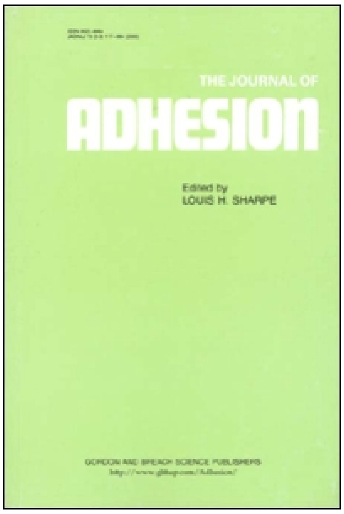

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MONITORING THE SURFACE TENSION OF REACTIVE EPOXY-AMINE SYSTEMS UNDER DIFFERENT ENVIRONMENTAL CONDITIONS

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MONITORING THE SURFACE TENSION OF REACTIVE EPOXY–AMINE SYSTEMS UNDER DIFFERENT ENVIRONMENTAL CONDITIONS

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Two commercially available amine-cured epoxy resin formulations were studied under different environmental conditions with regard to the surface tension evolution using axisymmetric drop shape analysis (ADSA). By employing a new strategy, ADSA was used to monitor simultaneously the surface tension and the density of these reactive mixtures from sessile drops. The kinetics of the bulk reactions were quantified by Fourier transform infrared (FTIR) spectroscopy, and the changes in the molecular composition of the surface region were studied by X-ray photoelectron spectroscopy (XPS).

In both formulations, the surface tension values of the amine hardeners were lower than those of the epoxy resins. For one system, the surface tension of the mixture was similar to the surface tension of the hardener. In this case, the hardener migrates to the surface and determines the surface tension of the mixture, as could be proved by XPS measurements. In the other case, the surface region contained

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only a very small amount of nitrogen, indicating that the nitrogen-containing groups of the hardener were not enriched in the surface region of this mixture. Its surface tension was similar to that of the pure epoxy resin.

In a controlled argon atmosphere, the surface tension of the reactive epoxy–amine systems considered here changed very little as the curing reaction proceeded. The time-dependent changes of the surface tension of the mixtures were caused by environmental factors, particularly the presence of carbon dioxide and water. Such factors can produce complicated surface tension responses due to surface reactions with the amine hardener. The extent of these changes can be controlled by the migration of the hardener to the surface region.

Keywords: Reactive epoxy–amine systems; Surface tension; Axisymmetric drop shape analysis; XPS

INTRODUCTION

Epoxy resin formulations are widely used in various applications such as adhesives, coatings, as matrix materials in fibre-reinforced composites, and in the microelectronic industry. For the end-use properties of these multicomponent materials, interfacial phenomena play a decisive role. The adhesion quality and optical appearance of the coatings are determined by the film-forming process where several factors, such as the rheological behaviour and interfacial properties, interact in a complicated manner. Without going into details, surface tension can be regarded as the *driving force* and viscosity as the *resistance* of wetting and levelling [1–4]. Moreover, surface defects can be caused by surface flow due to local surface tension differences [5].

In the case of fibre-reinforced composites, a spontaneous fibre impregnation can only be obtained when the resin has a low surface tension and wets the fibre surface [6, 7]. In the case of complete wetting, an intimate contact between the fibres and the resin can be achieved, which is a necessary condition for good adhesion and good mechanical properties of composites [8]. Therefore, it is of great practical importance to control and adjust the surface tension of resins. However, only very few reliable surface tension data are available for these materials. One major reason for the scarcity of information is that epoxy resin formulations are complex multicomponent, reactive systems (binder, hardener, additives) which cause difficulties in surface tension measurements. The cross-linking reaction results in an increase of the viscosity and a “freezing” of the resin. Thus, in order to quantify the surface tension, sophisticated measuring techniques are needed.

In previous studies, the influence of several binder parameters (*e.g.*, type, molecular weight, and branching) and the effect of additives on the surface tension of pure resins was studied by means of a modified

Wilhelmy technique [6, 9, 10]. Recently, a new technique based on axisymmetric drop shape analysis (ADSA) was developed [11, 12]. By employing a new strategy, ADSA was used to determine simultaneously the surface tension and the density of polymer melts from sessile drops at elevated temperatures. This method was used to investigate the relationship between the chemical structure of selected levelling additives and their influence on the melt surface tension of non-reactive powder coating binders [4].

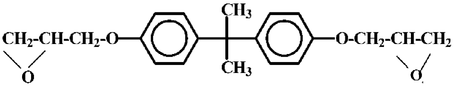
It is the purpose of this study to elucidate the rather complex behaviour of amine-cured epoxy resin formulations. The kinetics of the bulk reactions was studied by Fourier transform infrared spectroscopy (FTIR) and is well known from the literature [13–18]. The network formation results in an increase of the viscosity over time that was quantified by viscosity measurements. In the literature, the surface tension behavior of these systems was explained by the competition between diffusion of molecules with lower surface tension to the liquid–vapor interface and curing reactions of the amine hardener with the epoxy resin [19, 20]. In this article it will be shown that environmental factors also have to be considered and can cause complicated surface-tension responses of these reactive systems. A deeper understanding of these macroscopic interfacial phenomena can be obtained by the additional characterization of the molecular composition of the surfaces by X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL METHODOLOGY AND RESULTS

