JOURNAL OF MATERIALS SCIENCE **38** (2003) 413–420

Vinylester/epoxy-based thermosets of interpenetrating network structure: An atomic force microscopic study

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The morphology of vinylester (VE) and epoxy (EP) resins, and their combination (VE/EP at a ratio 1/1) was studied by atomic force microscopy (AFM). AFM scans taken on the ion-etched surface of EP showed a featureless homogeneous structure. On the other hand, VE exhibited a two-phase microgel, whereas VE/EP a two-phase interpenetrating network (IPN) structure. A vinylester-urethane hybrid resin (VEUH) showed also the formation of an IPN-like morphology. It was concluded that cross-reactions between the hydroxyl functionality of VE and additional functional groups, such as isocyanate in VEUH or epoxy in VE/EP combinations, strongly favour the IPN formation. AFM scans revealed the compaction of the IPN structure of VE/EP upon post-curing which was associated with a prominent increase in the glass transition temperature (T_g) according to dynamic-mechanical thermal analysis.

1. Introduction

Similarly to thermoplastics, the dispersion-type morphology strongly affects the toughness response also of thermosetting resins. The role of the modifier particles, produced either by phase segregation during curing or incorporated in preformed shape, is to relieve the triaxial stress state in the crack tip upon loading. Just after that, however, the matrix deformability will be the key toughness controlling parameter. It was early recognised that the crosslink-density of the resin influences the toughness. Further, the theory of the rubber elasticity can be adopted also for thermosets. Accordingly, the fracture energy changes linearly with the square root of the mean molecular mass between crosslinks. It has been proved for both vinylester- (VE) [1] and epoxy resin (EP)-based ([2] and references therein) systems. Reduced crosslinking degree is associated with lowering of the T_g and stiffness. However, to keep these parameters on a high level is of paramount importance for many applications. There is a third possibility to improve the toughness of thermosets: creation of interpenetrating network (IPN) structure. This became under spot of interest only recently for VE/EP combinations [3–6]. For the presence of an IPN structure usually indirect evidences were listed. The reason behind this fact is obvious: unlike to thermoplastic blends selective chemical etching can not be used to remove the one or other phase in thermosets. On the other hand, a deeper understanding of the IPN structure and its development would be very helpful for further material development. It is therefore indispensable to find a direct way for the detection of IPN. Atomic force microscopy (AFM) seems to be a suitable tool for that purpose provided that a suitable "etching" technique can be found. So, this work was aimed at studying the morphology of VE/EP resins with a supposed IPN structure using the technique of AFM. In order to get a more complete picture this work was extended for VE, vinylester-urethane hybrid (VEUH) and EP resins, as well.

2. Experimental

2.1. Resins and their curing

In this study the following thermosetting resins were involved: commercial VE, commercial VEUH, various EP and proprietary VE/EP (1/1) [7] formulations. The commercial VE (bisphenol-A based bismethacryloxy type) was a product of DSM Composite Resins (Daron® XP-45-A-2; styrene content: 30 wt%, ratio of the double bonds VE/styrene = 1 : 1.2). For its curing 0.75 phr (parts per hundred resin) dibenzoylperoxide, and 0.15 phr N,N-diethylaniline as accelerator were used. In case of VEUH 38 phr polyisocyanate (Daron® XP-40-B-1, NCO functionality: 2.7, from DSM Composite Resins) was added to the above VE composition. Note that VE copolymerises with styrene, while in VEUH an additional crosslinking mechanism, namely the reaction between the secondary —OH group of VE and —NCO group of a polyisocyanate, takes place [8–10].

The EP resins selected for this study were of aliphatic (Al) and cycloaliphatic (Cal) type. As aliphatic (Al-EP)

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1,4-butandioldiglycidylether and as cycloaliphatic EP (Cal-EP) 1,6-cyclohexanedimethanoldiglycidylether (Polypox R3 and R11 respectively from UPPC) served. Al-EP was cured by a cycloaliphatic diamine (Cal-Am) procured from Vantico Ltd. (HY2954 grade: 2,2′-dimethyl-4,4′-methylenbis(cyclohexylamine)), whereas Cal-EP with an aliphatic diamine (Al-Am) purchased from Aldrich (1,2-bis(2-aminoethoxy)ethane). Note that these EP formulations yielded the highest toughness values when combined with VE [11]. The hardener/EP ratio was stoichiometric in all EP formulations.

The cure regime (except VEUH) of the plaques produced in an open PTFE-mould was as follows: room temperature for 12 hours, 80°C for 3 hours and 150°C for 3 hours. In same cases a further post-curing step was also inserted (200°C for 3 hours) in order to check a potential improvement in T_g. In case of VEUH the room temperature curing (12 hours) was followed by the following sequence: 80°C for 30 min, 140°C for 30 min and 200°C for 1 hour. Further information to the preparation of the resins and their curing is given in our previous papers [6, 9–11].

