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Clear and pigmented water epoxy systems: a study on the hardening kinetics on the basis of the variations of the viscoelastic moduli

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Abstract The hardening reaction of a two-can water epoxy polyamide system was investigated on the basis of the variation of the viscoelastic moduli G' and G'' . Unpigmented (clear varnish) and TiO_2 pigmented formulations, at two different TiO_2 concentrations, were taken into account. Time and frequency sweep procedures were carried out using the stress-controlled rheometer Haake RS 150. The behavior of G' and G'' vs time was fitted to a four-parameter asymptotic model through the whole course of the hardening process. Frequency sweep

data, obtained at increasing times during the whole hardening process, were plotted to the generalized Cole and Cole behavior model and the corresponding mechanical spectra were drawn. An interpretation for some aspects of the cross-linking progress is discussed and possible future developments are briefly outlined.

Key words Water-epoxy-systems · Hardening process · Asymptotic model · Generalized Cole and Cole model

Introduction and objective

For the application of traditional paints, both of the protective and decorative types, a conspicuous quantity of volatile organic solvents (VOC) is required, in order to obtain the consistency suitable for the laying-down operations with the various techniques: brushing, traditional and air-less spraying, dipping, etc. The chemical nature of the solvents employed depends, in turn, on the chemical nature of the other paint components, mainly binders and additives. Besides alkanes, VOC often comprise, among others, aromatics, ketones, esters, and glycols; all these substances have a certain degree of toxicity, which may turn out to be harmful to both the paint manufactures and the applicators since, during the film forming process, VOC are released into the atmosphere. VOC contribute to atmospheric pollution.

At present, three main solutions are available to reduce the presence, or even to eliminate, VOC in paint formulation: the use of the so-called high solids coatings, characterized by a VOC content less than 30 wt% in the

ready mixed paint; the water emulsion paints, with a very few percent, if any, of VOC, and, finally, powder coatings, characterized by the total absence of VOC.

Today, water emulsion paints are largely used (Wicks et al. 1992). Among the binders employed in the formulation of water-emulsified coatings, epoxy systems play an important role in producing good properties of the films laid down from them. In the praxis, they are supplied in two separate cans, to be mixed just before use; they are laid down within a pot life in the order of hours, this being strongly dependent on the temperature. Film formation takes place with the reaction of a low molecular weight liquid epoxy resin with an emulsified hardener of the polyaminic and/or the polyamidic types. An exhaustive review on the rheological aspects near the gel point is given in Winter and Mour (1997).

The interest in epoxy systems with resistance against specific destructive agents and with specific properties is still noticeable and exhaustive references on the subject are available. Here mention is made only of patents DE no. 1985 1855.12.5.1999 (Gasche 1998) and JP no.

2000159584 (Kaibara and Miyama 1998), the former describing a method for laying down rapidly walkable cement floors by coating the fresh mortar with epoxy, the latter describing an epoxy-polyamide emulsion paint, that enhances the general resistance of cement-based substrates and prevents degradation by water absorption. The problem of replacing solvent epoxy systems with epoxy water systems is always present (Hedrick et al. 1997). For epoxy coatings see Lapasin et al. (1986, 1987, 1988), Lapasin and Torriano (1988), and Torriano et al. (1997).

This investigation is aimed at bringing a contribution to the knowledge of the flow properties during the hardening process of a system of the water epoxy type that is largely employed for floors and, more generally, for any surface exposed to water and chemicals. The variation of flow properties with the progress of the chemical reaction was followed on the basis of the evolution of the viscoelastic parameters G' and G'' , starting from the mixing of the epoxy component with the hardener, up to when the material could be charged into and removed from the viscometer. Both a clear varnish and pigmented coatings at two different TiO_2 contents were taken into account, in order to conduct a detailed investigation of the viscoelastic behavior of these industrially important products.