Materials

Two commercially available products, HT 2 (epoxy resin)/HT 2 (amine hardener) (Bakelite AG, Duisburg-Meiderich, Germany) and L 1000 (epoxy resin)/VE 5194/H (amine hardener) (Bakelite AG), were studied. The mixtures HT 2/HT 2 and L 1000/VE 5194/H are designated as systems *A* and *B*, respectively. Both mixtures are cold-curing, amine-hardening systems. The chemical composition of the resin and the amine is shown in Table 1. It can be seen that the two systems contain different additional components. The main components are bisphenol-A-epichlorhydrin and isophorone diamine (1,3-diamino-3,5,5-trimethyl-cyclohexane).

Bisphenol-A-epichlorhydrin



Isophorone diamine

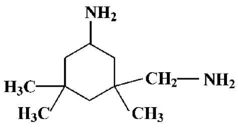


TABLE 1 Chemical Composition of the Individual Components of Reactive Systems *A* and *B*

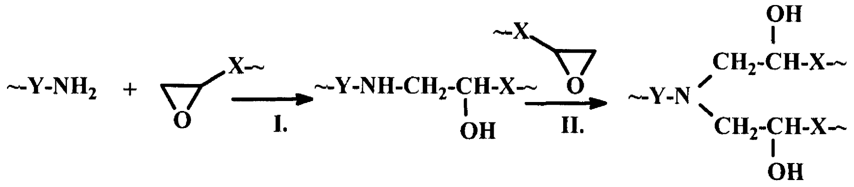
Reactive system	Composition	
	Epoxy resin	Hardener
Epoxy resin HT 2/ Hardener HT 2 (*A*)	bisphenol-A-epichlorhydrin $> 50\%$ (MW = 700 g/mol) epoxy derivate components < 50 wt% (MW = 700 g/mol)	isophorone diamine 50 wt% benzylalcohol 25–50 wt% nonylphenol < 5 wt%
Epoxy resin L 1000/ Hardener VE 5194/H (*B*)	bisphenol-A- epichlorhydrin > 50 wt% (MW = 700 g/mol) C12-C14-alkylglycolether < 50 wt%	isophorone diamine 50 wt% alkyletheramine 25–50 wt%

The weight ratio of epoxy to amine was 2:1 for system *A* and 3:1 for system *B* for all mixtures investigated. This corresponds to an equivalent ratio 1:1 of epoxy to amine groups in the two cases.

FTIR Spectroscopy

FTIR spectroscopy was used to study the chemical bulk reactions of the epoxy–amine systems. Upon the curing reaction epoxy groups disappear while hydroxyl groups develop (Scheme 1).

To determine the kinetics of the curing reaction we used the band at 915 cm^{-1}, which corresponds to the amount of epoxy groups in the mixture. The mixtures were prepared as thin liquid films between two KBr discs and placed on the horizontal sample stage of an IR microscope with the MCT detector attached to a Bruker IFS66 spectrometer (Ettlingen, Germany). Then, the mid infrared transmission spectra were recorded *in situ* as a function of the cross-linking reaction time at 23°C while purging with dry air. One hundred scans per spectrum were performed with a spectral resolution of 2 cm^{-1}. The spectra were normalized to a constant absorbance value A = 0.8 of the aromatic ring band at 1510 cm^{-1}. By dividing the integral absorbance



SCHEME 1 Reaction between epoxy and amino groups.

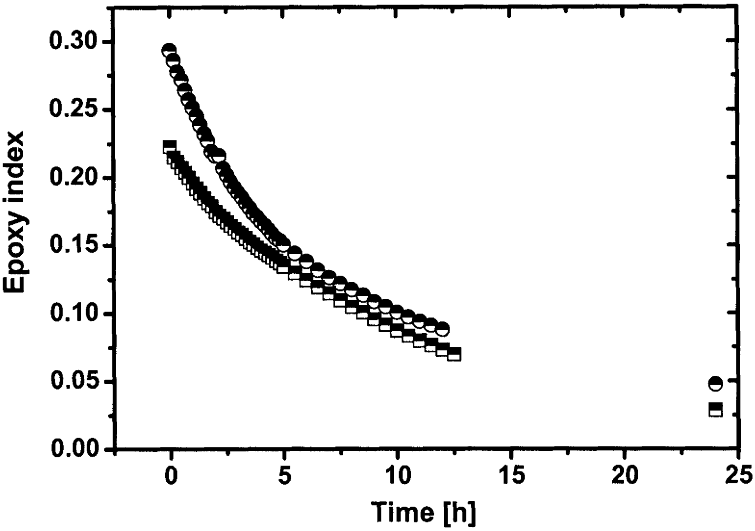


FIGURE 1 Epoxy index evolution (●, system *A*; ■, system *B*) *versus* curing time.

of the epoxy ring band at 915 cm^{-1} by that of the aromatic ring band at 1510 cm^{-1} (*i.e.*, $= A_{915}/A_{1510}$; internal standard) [21], the so-called epoxy index is obtained. Upon curing, epoxy groups disappear, whereas the amount of aromatic rings remains constant. Thus, the epoxy index is an indicator of the concentration of unreacted epoxy groups in the reactive mixture and can be used to describe the curing kinetics of both systems.