2.2. Material characterisation

The resins were characterised by dynamic-mechanical thermal analysis (DMTA). DMTA spectra were taken on rectangular specimens (50 × 10 × 4; length × width, thickness) in flexural mode at 10 Hz using a Eplexor 25N device of Gabo Qualimeter. DMTA spectra, viz. complex modulus (E*) and its constituents (E′ and E″), mechanical loss factor (tan δ) as a function of temperature (T), were measured in the interval $T = -100$ to +200°C (in case of VEUH the upper threshold was set for 300°C) a heating rate of 1°C/min. More fundamental information on the morphology of the VE, VEUH, EP and VE/EP systems was expected from atomic force microscopic (AFM) studies. Polished surface of the specimens was eroded by Ar^+ ion bombardment. This occurred in a secondary neutron mass spectrometer (INA3 of Leybold) working at 500 eV energy. The beam was focused perpendicular to the polished surface of the specimen. The overall ion dose was 1.9×10^{18} Ar^+/cm^2 which resulted in a surface roughening of ca. 200 nm (see later). The surface profile was scanned by AFM (Digital Instruments) in tapping mode and the related amplitude- and height-contrast images captured.

3. Results and discussion

Fig. 1 depicts the mechanical loss factor vs. temperature (tanδ-T) traces for the VE and VEUH resins, respectively. One can notice a strong shift in the α-relaxation peak (T_g) towards higher temperatures. Recall that this shift is due the "polyurethane chemistry" applied, i.e. the additional crosslinking between the secondary —OH of the VE and —NCO group of the polyisocyanate compound. The AFM scans for these resins are displayed in Fig. 2a and b. Fig. 2a clearly shows the nodular structure (also called microgel) of the VE. Accordingly, VE exhibits a two-phase structure. More or less spherical VE nodules are dispersed in a polystyrene (PS) matrix. The size of the VE nodules is mostly in the range of 60–80 nm. The presence of such a two-phase dispersion was shown also by Mortaigne *et al.* [12] who used laser ablation for the "physical etching" of VEs. The morphology of VEUH strongly differs from that of the VE (see Fig. 2b). Instead of nodules greater interconnected domains are present in VEUH which looks like as an IPN structure. Nevertheless, the mean size of the ribbon-like entities agrees with that of the VE nodules. Recall that the only difference between VE and VEUH is the onset of an additional crosslinking reaction in the latter resin. The reaction between the secondary —OH of VE and —NCO of polyisocyanate should preferentially occur between two VE molecules (intermolecular reaction connecting two nodules) which triggers the formation of an IPN-like structure. A further indication for the onset of an IPN-like structure in VEUH delivers