Experimental

Materials

The binder used in all formulations was a low molecular weight liquid epoxy resin, modified with glycidyl ether, to be reacted with an emulsified cycloaliphatic amine adduct. The adduct had an NH-equivalent weight of 300 ± 50 , an amine value between 145 mg and 165 mg KOH, a viscosity between 5 Pa.s and 10 Pa.s, a density of 1.080 g cm^{-3} at 20°C , a pH value of 9.8, and a solid content of $55 \pm 2\%$ after 1 h at 135°C . The investigation considered both a non-pigmented system (clear varnish) and systems pigmented with rutile TiO_2 at the weight on weight (w/w) pigment concentration of 4% and 15%, respectively. The pigment used was a rutile titanium dioxide, with a TiO_2 content between 93% and 95%, an $(\text{Al}_2\text{O}_3 + \text{ZrO}_2)$ content between 3% and 5%, a density of 4.1 g cm^{-3} , a sieve residue of 0.01% on a $45\text{-}\mu\text{m}$ sieve, a pH value of 7, and an average particle size of $0.25 \mu\text{m}$. The ratio: 9.2:14.4 for the 100% epoxy resin and the 55 wt% hardener was selected for the binder of both the non-pigmented and the pigmented samples. Pigmented samples were obtained by dispersing the solid phase in a high-speed impeller disperser. The dispersion process was continued up to when the suspended phase contained primary particles and pigment clusters with mean diameters lower than $2\text{--}3 \mu\text{m}$.

Apparatus

The study was performed with a Haake Stress Controlled Rheometer RS 150, equipped with the truncated cone and plate system C 35/2, with a diameter of 35 mm, an angle of 2° , and a gap between the plate and the flat surface of the truncated cone of $137 \mu\text{m}$. This experimental setup allowed no corrections for wall effect to be made even for the pigmented samples, since they

contained primary particles of $0.25 \mu\text{m}$ and particle clusters with average diameters lower than $2\text{--}3 \mu\text{m}$. Indeed, the gap magnitude/particle diameter ratio was higher than 30. Thus it was possible to operate within the linear range for a consistent part of the cross-linking reaction. The temperature was controlled with a Haake F3 thermostat, with a precision of $\pm 0.02 \text{ K}$.

Tests and procedure

Time and frequency sweep tests were carried out to characterize the viscoelastic behavior of the systems considered. Epoxy base, both pigmented and non-pigmented, and hardener were weighed with a Mettler balance, with a precision of $3 \times 10^{-5} \text{ g}$ and subsequently hand-mixed for 1 min in a 100-cc cup with a spatula: Nickel/SS rod, one scraper/spoon end, $6 \frac{7}{16} \text{ in.}$ long, at a speed of $60 \pm 10 \text{ rpm}$ and poured into a 100-cc sealed flask, maintained at the testing temperature. Time sweep tests were accomplished within a time interval between 2.5 min and 4 min, while frequency sweep tests were performed within a time interval of around 3 min. Time sweep tests were repeated at successive times during the hardening process until the consistency of the reacting material still allowed the sample to be charged and removed from the measuring device. Frequency sweep tests were performed immediately after the time sweep tests, on the same charge. All time sweep tests were performed on fresh samples, taken out each time from the flask of the ready mixed product just before testing. To achieve thermal stability, readings started not earlier than 15 min after charging the material into the instrument. For the pigmented systems, tests were performed at 25°C . For the clear system, the testing temperature ranged between 15°C and 35°C . In the time sweep tests, the applied frequency was 6.28 rad s^{-1} and the applied deformation was equal to 0.005. In frequency tests, frequency was varied between 62.8 rad s^{-1} and 0.628 rad s^{-1} and the applied deformation was again 0.005. A 0.005 deformation was selected as a compromise between operating at the lowest strain and obtaining reliable results.

Results and discussion

Time sweep tests

Figure 1 shows a typical behavior of parameters G' and G'' for this class of material. Experimental data were obtained from about 30 min after mixing base and

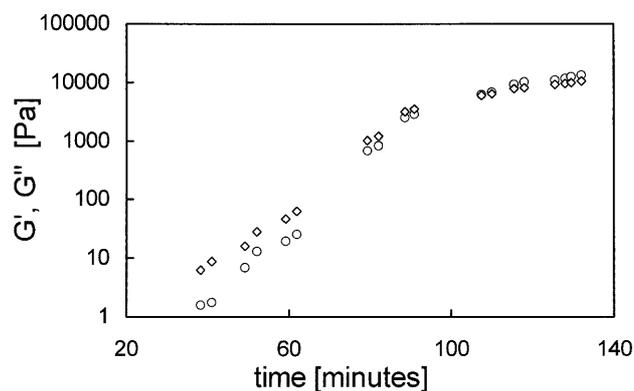


Fig. 1 Typical experimental data obtained from time sweep tests: G' (\circ), G'' (\diamond) at 25°C