Figure 1 shows the change in the epoxy index as a function of the curing time for systems *A* and *B*. It can be seen that the curing kinetics are similar for both systems.

Viscosity

In addition to the chemical changes of the bulk due to the curing reaction, the viscosity of the reactive mixtures will also change with time. Due to the network formation an increase of the viscosity is expected. Therefore, the viscosity of the reactive systems was measured by means of a commercial rotation rheometer (PHYSIKA, Rheolab MC 20, Graz, Austria) at a constant frequency of 1 rad/s at room temperature (23°C). The apparatus is equipped with a disc and plate system (disc diameter of 25 mm; gap width of 2 mm). The results are shown in Figure 2. Up to 1 h both reactive systems have low viscosities of

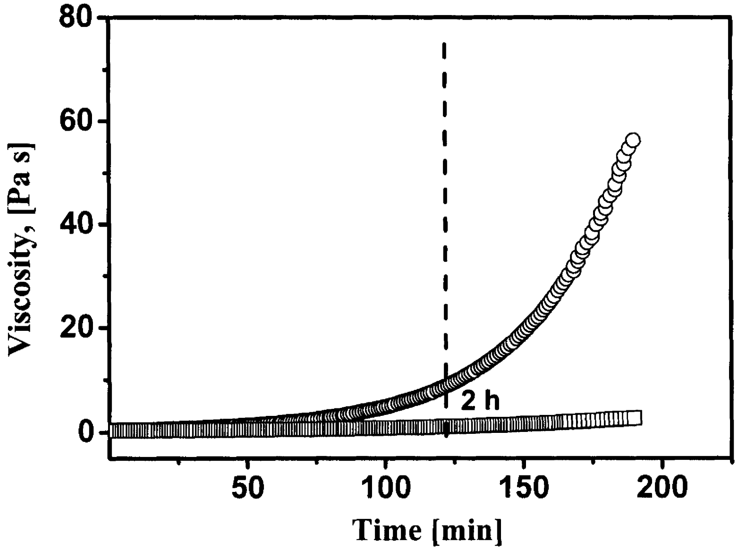


FIGURE 2 Viscosity *versus* time for reactive systems (○, system *A*; □, system *B*).

about 1 Pa.s, comparable with the viscosity of low molecular liquids such as glycerol. Then the viscosity of system *A* increases, reaching a value of about 10 Pa s after 2 h and 50 Pa.s after 3 h, while the viscosity of system *B* remains rather low, with only several Pa.s.

X-Ray Photoelectron Spectroscopy (XPS)

The elemental surface composition of the resins, the hardeners, and the reactive mixtures were studied by XPS. The liquids were placed on a sample holder and spread to a thick film. Then the samples were quickly frozen in liquid nitrogen at −196°C. To record XPS spectra the samples had to be transferred in their deep-frozen state into a separate preparation chamber that was directly connected to an AXIS ULTRA photoelectron spectrometer (KRATOS ANALYTICAL, Manchester, England). Cooling with liquid nitrogen was continued during the whole time of spectrum acquisition. The spectrometer was equipped with a monochromatic Al Kα (h·ν = 1486.6 eV) X-ray source of 300 W at 15 kV.

The results of the XPS measurements are summarized in Table 2. Since nitrogen atoms are unique to the hardener, the ratio of nitrogen to carbon was used as a measure of the concentration of the hardener

TABLE 2 Elemental Surface Composition (XPS Data) of Systems *A* and *B* and Their Individual Components

		Curing time, min	Atomic surface ratios	
			[N]:[C]	[O]:[C]
A	Resin	—	—	0.18
	Hardener	—	0.11	0.07
	Reactive mixture	116	0.10	0.12
B	Resin	—	—	0.09
	Hardener	—	0.17	0.19
	Reactive mixture	120	0.04	0.09

in the surface region of the reactive mixtures. The data show that the surface concentration of nitrogen of the reactive mixture *A* is comparable with the nitrogen content in the surface region of the pure hardener. Thus, it can be concluded that the hardener is enriched in the surface region. In contrast to this result, the surface region of the mixture *B* contains only a very small amount of nitrogen, indicating that the nitrogen-containing groups of the hardener are not enriched in the surface region of this mixture.

ADSA—Density and Surface Tension Measurements Using Sessile Drops

ADSA was used to determine the surface tension of the individual components (epoxy resin and amine hardener) and of the reactive mixtures. Details of the methodology of ADSA have been described previously [11, 12, 22–25]. A modified algorithm of ADSA in which the density was replaced by the mass of the drop as an input parameter was used. Since the ADSA algorithm also yields the drop volume, the density becomes output rather than input. The mass of a sessile drop during the experiment is available since the drop and its holder were placed on a microbalance.