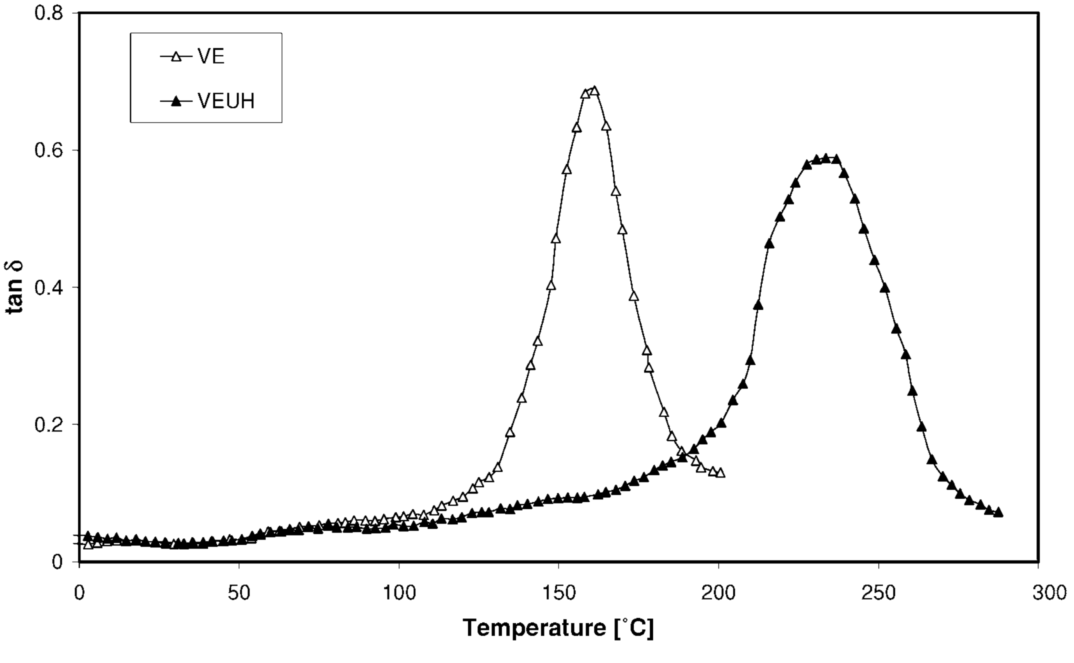
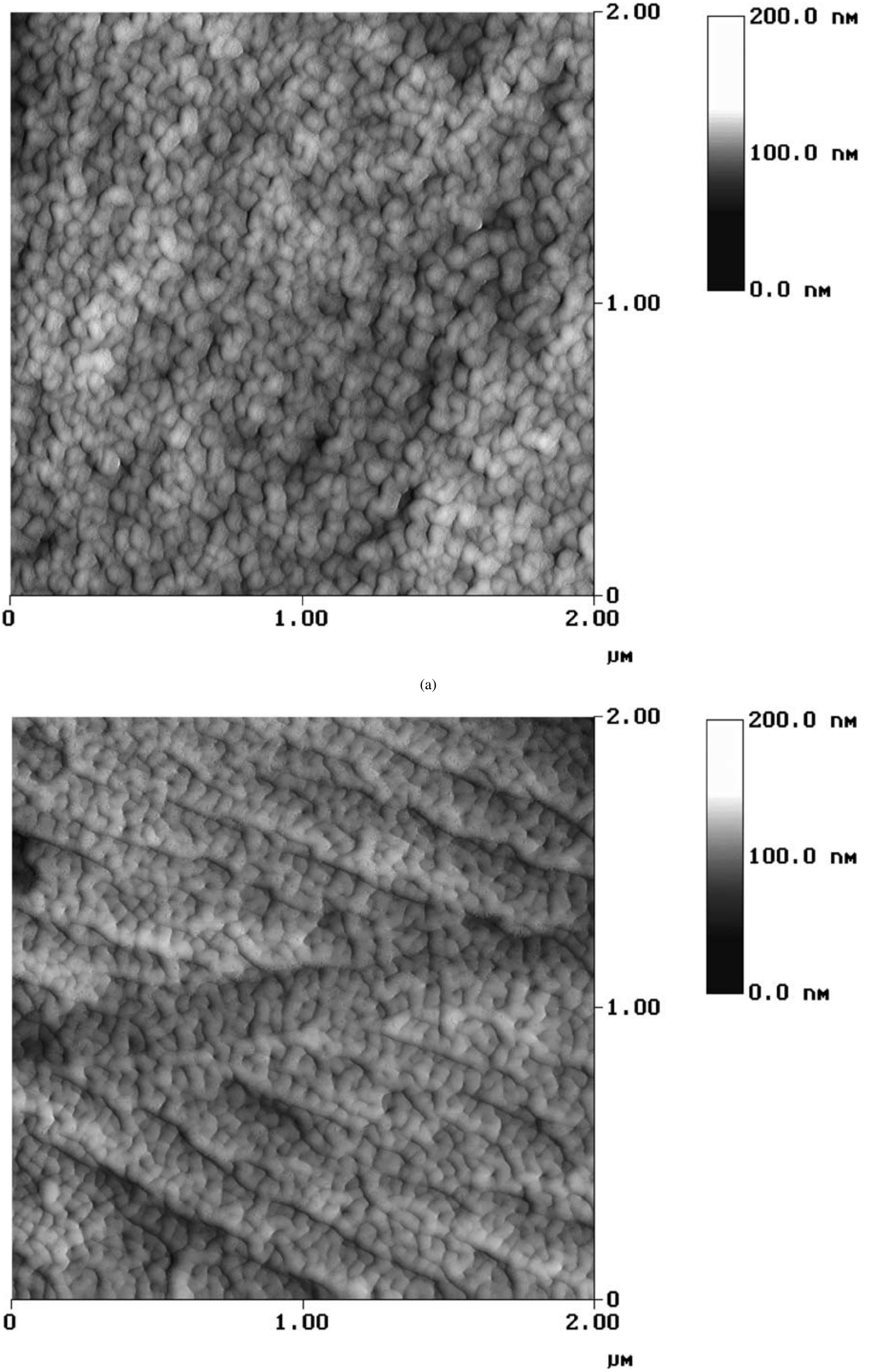


Figure 1 tanδ vs. T traces for the VE and VEUH resins.



(a)

(b)

Figure 2 AFM pictures (height images) taken on the ion-etched surface of VE (a) and VEUH (b) resins.