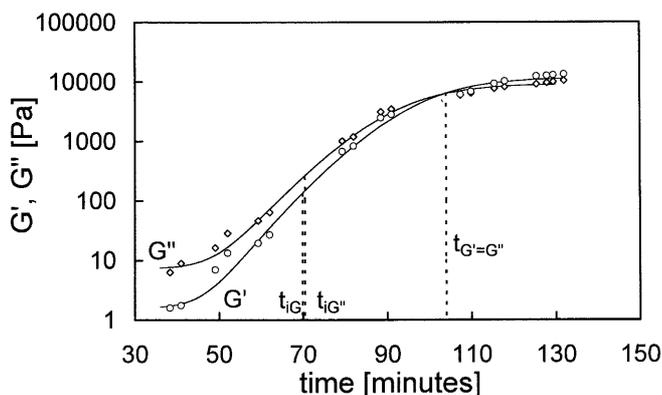


Fig. 2 Application of the asymptotic model (1) to G' (○) and G'' (◇) for a TiO_2 15% pigmented system at 25 °C

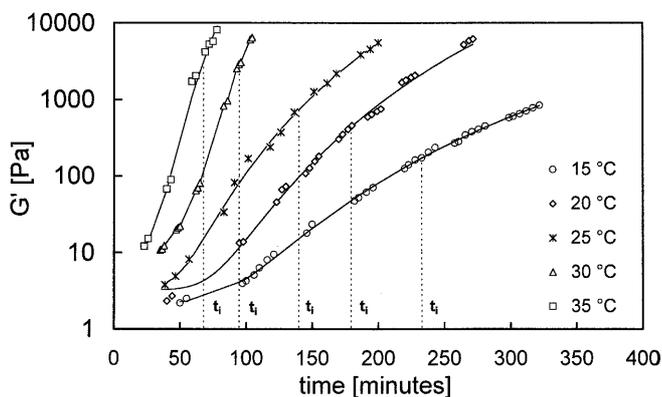


Fig. 3 G' behavior vs temperature for the clear system. Experimental data at 15 °C (○), 20 °C (◇), 25 °C (*), 30 °C (△), 35 °C (□) and asymptotic model application (1)

hardener up to when it was possible to keep the reacting material in the apparatus.

As can be inferred from Fig. 1, initially the reaction rate tend to increase with time; subsequently it decreases and becomes slower and slower. A description of the whole hardening process on the basis of the G' and G'' variations could be obtained for both the moduli (and

the dynamic viscosity) by means of the same asymptotic model that is reported below for the case of G' :

$$G' = G'_\infty - \frac{G'_\infty - G'_0}{1 + \left(\frac{t}{t_{i[G']}}\right)^{n_{[G']}}} \quad (1)$$

Here G'_∞ represents the value of G' at infinite time, G'_0 represents the value of G' immediately after mixing, $t_{i[G']}$ is a system characteristic time, and $n_{[G']}$ is an exponent. The analytic expressions for G'' and η^* are utterly analogous, with the obvious meanings of the relevant parameters. From the equation parameters the corresponding curve inflection times $t_{i[G']}$ and $t_{i[G'']}$ were derived; these two parameters are useful, since they bring out the time of the change of the behavior of the reaction rate. Besides, from the model application, the time $t_{[G'=G'']}$ was evaluated. $t_{[G'=G'']}$ is the time in which the initially lower, but faster growing, G' equals G'' . A typical model application for a TiO_2 pigmented system is shown in Fig. 2.

Model (1) was applied to the clear system, tested at five temperatures. Results obtained for G' vs time are reported in Fig. 3.

Analogous evidences were obtained for G'' and η^* , and are not reported here for the sake of brevity.

