal ion viscosity, which should be comparable with a maximum conversion rate between 55 and 75% for light-curing methacrylate systems [20]. These findings match up with results by differential scanning analysis of experimental resin monomers [21]. Whether the approached horizontal maximum of the ion viscosity corresponds with a maximum detectable conversion rate has to be clarified in further investigations.

To guarantee sufficient local light exposure and resulting optimal polymerisation, we reduced the sample size on the sensor to about 20 mm² (diameter polymerisation light: 10 mm), 1/8 of the sensor area. This may have effected the A/D ratio of the capacitor, what may explain that the position of the specimen on the sensor had an influence on the maximum ion viscosity and affinity. Therefore it was essential to position the specimen reproducibly and to cover the whole sensor area to avoid environmental effects. In a control measurement without specimen we found no influence of the mask film on the ion viscosity. Applying the composite without light activation also led to no significant changes of the ion viscosity.

As expected, a relation between the distance light-to-specimen was found. The maximum ion viscosity was not significantly different, but the chart slope (progress of the polymerisation) decreased with increasing distance. This confirmed basic physical considerations, because with increasing distance, the light intensity decreases exponentially [22]. The reaction showed different speed and the light intensity was sufficient to start the polymerisation enduring with a chemical “dark” reaction of the resin. With increasing layer thickness an incomplete curing should be expected.

The time of light exposure affected both, amount of conversion and affinity. There was no linear correlation, but a maximum ion viscosity was found for 40 s light exposure. We only may suppose that this light intensity makes available a high amount of radicals, culminating in an optimum chain reaction. The softstart polymerisation (ecp)—with a stepwise increasing light power—led to a lower conversion and slower reaction. The polymerisation with half light power (med) resulted in a slower reaction, but higher conversion compared to the standard procedure. This results may be explained by the diffusion controlled reaction of the methacrylate polymerisation indicating a relation between light intensity (I_0) and rate of polymerisation (R_p): $R_p \cong (I_0)^{0.5-1.0}$ [21, 23, 24].

Up to a specimen thickness of 3 mm all specimen were completely polymerised, but the thicker the material the slower the reaction. The light penetration through the composite seemed to be hindered by the high content of opaque inorganic fillers. The manufacturer instructions to restrict the polymerisable composite thickness to 2 mm may take that fact into account.

It was evident, that the conversion was higher and the reaction faster with higher surrounding temperature. The reaction at room-temperature started at a 0.6 decade higher level of the ion viscosity, indicating the strong influence of temperature. With a higher temperature, the kinetic constants of a methacrylate reaction typically increases [21]. The higher the temperature, the higher chain- and radical mobility. This allows the reaction to continue for longer times and achieve higher conversions—before the reaction propagation finally becomes diffusion-limited.

To examine the influence of the composite viscosity, two materials were investigated in a standard composition and their comparable “flow”, high viscous alternative. Both flowables showed lower conversion and a slower reaction due to light activation. In contrast to the expectations, the high mobility of the reactive components in high viscous resin systems did not culminate in a higher conversion rate and faster reaction. A different

ratio of diluent resin (e.g. TEGDMA) and basic resin (e.g. bisGMA) may influence the final conversion and reaction affinity [21]. We suppose that different or additional filler and resin components of the “flowable” and “standard” composites may limit the comparison of the materials.

The small distance between the electrodes of 115 μm limited the penetration of the current field into the composite layer. This performance should be preferred when investigating thin films, but a high filler content and filler size or superficial oxygen-inhibition reactions may influence the results. The detach of the composite from the sensor due to polymerisation shrinkage may lead to a falsification of the results and had to be investigated further. Exemplary tests with a monotrode sensor ($\varnothing = 6 \text{ mm}$) showed a deeper field penetration and may be recommended evaluating bulk materials.

FTIR and thermal investigations provide information about the degree of conversion (DC) and the affinity of the exothermal reaction. The FTIR absorptions at 1610 cm^{-1} (C=C methacrylate group) and 1637 cm^{-1} (C=C aromatic ring) were used to determine the DC [25], but a high filler content may disturb the relevant absorption spectra or differences in the often unknown methacrylate composition and silane components may influence the calculation of DC [26]. The sample preparation (grinding and mixing with Kalimubromid e.g.) may limit the validity and may forbid further investigations (hardness e.g.) on the sample. Thermal investigations are influenced by the reactivity of the thermocouple, the heat dissipation and may only be performed inside of bulk materials. The combination of the described experimental procedures with DEA investigation with dielectric analysis would therefore be desirable. A direct comparison of the FTIR and thermal approaches with DEA should be performed in further investigations.