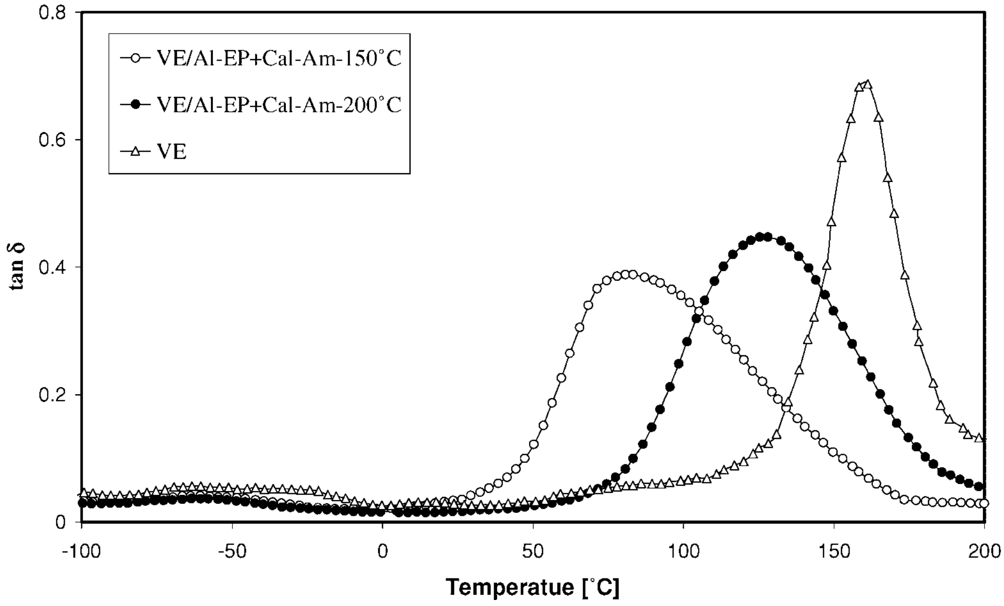
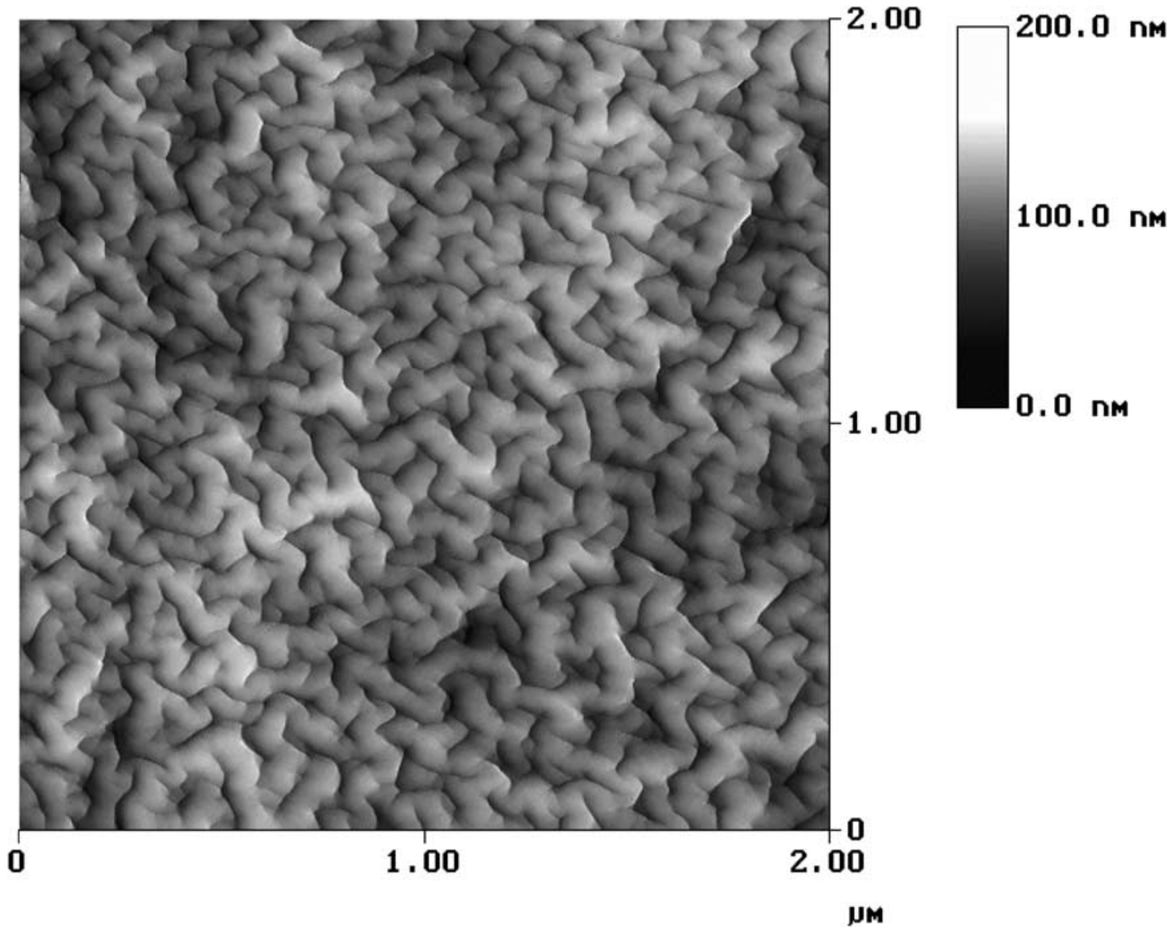


Figure 3 tanδ vs T traces for VE/Al-EP + Cal-Am (1/1) after curing at max. $T = 150$ and $=200$°C, respectively. (Note: This figure contains the related trace of VE for comparison purpose.)