The behavior of $t_{i[G']}$, $t_{i[G'']}$, and $t_{[G'=G'']}$ vs the temperature is reported in Table 1 together with the results of a parameter fitting to an exponential law. Table 1 how that $t_{[G'=G'']}$ decreases with increasing temperature, i.e., with increasing temperature the material passes earlier from a condition of prevailing viscous contributions to a condition of prevailing elastic contributions. An analogous decreasing behavior is given by both $t_{i[G']}$ and $t_{i[G'']}$. At 15 °C, 20 °C, and 25 °C the inflection temperatures are lower than $t_{[G'=G'']}$, the inflection occurs in a region of prevailing viscous components, and the differences $t_{i[G']} - t_{[G'=G'']}$ and $t_{i[G'']} - t_{[G'=G'']}$ are negative. The opposite is found at 30 °C and 35 °C; here $t_{[G'=G'']}$ is lower than of $t_{i[G']}$ and $t_{i[G'']}$, the differences $t_{i[G']} - t_{[G'=G'']}$ and $t_{i[G'']} - t_{[G'=G'']}$ are positive, and $t_{i[G']}$ and $t_{i[G'']}$ are longer times than $t_{[G'=G'']}$. This fact shows that the inflection of the curves

Table 1 Clear system, asymptotic model application. Temperature dependence of the parameters $t_{[G'=G'']}$, $t_{i[G']}$, $t_{i[G'']}$, $t_{i[G']} - t_{[G'=G'']}$ and $t_{i[G'']} - t_{[G'=G'']}$ evaluated in minutes and the parameters a and b of their fitting to an exponential model

Temperature	$t_{[G'=G'']}$	$t_{i[G']}$	$t_{i[G'']}$	$t_{i[G']} - t_{[G'=G'']}$	$t_{i[G'']} - t_{[G'=G'']}$
15 °C	317 ^a	233	234	-84	-83
20 °C	210	173.9	179.4	-36.1	-30.7
25 °C	160	127.7	137.7	-32.3	-22.3
30 °C	65	95	95	30	30
35 °C	57	63.1	67.8	6.1	10.8
a	1363	623	615.5		
b	-0.0903	-0.0643	-0.0622		
σ^b	0.2004	0.0396	0.0421		

^a Extrapolated

^b $\sigma = \text{SQRT}[(x_{\text{spcr}} - x_{\text{calc}})^2 / (N_{\text{data}} - n_{\text{param}})^2]$

Table 2 Pigmented systems, 25 °C. Asymptotic model application. TiO₂ dependence of the parameters $t_{[G'=G'']}$, $t_{[G]}$, $t_{[G']}$ evaluated in minutes

TiO ₂ content	$t_{[G'=G'']}$	$t_{[G]}$	$t_{[G']}$	$t_{[G]}-t_{[G'=G'']}$	$t_{[G']}-t_{[G'=G'']}$
0	160	127.7	137.7	-32.3	-22.3
4 wt%	142	103.5	94.2	-38.5	-47.8
15 w%	104	69.9	70.3	-34.1	-33.7

takes place in conditions of prevailing elastic contributions.

The behavior of the model parameters at infinite time G'_{∞} and G''_{∞} (see Eq. 1) vs temperature can be described by means of the Andrade model. The results of the Andrade model application are shown in Fig. 4.

Pigmented systems were tested at 25 °C only. Experimental data were fitted to the asymptotic model given by Eq. (1). Figure 2, reported above as a general example of the behavior of this class of materials, actually gives the results obtained with the 15% TiO₂ pigmented system. As was found for the clear system at 25 °C, for this pigmented systems $t_{[G]}$ and $t_{[G']}$ are also lower than $t_{[G'=G'']}$. They decrease if the TiO₂ concentration is increased. Besides, $t_{[G]}$, $t_{[G']}$, and $t_{[G'=G'']}$ of the pigmented systems are lower than the corresponding parameters of the clear system at the same temperature. The same observation can be extended to the 4 wt% pigmented system. No parameter fitting to models was possible, too few data being available, see Table 2.

A correlation between TiO₂ content and $t_{[G'=G'']}$ is reported in Fig. 5. Very similar results are found for $t_{[G]}$ and $t_{[G']}$ and are not reported here for the sake of readability.