A schematic of the experimental setup is shown in Figure 3. A special chamber, consisting of a sample holder inside a cuvette, was constructed. The sessile drop was formed by deposition of the drop on the top of a small stainless-steel holder (10 mm in height, 5 mm in diameter). The drop spreads to the edge of the sample holder and covers it completely. Hence, the drop is axisymmetric due to the axisymmetry of the holder. The sample holder with the drop was placed onto the microbalance and covered by the cuvette. Typically,

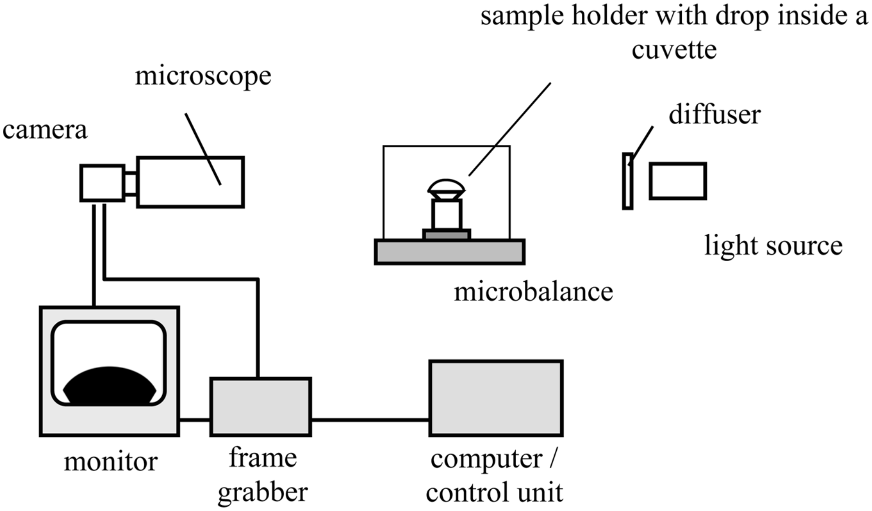


FIGURE 3 Experimental setup for sessile drop measurements.

about 23–24 mg of the component or reactive mixture was used. The mass of the sessile drop was determined simultaneously during the surface tension measurement. Since the mass of the cylinder was known, it was a simple calculation to determine the mass of the mixture. All sessile drop experiments were performed in standard laboratory air conditions (T = 23°C, relative humidity (RH) = 40%). Pictures were acquired at a rate of one picture every 10 s. Mixing of components was performed during 1 min, and the next 8 min were needed for removing air bubbles and placing the drop on the microbalance and weighting. The surface tension was then measured as a function of time.

As stated above, ADSA can be used to determine simultaneously the density and surface tension of liquids. The average density results for resins and hardeners are summarized in Table 3, and the results for the mixtures are summarized in Table 4. The average values of

TABLE 3 Densities of Individual Components of Systems *A* and *B*

System	Component	Mean value of density $\bar{\rho}$ [g/cm^3]
A	epoxy resin HT 2	1.11 ± 0.01
	hardener HT 2	0.97 ± 0.01
B	epoxy resin L 1000	1.14 ± 0.02
	hardener VE 5194/H	0.95 ± 0.01

TABLE 4 Densities of Systems *A* and *B* After Different Times of Curing

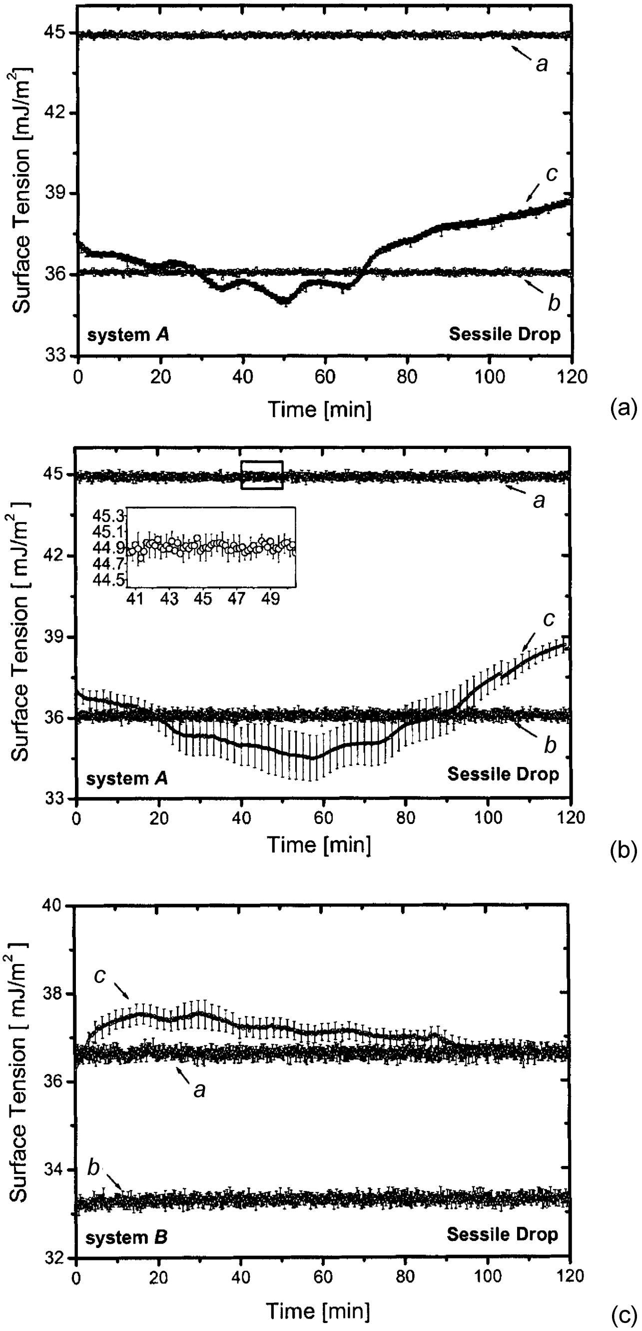
	$\bar{\rho}$ [g/cm^3]		
System	0 h	1 h	2 h
A	1.11 ± 0.01	1.11 ± 0.01	1.11 ± 0.01
B	1.09 ± 0.01	1.08 ± 0.01	1.09 ± 0.01