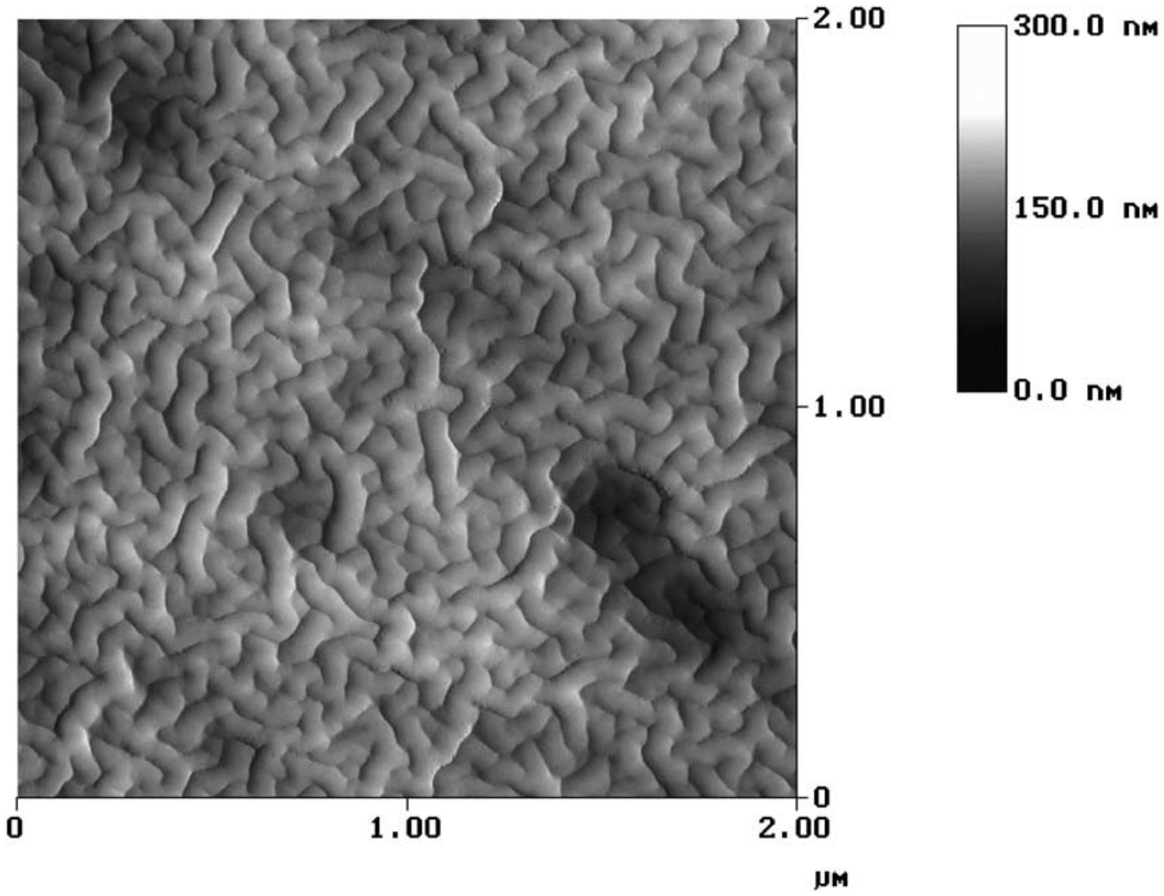
the comparison of the tanδ-T traces in Fig. 1. When VE nodules are present in a PS matrix then one would expect a T_g not far from that of PS. This is the case, in fact, in Fig. 1. The high T_g of VEUH can be assigned to the formation of the above discussed IPN-like structure in which the VE forms a more or less continuous phase.

Fig. 3 displays the tanδ-T traces for the VE/Al-EP + Cal-Am combination cured at $T = 150$ and $=200$°C, respectively. For comparison purpose the related traces of VE is also indicated. Note that the α-relaxation (T_g) peak shifts towards higher temperatures owing to post-curing. In case of an IPN structure one would expect a doubling or at least a rather complex shape in the T_g peak. In contrast, a single α-peak was often reported for thermosets with an IPN structure. So, the tanδ-T trace can hardly evidence the presence of



(a)

Figure 4 AFM pictures (height images) taken on the ion-etched surface of VE/Al-EP + Cal-Am after curing at max. $T = 150$ (a) and $=200$°C (b). (*Continued.*)



(b)

Figure 4 (*Continued*).