The presence of the pigment plays a simple role in the behavior of these systems. It is beyond the scope of this work to put forward an explanation for the behavior difference between clear and pigmented systems, since this would involve an investigation on the effects of secondary forces, like polar and hydrogen bonding

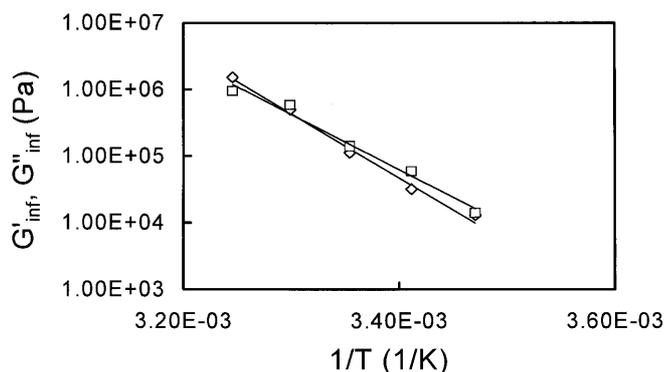


Fig. 4 Linear dependence of parameters G'_{inf} (\diamond) and G''_{inf} (\square) on $1/K$ for the clear system (Andrade behavior)

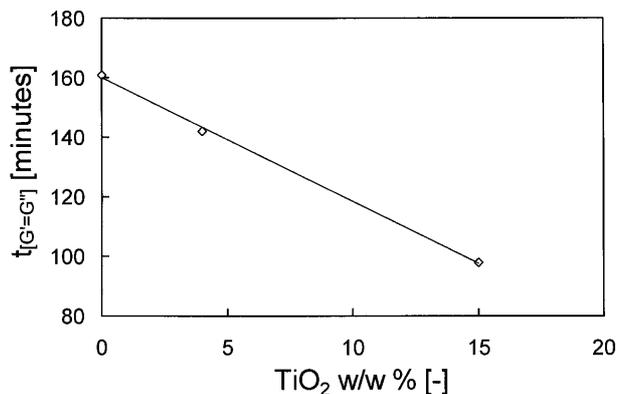


Fig. 5 Linear dependence of $t_{[G'=G'']}$ on the TiO₂ content (\diamond) at 25 °C

forces, which develop between binder and TiO₂, the binder absorption phenomena on the surface of the TiO₂ particle, etc. Nevertheless, it can be emphasized that a comparison between the behaviors of the clear and pigmented systems shows that the trend of G' and G'' with time is quite similar and that the differences found, that are sometimes even strong, are essentially quantitative. Indeed, the presence of the pigment seems not to alter the cross-linking mechanism but acts only on the reaction rate and on the magnitude of the parameters. This is also confirmed by the quantitative effect of the variation of the pigment content. The effect of presence and concentration of pigment on $t_{[G]}$, $t_{[G']}$, and $t_{[G'=G'']}$ are quantitatively important, as is shown by the strong linear dependence of the characteristic times on the pigment content seen in Fig. 5.

Frequency sweep tests

For a more extensive description of the water-epoxy coatings the relevant mechanical spectra were obtained

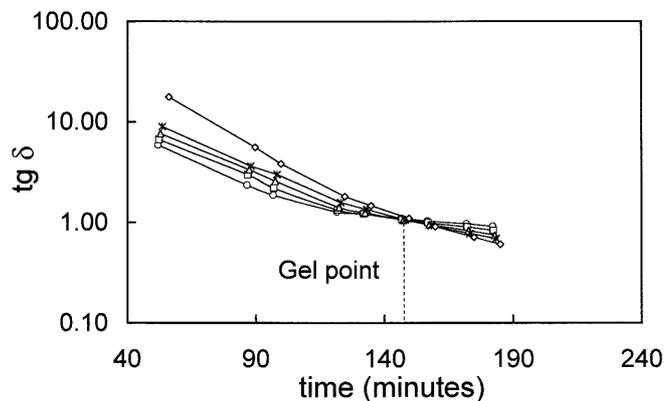


Fig. 6 Gel point for the clear system at 25 °C; at the frequencies of: 0.628 rad s⁻¹ (\diamond), 1.99 rad s⁻¹ (\blacksquare), 6.28 rad s⁻¹ (\triangle), 19.9 rad s⁻¹ (\square), and 62.8 rad s⁻¹ (\circ)