density at a given time were obtained by averaging the results of eight drops. The densities were averaged over the same pictures that were used for the calculation of surface tensions. The errors for eight drops over the whole time of the experiment are 0.01 g/cm^3 for all samples investigated. Table 4 shows also that the density values did not change with time of curing. The values given in Tables 3 and 4 were used for the calculation of the surface tension.

Figure 4a shows the surface tension for a typical sessile drop experiment of the reactive system *A* (curve *c*) and its individual components (curves *a* and *b* for epoxy resin and amine hardener, respectively) as a function of time. The error bars shown are the 95% confidence limits. The errors are in the range of 0.1–0.3 mJ/m^2 for individual components (epoxy resin, amine hardener) as well as for the reactive mixture. The surface tension was found to be constant over time for the resin and the hardener, and irregular for the mixture. It can be seen that the surface tension of the mixture decreases up to about 60 min and afterwards increases. All experiments were repeated at least eight times. The averages for system *A* are given in Figure 4b. The larger errors of the surface tension of the reactive system (0.4–0.8 mJ/m^2) compared with that of the individual components (0.3–0.4 mJ/m^2) is probably caused by different conditions resulting from the mixing procedure. This procedure described above was necessary before the surface tension experiment could be started.

In Figure 4c the surface tension curves obtained from eight experiments for the reactive system *B* and the corresponding individual components are plotted as a function of curing time. Again, the surface tension is shown to be constant for the epoxy resin and amine hardener and irregular for its mixture.

The reason for the time-dependent changes of the surface tension of the mixtures was not clear. Concentration gradients within the mixtures as well as interactions with the surrounding atmosphere (air) could result in the observed fluctuations of the surface tension. Since the sessile drop experiment could only be carried out under air and not under controlled environmental conditions, we performed pendant


Surface Tension [mJ/m2]
45
42
39
36
33
a
c
b
system A
Sessile Drop
0
20
40
60
80
100
120
Time [min]
(a)
Surface Tension [mJ/m2]
45.3
45.1
44.9
44.7
44.5
41
43
45
47
49
a
c
b
system A
Sessile Drop
Time [min]
(b)
Surface Tension [mJ/m2]
40
38
36
34
32
c
a
b
system B
Sessile Drop
Time [min]
(c)

drop experiments where the influence of the environmental conditions could be studied. The density data required as input were taken from the sessile drop results.

ADSA—Surface Tension Measurements Using Pendant Drops

Figure 5 shows the experimental setup for pendant drop experiments under different environmental conditions. A special chamber was used where the pendant drops could be formed in different atmospheres (argon; humid argon: RH = 80%; and mixtures of argon and carbondioxide) at T = 23°C.

Table 5 summarizes the results for the epoxy resins and the amine hardeners obtained from the pendant drop experiments in different environments and from the sessile drop experiments in air. The surface tension values are mean values obtained from eight experiments with different drops. It can be seen that the surface tension values determined from pendant and sessile drops under air are in good agreement. The values were independent of different environmental atmospheres except for both amine hardeners in an atmosphere containing a mixture of carbon dioxide and argon. In this case, the interaction between the amine hardener and carbon dioxide results in the formation of a skin on the droplets caused by surface reactions. The drop no longer has a Laplacean shape, which meant that the surface tension could not be calculated from the drop profile.

In Figure 6 the averaged surface tension values for the reactive systems *A* (Figure 6a) and *B* (Figure 6b) obtained from the pendant drop experiments under different environments (air, dry argon, and humid argon) are plotted as a function of time. It is clearly seen that different environmental conditions affect the surface tension of the reactive systems. In the inert gas atmosphere (argon), the surface tension of both reactive systems did not change over time. In humid argon, the surface tension increased with time. The experiments in air yielded lower surface tension values for both reactive systems compared with the measurements under dry and humid argon. Similar to the sessile drop experiments, the surface tension changed over time in air.

◀

FIGURE 4 Surface tension *versus* time for sessile drop experiments in air atmosphere: (a) typical sessile drop experiment for reactive system *A* (curve *c* as graph) and its components (a resin, b hardener); (b) averaged curves for reactive system *A* (curve *c* as graph) and individual components (curves *a* and *b* as graph) and (c) averaged curves for reactive system *B* (curve *c* as graph) and individual components (curves *a* and *b* as graph). The error bars are the 95% confidence limits calculated for eight experiments each.