IPN. This IPN structuring becomes, however, obvious in the height-contrasted AFM pictures in Fig. 4. One can see that the IPN structure become more compact due to post-curing. This compaction is accompanied with a higher resistance to Ar^+ ion bombardment. Accordingly, the surface roughness should decrease with increasing curing temperature. This is not evident when comparing Fig. 4a and b due to a deep area (see black region) in Fig. 4b. Note that this micro structural compaction upon post-curing rises the T_g (see Fig. 3). The mean width of the IPN constituting ribbons is still in the same range (i.e. 60–80 nm) as found for VE and VEUH. This means that the EP phase has been selectively removed by ion etching and the more stable VE remained.

Fig. 5 shows the tanδ-T traces for the VE/Cal-EP + Al-Am systems cured at $T = 150$ and $=200$°C, respectively. Again, the shift in the T_g peak toward

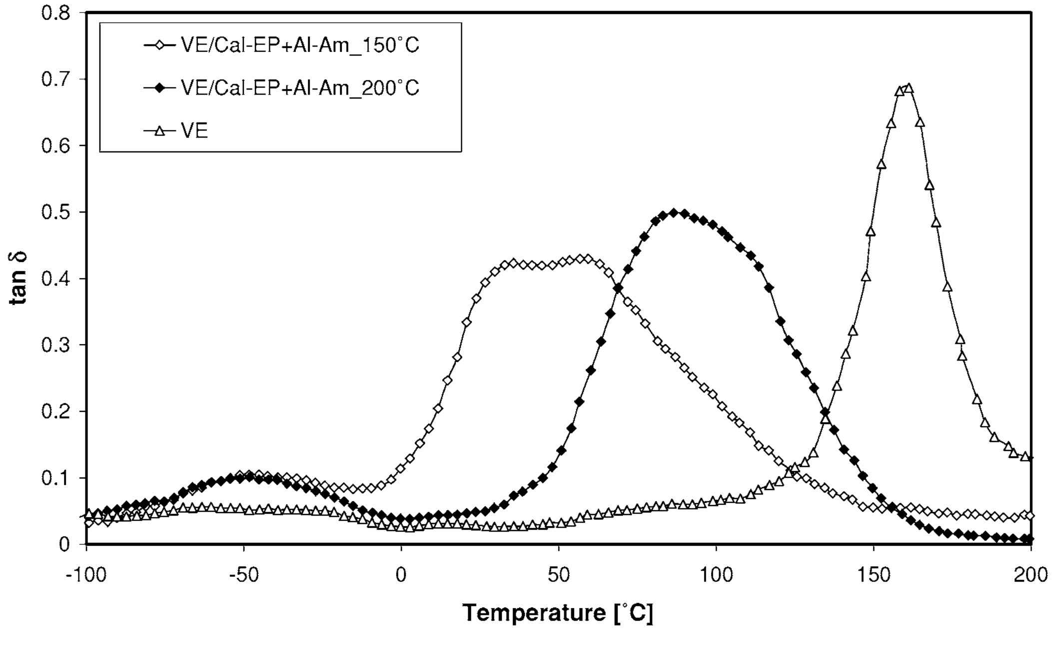


Figure 5 tanδ vs T traces for VE/Cal-EP + Al-Am (1/1) after curing at max. $T = 150$ and $=200$°C, respectively. For note cf. Fig. 3.