5. Conclusions

In conclusion, dielectric analysis of thin films or bulk layers may give some insight into the light-or chemical activated reaction of dental materials. Detailed basic investigations concerning the influence of fillers and monomer composition had to be performed, perhaps with chemically designed composites.

References

1. O. BALA, A. ÖLMEZ and S. KALAYCI, *J. Oral. Rehabil.* **32** (2005) 134.
2. G. ELIADES, G. VOUGIOUKLAKIS and G. PALAGHIAS, *Dent. Mater.* **3** (1987) 19.
3. M. ROSENTRITT, M. BEHR, A. LEIBROCK and G. HANDEL, *G. J. Mater. Sci. - Mater. Med.* **10** (1999) 91.
4. L. G. LOVELL, K. A. BERCHTHOLD, J. E. ELLIOT, H. LU AND C. N. BOWMAN, *Polym. Adv. Technol.* **12** (2001) 335.
5. H. JUNG, K. H. FRIEDL, K. A. HILLER, A. HALLER and G. SCHMALZ, *Clin. Oral. Investig.* **5** (2001) 156.
6. H. KIM and K. CHAR, *Bull. Korean. Chem. Soc.* **20** (1999) 329.
7. D. KRANBUEHL, S. DELOS, E. YI, J. MAYER and T. JARVIE, *Polym. Eng. Sci.* **26** (1986) 338.
8. J. R. S. HAVRILIAK and S. J. HAVRILIAK, *J. Polym. Sci., Part B: Polym. Phys.* **33** (1995) 2245.
9. F. LIONETO and A. MAFFEZZOLI, *J. Polym. Sci., Part B: Polym. Phys.* **43** (2005) 596.
10. J. Y. SHIEH, H. J. HWANG, S. P. YANG and C. S. WANG, *J. Polym. Sci., Part A: Polym. Chem.* **43** (2005) 671.
11. H. J. HWANG, C. H. LI and C. S. WANG, *J. Appl. Polym. Sci.* **96** (2005) 2079.
12. A. CHERFI, A. F. SANTOS, J. C. PINTO, G. SEYTRÉ, G. BOITEUX, T. F. MCKENNA and G. FEVOTTE, *Chem. Eng. Prog.* **42** (2003) 121.
13. G. GALLONE, S. CAPACCIOLI, G. LEVITA, P. A. ROLLA and S. COREZZI, *Polym. Int.* **50** (2001) 545.
14. Y. HE, DSC and DEA Studies of underfill curing kinetics, *Thermochim. Acta* **367** (2001) 101.
15. C. H. LIN, C. N. HSIAO, C. H. LI and C. S. WANG, *J. Polym. Sci., Part A: Polym. Chem.* **42** (2004) 3986.
16. C. Y. SHIQUE, R. G. S. DOS SANTOS, C. A. BALDAN and E. RUPPERT, *IEEE. T. Appl. Supercond.* **14** (2004) 1173.
17. L. NÚMEZ-REQUEIRA, C. A. GRACIA-FERNANDEZ and S. GÓMEZ-BARREIRO, *Polymer.* **46** (2005) 5979.
18. S. KNAPPE, *Europ. Coat. J. E.C.J.* in press.
19. K. ZAHOUILY, C. DECKER, E. KAISERSBERGER and M. GRUENER, *European. Coatings. Journal. E.C.J.* **11** (2003) 245.
20. B. KALIPCILAR, L. KARAAGACLIOGLU and U. HASAN-REISOGLU, *J. Oral. Rehabil.* **19** (1991) 399.
21. L. C. LOVELL, S. M. NEWMANN and C. N. BOWMAN, *J. Dent. Res.* **78** (1999) 1469.
22. F. A. RUEGGEBERG and D. M. JORDAN, *Int. J. Prosthodont.* **6** (1993) 364.
23. C. DECKER and K. MOUSSA, *Makromol. Chem.* **191** (1990) 963.
24. S. ZHU, Y. TIAN and A. E. HAMIELEC, *Macromolecules.* **23** (1990) 1144.
25. S. IMAZATO, J. F. MCCABE, H. TAUMI, A. EHARA and S. EBISU, *Dent. Mater.* **17** (2001) 178.
26. R. H. HALVORSON, L. E. ERICKSON and C. L. DAVIDSON, *Dent. Mater.* **19** (2003) 327.

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