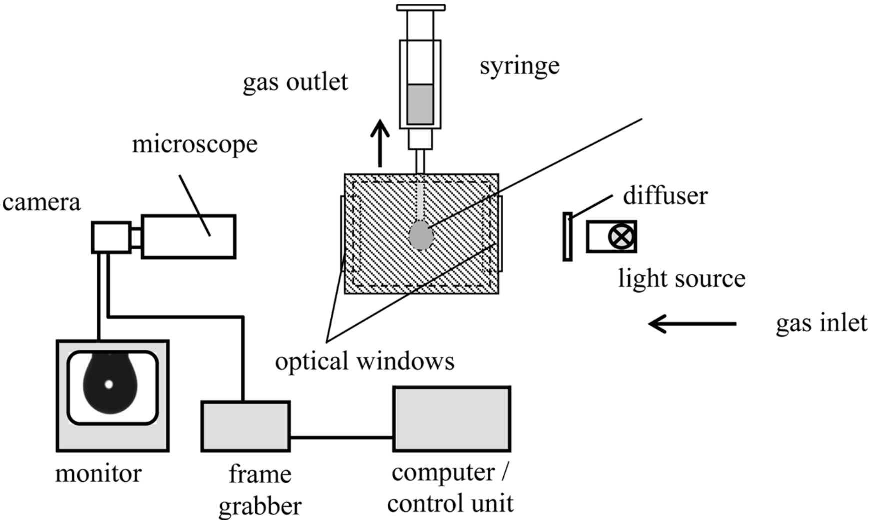


FIGURE 5 Experimental setup for pendant drop experiments under different environmental conditions.

DISCUSSION

The reactive epoxy-amine systems investigated in this study are widely used in ambient-temperature–cured coatings and fibre-reinforced composites. The surface tension results presented above enable one to obtain a more fundamental and quantitative understanding of the interfacial phenomena in these complicated systems. It is well known that wetting of a substrate and levelling of a fluid film strongly depend on the surface tension of the coating. In the case of composites, the flow of the resin into unidirectionally oriented fibres or anisotropically oriented fibre mats and their wetting is also influenced by the surface tension of the resin. For a given solid surface, low surface tension of the resin should improve wetting, which is a necessary condition for good adhesion. Within this context, the above surface tension results obtained for the pure epoxy resins seemingly suggest that better wetting can be achieved with the resin of system B. It has a surface tension of $36.6 \pm 0.35\,\mathrm{mJ/m^2}$, while the surface tension of the pure resin of system A is $44.1 \pm 0.2\,\mathrm{mJ/m^2}$ under ambient conditions. However, the characterization of the whole epoxy resin formulation reveals that this conclusion is misleading.

Since the epoxy resin formulations investigated here are multicomponent systems that also contain amine hardeners, the surface tension of the hardeners has also to be considered. In both systems, their

TABLE 5 Surface Tension Values for the Individual Components (Epoxy Resins, Amine Hardeners) in Different Environment (Measured by Sessile and Pendant Drop Methods)

	Surface tension [mJ/m^2]				
	Air		Argon	Humid argon	CO_2/argon
Component	Sessile drop	Pendant drop	Pendant drop	Pendant drop	Pendant drop
System *A*					
Epoxy resin	44.9 ± 0.40	44.1 ± 0.20	44.6 ± 0.30	44.9 ± 0.35	44.5 ± 0.28
Amine hardener	36.1 ± 0.30	35.7 ± 0.40	35.9 ± 0.20	35.4 ± 0.25	—*
System *B*					
Epoxy resin	36.3 ± 0.40	36.6 ± 0.35	36.3 ± 0.30	36.7 ± 0.35	36.6 ± 0.23
Amine hardener	33.3 ± 0.40	33.3 ± 0.20	33.3 ± 0.25	34.9 ± 0.40	—*

*The surface tension of both hardeners in argon atmosphere containing CO_2 was not measurable due to an irregular drop shape caused by the formation of a skin on the drop surface.

surface tension values were lower than those of the epoxy resins (see Table 5) so that the surface tension values of the mixtures should be somewhere between the values of the resin and the hardener or similar to that of the hardener if the hardener acts as a surface active agent. This was the case for system *A*, where the surface-tension values of the mixture are very similar to the surface tension of the hardener (see Figure 4). The results imply that the hardener migrates to the surface and determines the surface tension of the mixture. This conclusion could be proved by XPS measurements, where a high amount of nitrogen was found in the surface region of the mixture, which was comparable with the N/C ratio at the surface of the pure hardener. In contrast to these results, the surface tension of the mixture of system *B* was similar to that of the pure epoxy resin, as can be seen in Figure 4. The surface region of this mixture contained only a very small amount of nitrogen, indicating that the nitrogen-containing groups of the hardener were not enriched in the surface region of this mixture (see Table 2). Comparison of the two systems shows a slightly higher surface tension for the epoxy–amine system *B*, even though the epoxy resin of system *A* has a much higher surface tension than the epoxy resin of system *B*. These results suggest similar wetting behaviour of both reactive epoxy–amine systems.