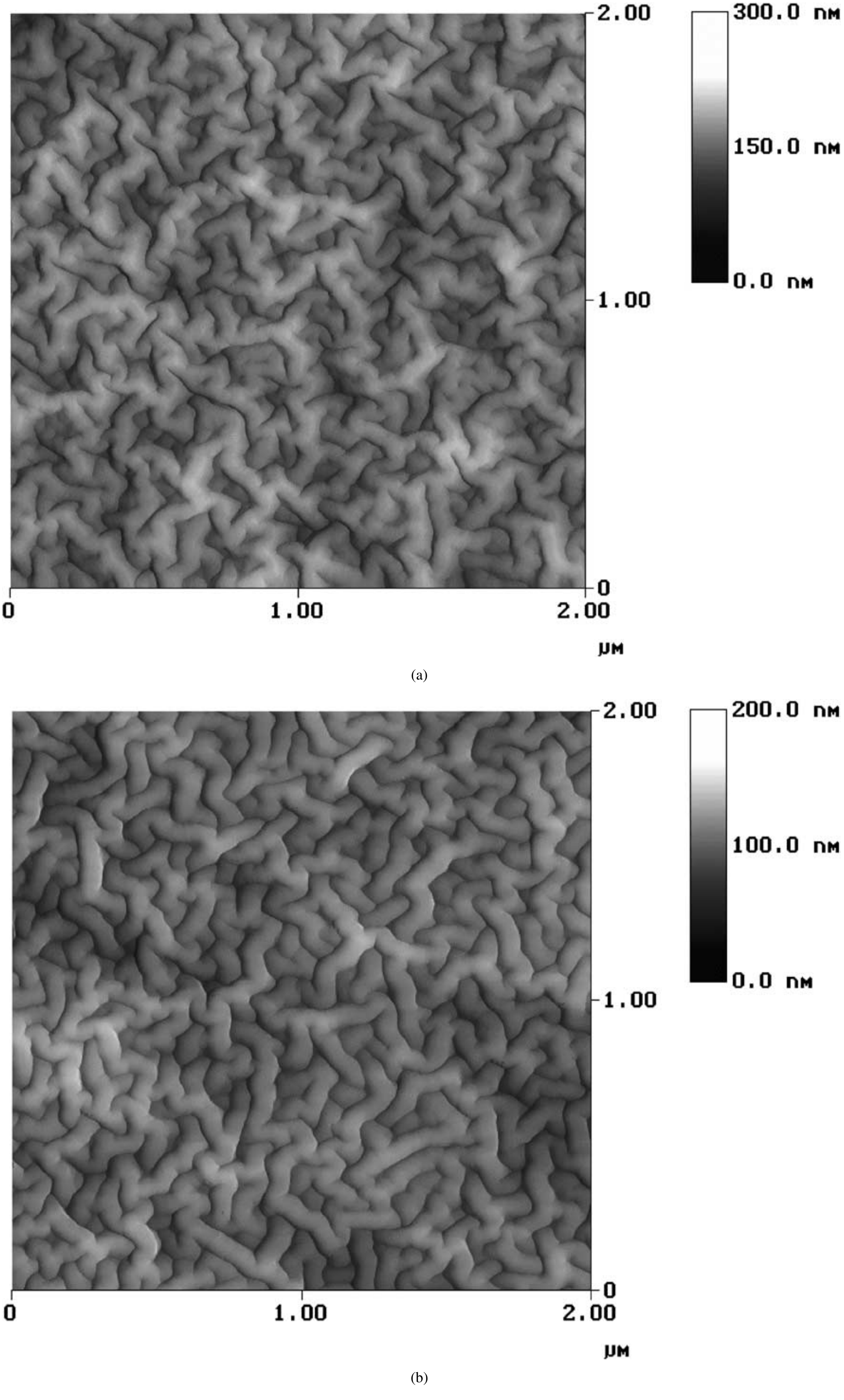


Figure 6 AFM pictures (height images) taken on the ion-etched surface of VE/Cal-EP + Al-Am after curing at max. $T = 150$ (a) and $= 200°\mathrm{C}$ (b).