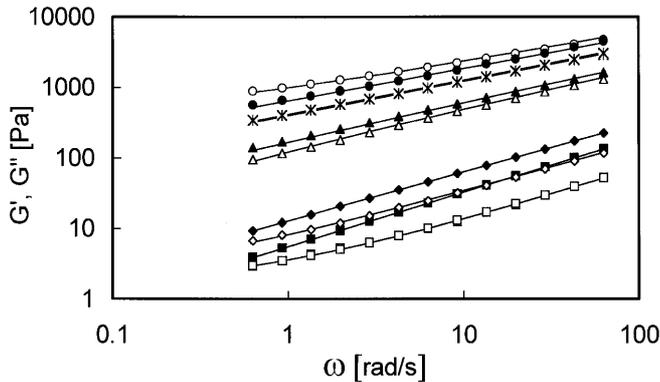


Fig. 7. The application of the Cole and Cole generalized model to the 4% TiO₂ pigmented system. After 44 min: G' (□), G'' (■); after 79 min: G' (◇), G'' (◆); after 114 min: G' (△), G'' (▲); after 137 min: G' (×), G'' (✕) [similar symbols because the lines practically coincide]; after 164 min: G' (○), G'' (●)

in frequency sweep tests. Tests always started immediately after a time sweep test. Since the cross linking reaction brings about transition from a condition of prevailing liquid contributions ($G'' > G'$) to a condition of prevailing solid contributions ($G' > G''$) the gel point (Fig. 6) was determined on the basis of the reaction time in which for a short while $\text{tg } \delta$ is independent of the frequency (Winter and Mour 1997).

It was observed that in all the systems tested the time of the gel point obtained with the $\text{tg } \delta$ method generally coincides with the time $t_{[G'=G'']}$, determined in the time sweep tests; otherwise the differences between the two times are restricted to a few minutes.

Frequency sweep tests showed the same qualitative behaviors at increasing times after mixing at different temperatures and at different levels of pigmentation. Data were fitted to the below-reported generalized Cole and Cole model (Friedrich and Braun 1992):

$$G'(\omega) = G_{\infty} + \Delta G \frac{(\lambda\omega)^d [\cos(d\frac{\pi}{2}) + (\lambda\omega)^c \cos((d-c)\frac{\pi}{2})]}{1 + 2(\lambda\omega)^c \cos(c\frac{\pi}{2}) + (\lambda\omega)^{2c}} \quad (2a)$$

$$G''(\omega) = \Delta G \frac{(\lambda\omega)^d [\sin(d\frac{\pi}{2}) + (\lambda\omega)^c \sin((d-c)\frac{\pi}{2})]}{1 + 2(\lambda\omega)^c \cos(c\frac{\pi}{2}) + (\lambda\omega)^{2c}} \quad (2b)$$

Table 3 Parameters of the generalized Cole and Cole model – clear system, 25 °C

Time	42 min	86 min	121 min	148 min	170 min
G_{inf} [Pa]	0.001	0.0001	0.001	35.24	399
ΔG [Pa]	8.06	24.90	41.873	72.67	95
λ [min.]	1	0.97548	12.4633	78.11	217
c	0.132	0.289	0.350	0.503	0.468
d	0.990	0.990	0.886	0.999	0.946

where G_{∞} is the equilibrium modulus for $\omega \rightarrow 0$, ΔG is a parameter which governs the increment of the both the moduli G' and G'' when ω increases, λ is a time characteristic of the system, and c and d are fractional derivative orders, whose values range between 0 and 1.

All samples were successfully fitted to this model. Figure 7 shows the behavior of the clear system at 25 °C, as an example. The parameters are reported in Table 3.

An inspection of Fig. 7 shows that after 42 min from the mixing, G' is much lower than G'' at all the frequencies tested. After 86 min the difference becomes lower, and it is still lower after 121 min; up to this time liquid components are prevailing. After 148 min G' and G'' have similar values; between the successive frequencies of 6.28 rad s⁻¹ and 0.628 rad s⁻¹ they are equal. This indicates that the reaction is at the gel point. Further on, after 170 min G' is higher than G'' . Here solid components are prevailing. It is emphasized that for the same sample in time sweep tests $t_{[G'=G']}$ falls between 148 s and 149 s.