The surface tension measurements also revealed a time-dependent behaviour of the surface tension of the reactive mixtures under ambient conditions (Figure 4). Within the time period of 2 h investigated

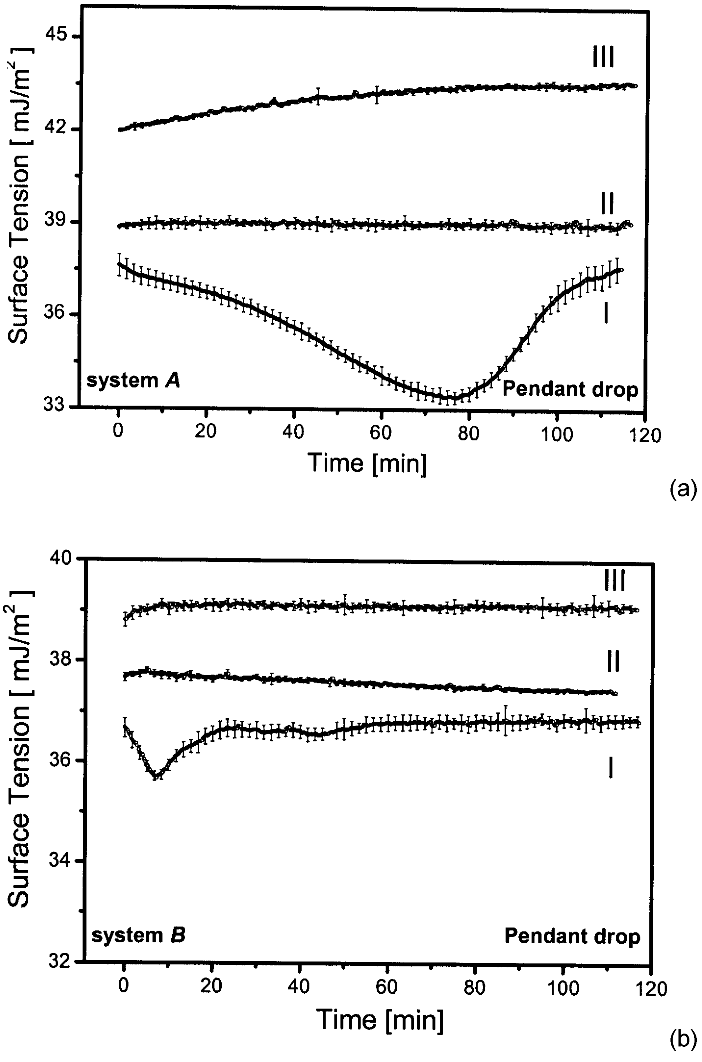


FIGURE 6 Surface tension *versus* time for pendant drop experiments in different atmospheres for reactive systems (a) A and (b) B (I, air; II, dry argon; III, humid argon). The error bars are the 95% confidence limits calculated for eight experiments each.

curing reactions are proceeding in the bulk of the two mixtures (see Figure 1), resulting in a network formation. Since the measured viscosities of one up to several Pa s were rather low in this period of time (Figure 2), we assume that the formation of the shape of the sessile drops may be fast enough to obtain equilibrium shapes necessary for the surface tension measurements. The question was, what are the causes for the time-dependent alteration of the surface tension of the mixtures? Chen *et al.* [19, 20] also monitored time-dependent changes of the surface tension of reactive epoxy–amine mixtures under ambient conditions. They observed a decrease of surface tension at the beginning of the curing reaction, followed by an increase. The changes were explained by a migration of the low energy component (amine hardener) to the surface. If this concept is correct the alteration of the surface tension should occur independent of the environment, either air or argon atmosphere. Our results show that the surface tension of the two reactive epoxy–amine systems was nearly constant as the reaction proceeds when the experiments were carried out in dry argon atmosphere (see Figure 6). From this observation we concluded that the time-dependent changes of the surface tension of the mixtures were caused by environmental factors and not by the segregation of different components of the reactive mixture from the bulk to the surface region. This hypothesis was supported by additional surface tension experiments in humid argon and in argon containing CO_2. Both water and CO_2 are constituents of the air atmosphere under ambient conditions. In the case of humid air, the surface tension of both mixtures was increased compared with dry argon atmosphere (Figure 6). When the experiments were carried out under a mixture of argon and CO_2 a skin was formed at the surface of the drops, preventing a surface tension measurement. The chemistry that is involved when sorption of moisture and carbon dioxide occurs during the curing of epoxy–amine systems is well known and is called “blushing” [26, 27]. The amine compounds used as epoxy curing agents readily scavenge carbon dioxide (and sometimes moisture) from the atmosphere. They react with carbon dioxide to form carbamate zwitterions. In the case of isophorone diamine, the reaction products are insoluble in the amine and result in the formation of a skin. The addition of water strongly increases the sorption capacity and rate.