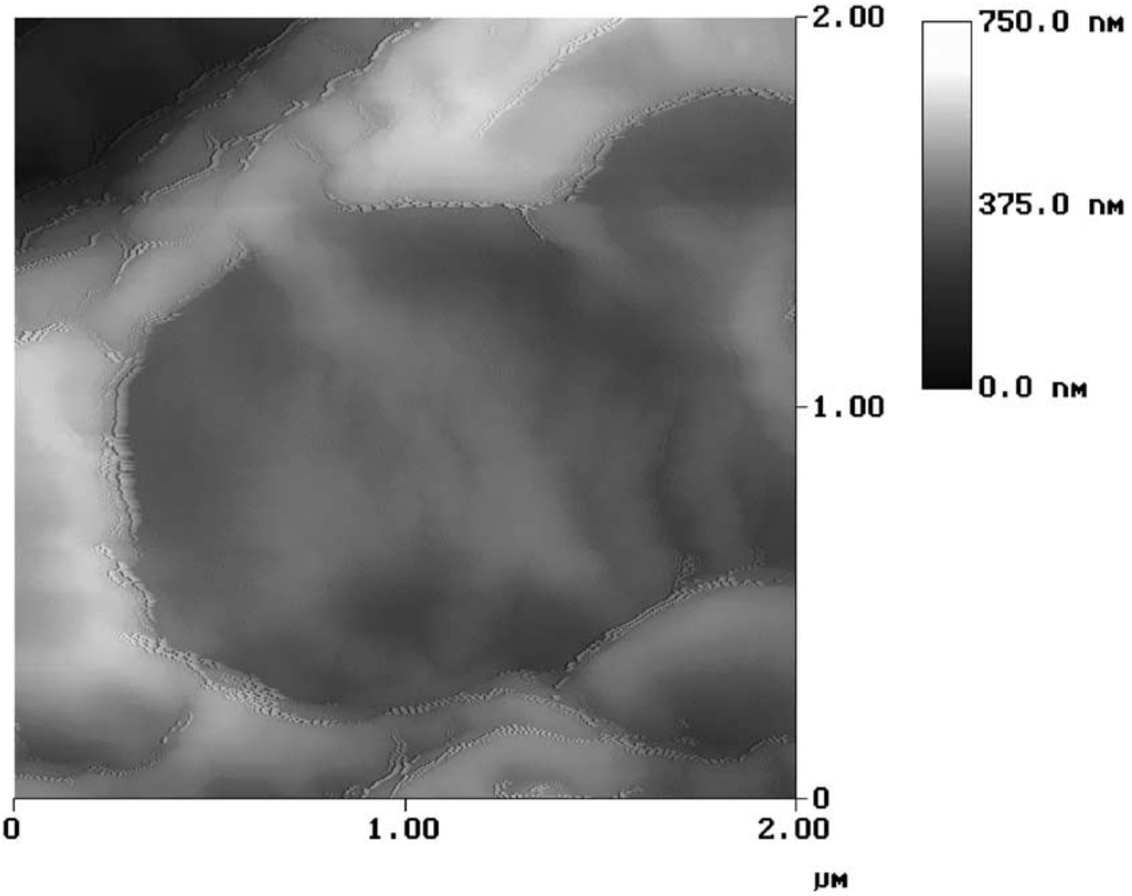


Figure 7 AFM picture taken on the ion-etched surface of cured (at $T = 150°C$) EP composed of Cal-EP + Al-Am.

higher temperatures is prominent. Comparing the related traces in Figs 3 and 5 one can conclude that the rigidity of the idealized EP crosslink unit of Al-EP + Cal-Am is higher than that of Cal-EP + Al-Am. This is in line with the expectation as Cal-Am contain two cyclohexylene units, whereas Cal-EP only one. As a consequence, the idealized crosslink unit of the latter is more flexible and thus yields a lower T_g [11]. The AFM scans in Fig. 6 demonstrate the formation of IPN which is highly compacted during additional heat treatment. Comparing Fig. 6a and b one can now recognize how the structural rearrangement (i.e. compaction) reduces the surface roughness. It is the right place to discuss the possible driving force of this morphology compaction. One should keep in mind that albeit the VE copolymerisation with styrene is independent from the polyaddition reaction between the EP and hardener, several by-side reactions may occur. It is highly probable for example that the secondary —OH of the VE (which has been used to react with the polyisocyanate in VEUH) enter in a polyaddition reaction with the epoxy group of the related EP. This means a potential cross-reaction between the VE and EP phases which become thus chemically linked to each other [11]. The related IPN structure is termed "grafted IPN". It is worth of calling the attention that the IPN formation in VE/EP depends on both thermodynamical (compatibility) and kinetical (crosslinking-induced phase segregation) aspects. Further on, the mathematical description of the IPN structure represents a great challenge.

It was speculated above that the resistance to ion etching of EP is likely much less than VE. Fig. 7 delivers a prove for this assumption. The etched surface of the Cal-EP + Al-Am cured at $T = 150°C$ is very rough, the height relief is in the range of 750 nm. Note that in case of VE/EP combinations the height difference was less than 300 nm (see Figs 4 and 6). This indicates that EP was preferentially removed by the Ar^+ ion bombardment. Fig. 7 also demonstrated that the EP surface is featureless. This suggests that the EP is a single-phase system in contrast to the plain VE.

4. Conclusions

Based on this work devoted to study the morphology of vinylester (VE), vinylester-urethane hybrid (VEUH) and VE/epoxy (EP) resins using atomic force microscopy (AFM), the following conclusions can be drawn:

- ion etching (Ar^+ ion bombardment) is a useful technique to detect the morphology of thermosetting resins
- cured VE has a two-phase (microgel) structure: VE nodules dispersed in a polystyrene (PS) matrix. When additional crosslinking mechanism is at work then an interpenetrating network (IPN) like structure may appear. This was shown on the example of VEUH which is cured by two reactions: polymerisation (copolymerisation with styrene) and polyaddition (—OH of VE with —NCO of an additional polyisocyanate)

- the VE/EP systems at a ratio of 1/1 exhibited a clear IPN structure which became more compact with increasing curing temperature. This compaction in the morphology was traced to the formation of a grafted IPN (chemical reaction between the –OH of VE and epoxy group of the EP). The mean width of the IPN constituting ribbons agreed with that of the size of the nodules in the plain VE (60–80 nm).

Acknowledgements

The authors wish to thank the German Science Foundation for the financial support of this project (DFG FOR 360; Ka 1202/9). Thanks are also due to DSM Composite Resins and U. Prümmer Polymer-Chemie GmbH (UPPC) for providing us with material samples.

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Received 22 May
and accepted 20 August 2002