The Cole and Cole parameters for the clear varnish at 25 °C are reported in Table 3.

The Cole and Cole parameters were fitted to the asymptotic model. Figure 7 reports the behavior of ΔG , λ , and G_{∞} vs time for the 4 wt% TiO₂ pigmented system.

Figure 8 reports the behavior of G' and G'' vs time at three different frequencies during the cross-linking reaction for the clear system. As can be seen from this

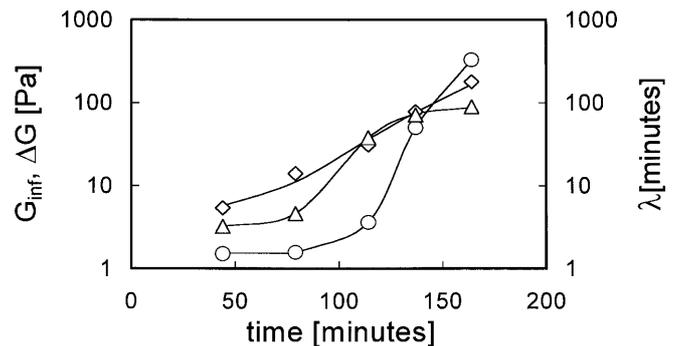


Fig. 8 Asymptotic model application to the behavior vs time of the Cole and Cole model parameters G_{∞} (○), ΔG (△), and λ (◇) for the 4% TiO₂ pigmented system at 25 °C

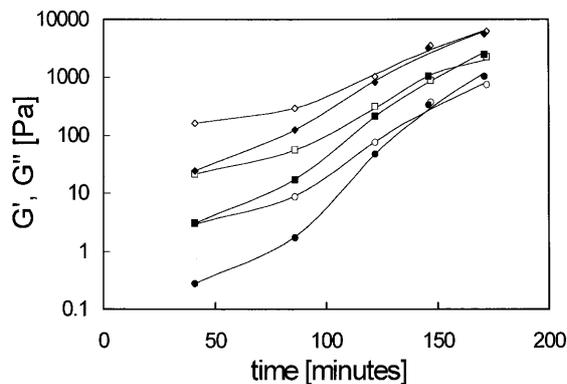


Fig. 9 Asymptotic model application to the behavior vs time of G' (filled symbols) and G'' (blank symbols) at 62.8 rad s^{-1} (\diamond , \blacktriangle), at 6.28 rad s^{-1} (\square , \blacksquare) and at 0.628 rad s^{-1} (\circ , \bullet) for the clear system at $25 \text{ }^\circ\text{C}$

figure, a change in frequency only results in a quantitative effect. The behavior of G'' and of η^* is quite similar and, therefore, not reported. All these behaviors were successfully fitted to the asymptotic model (Fig. 9).

G' and G'' vs frequency data were fitted to a power law. Parameters for the clear system at three temperatures and for the 4 wt% pigmented system at $25 \text{ }^\circ\text{C}$ are reported in Tables 4, 5, 6, and 7.

The parameters of the power law were fitted to an exponential and the relevant plots are reported in Fig. 10.

Final considerations and future developments

The most significant result of this investigation is represented by the identification of an asymptotic

Table 4 Parameters a, b and R-square of the power law for the clear system, $15 \text{ }^\circ\text{C}$

Time	G'			G''		
	a	b	R^2	a	b	R^2
182	6.6939	0.6539	0.9548	10.187	0.8449	0.9896
196	9.4044	0.6857	0.9682	16.34	0.799	0.9944
223	19.93	0.7187	0.9983	44.23	0.6528	0.9999
234	28.19	0.7003	0.9994	56.32	0.6378	1
262	70.88	0.5988	0.9999	107.33	0.5651	0.9998
272	96.69	0.5859	0.9996	136.1	0.5642	0.9998
302	198.2	0.5315	0.9999	233.4	0.5307	0.9996
313	252	0.5162	0.9998	258.5	0.5208	0.9993