Since “blush” formation is associated with carbon dioxide sorption by the amine, a decrease of the amine group concentration in the surface region should also decrease the tendency of a formulation to “blush.” In our study, this behaviour was observed in the case of the reactive mixture *B*. Here, the nitrogen-containing groups of the hardener were not enriched in the surface region so that the extent of the surface reactions described above was limited. This was concluded from the observed time-dependent changes in the surface tension under ambient conditions. These changes were less pronounced for the reactive mixture *B*. For system *A*, where the hardener was enriched in the surface region, the surface tension response caused by the surface reactions between the hardener and carbon dioxide was more pronounced. In dry argon, the surface tension was constant for both reactive systems. In this inert gas atmosphere, no surface reactions can take place. Hence, surface tension measurements can be used to monitor surface reactions of epoxy–amine systems. With respect to an increase of the surface tension of both reactive mixtures under humid argon atmosphere, we suggest chemical reactions between the epoxy resin and water, resulting in a hydrolytic splitting of the oxirane ring and the formation of hydroxyl groups.

CONCLUSIONS

1. Surface tension and density in reactive epoxy–amine systems can be determined simultaneously by ADSA.
2. The surface tension of the epoxy resin and the hardener components are not necessarily a measure for the surface tension of the mixture, *i.e.*, the reactive system.
3. Surface tension in such systems can be sensitive to environmental factors, particularly the presence of carbon dioxide and water vapour. Such factors can produce complicated surface tension responses.
4. In a controlled argon atmosphere the surface tension of the reactive epoxy–amine systems considered here changes very little as the curing reaction proceeds.

REFERENCES

[1] DeLange, P. G., *J. Coat. Technol.* **56**, 23–33 (1984).
[2] Orchard, S. E., *Prog. Org. Coat.* **23**, 341–350 (1994).
[3] Misev, T. A., *Powder Coatings Chemistry and Technology* (John Wiley & Sons Ltd., Chichester, UK, 1991).
[4] Wulf M., Uhlmann, P., Michel, S., and Grundke, K., *Prog. Org. Coat.* **38**, 59–66 (2000).
[5] Bierwagen G. P., *Prog. Org. Coat.* **19**, 59–68 (1991).
[6] Grundke, K., Uhlmann, P., Gietzelt, T., Redlich, B., and Jacobasch, H.-J., *Colloids Surf.* **116**, 93–104 (1996).
[7] Mäder, E., Grundke, K., Jacobasch, H.-J., and Wachinger, G., *Composites* **25**, 739–744 (1994).
[8] Pocius, A. V., *Adhesion and Adhesive Technology: An Introduction*, 2nd ed. (Hanser Gardner, New York, 2002).
[9] Uhlmann, P., and Grundke, K., *Farbe Lack* **102**, 48–55 (1996).
[10] Grundke, K., Michel, S., and Osterhold, M., *Prog. Org. Coat.* **39**, 101–106 (2000).
[11] Wulf, M., Michel, S., Grundke, K., Del Rio, O. I., Kwok, D. Y., and Neumann, A. W., *J. Colloid Interface Sci.* **210**, 172–181 (1999).

[12] Wulf, M., Michel, S., Jenschke, S., Uhlmann, P., and Grundke, K., *PCCP, Phys. Chem. Chem. Phys.* **1**, 3899–3903 (1999).

[13] Rozenberg, B. A., *Adv. Polym. Sci.* **75**, 113–165 (1985).

[14] Mijovic, J., Fishbain, A., and Vijova, J., *Macromolecules* **25**, 979–985 (1992).

[15] Dusek, K., *Adv. Polym. Sci.* **78**, 1–59 (1986).

[16] Matejka, L., *Macromolecules* **33**, 3611–3619 (2000).

[17] Dean, K., Cook, W. D., Rey, L., Galy, J., and Sautereau H., *Macromolecules* **34**, 6623–6630 (2001).

[18] Cheng, Y.-C. and Chiu W.-Y., *Macromolecules* **33**, 6672–6684 (2000).

[19] Chen, D. and Pascault, J. P., *Macromol. Chem.* **192**, 867–882 (1991).

[20] Chen, D. and Pascault, J. P., *Macromol. Chem.* **192**, 883–889 (1991).

[21] Cole, K. C., Pilon, A., Noel, D., Hechler, J.-J., Chouliotis, A., and Overbury, K. C., *Appl. Spectroscopy* **42**, 761–770 (1998).

[22] Lahooti, S., Del Rio, O. I., Cheng, P., and Neumann, A. W., *Applied Surface Thermodynamics*, A. W. Neumann and J. K. Spelt, Eds. (Dekker, New York, 1996), Vol. 63, Chap. 10, pp. 441–505.

[23] Rotenberg, Y., Boruvka, L., and Neumann, A. W., *J. Colloid Interface Sci.* **93**, 169–183 (1983).

[24] Cheng, P., Li, D., Boruvka, L., Rotenberg, Y., and Neumann, A. W., *Colloids Surf.* **43**, 151–167 (1990).

[25] Del Rio, O. I. and Neumann, A. W., *J. Colloid Interface Sci.* **196**, 136–147 (1997).

[26] Croll, S. G., *J. Coat. Technol.* **58**, 41–49 (1986).

[27] Bell, J. P., Reffner, J. A., and Petrie, S., *J. Appl. Polym. Sci.* **21**, 1095–1102 (1977).