Table 5 Parameters a, b and R-square of the power law for the clear system, $20 \text{ }^\circ\text{C}$

Time	G'			G''		
	a	b	R^2	a	b	R^2
95	0.8799	0.9276	0.9813	4.4635	0.84	0.9989
120	5.0723	0.6882	0.9883	13.506	0.7246	0.9976
145	14.784	0.7798	0.9977	38.503	0.6744	0.9999
170	75.884	0.6338	0.9985	126.6	0.5703	1
192	225.63	0.5337	0.9994	257.86	0.4934	1
218	797.71	0.4799	0.9998	731.58	0.5018	1
266	4698.9	0.3581	0.9979	2862.4	0.4522	0.9983

Table 6 Parameters a, b and R-square of the power law for the clear system, $25 \text{ }^\circ\text{C}$

Time	G'			G''		
	a	b	R^2	a	b	R^2
41	0.461	1.008	0.9931	4.4203	0.872	0.9993
86	3.061	0.9029	0.99802	13.375	0.7619	0.9984
121	65.42	0.623	0.9993	105.1	0.562	0.9988
148	427.9	0.4906	1	460.8	0.4881	0.9995
170	12105	0.3979	0.9982	895.9	0.4644	0.9978

Table 7 Parameters a, b and R-square of the power law for the 4 wt% pigmented system, 25 °C

Time	G'			G''		
	a	b	R ²	a	b	R ²
47	3.4475	0.6269	0.9924	5.7057	0.7588	0.9993
82	8.1250	0.6317	0.9992	13.559	0.6749	0.9973
117	123.45	0.5784	0.9996	179.24	0.534	1
140	423.30	0.4686	0.9999	416.75	0.4767	0.9996
167	1011.5	0.369	0.9983	667.20	0.4528	0.9981

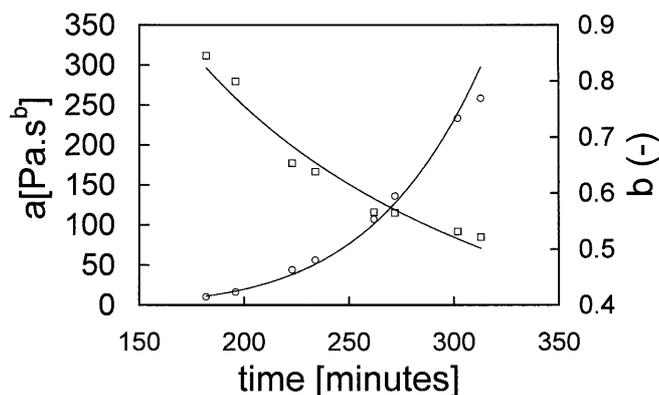


Fig. 10 Exponential plot of the coefficients a (○) and b (□) vs time, G'', clear system, 15 °C

behavior of G' and G'' with an inflection point during the hardening process. Moreover, the gel point evaluated by means of the $\text{tg } \delta$ method from frequency sweep tests and $t_{[G'=G'']}$ obtained from time sweep tests were compared and found coincident in the most cases. The inflection point was determined. For the clear system, at a temperature between 25 °C and 30 °C an inversion in the behavior between the inflection point and $t_{[G'=G'']}$

was found. So the inflection point occurs at the three lower temperatures in a field of prevailing liquid contributions; the opposite occurs at the two higher temperatures. For the pigmented systems, tested at 25 °C only, the behavior was qualitatively similar to that of the clear system at 25 °C; quantitative differences, on the other hand, were appreciable. The influence of the pigment concentration is high, both on the inflection point and $t_{[G'=G'']}$. To obtain the mechanical spectra, recourse was made to the generalized Cole and Cole model as a suitable model to describe the behavior of G' and G'' vs the frequency. Frequency sweep G' and G'' were fitted to a power law. The coefficient a and b were fitted in turn to an exponential with good quality indexes.

Among the possible future developments (study of the effects of different pigmentations, dilution, epoxy/polyamide ratio variations, etc.), one is of the practical type, is immediate, and seems to be attractive. On the basis of the behavior of η^* vs time the pot life of a two-can coating can be evaluated with a very good approximation under different conditions of temperature and in accordance with the type of the laying down apparatus and of the selected procedure.

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