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Fabrication of thermally stable porous films from a cured epoxy resin via the *Breath Figures* process

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Abstract In the current work, porous films based on epoxy resin have been obtained via the *Breath Figures* method. It was shown that the use of a low-temperature curing agent and fluoro-containing organosilicon copolymer, compatible with epoxy resin, makes it possible to obtain porous, thermostable, highly hydrophobic coatings with a pore diameter of 3–4 μm. When the epoxy resin/copolymer mixture is homogenous, the modifier prevents water droplet coalescence; otherwise, the mixture becomes heterogeneous, and the positive influence of the modifier is lost. The obtained modified porous films are highly hydrophobic and maintain their porous structure until polymer devitrification occurs. The simplicity of the *Breath Figures* method shows great potential for the manufacture of water-repellent paint coatings based on epoxy resin for use in a variety of applications.

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Introduction

Porous structured films are of great interest in various technology fields such as microelectronics,[1] photonics,[2] membranes,[3] and hydrophobic coatings.[4,5] The methods based on surface instability principles fulfill a specific function in the preparation of this type of film.[6] In particular, the structural features of the film surface result from the adsorption–desorption processes that occur in a humid atmosphere. This approach is also known as the *Breath Figures* method.[7] In the first stage of the process, water droplets condense onto the surface of a polymer solution as they cool due to endothermic solvent evaporation. Next, the droplets grow and can be ordered in a hexagonal packing arrangement. Following complete evaporation of both solvent and water droplets, a porous structured polymeric film is formed. Its morphology depends on multiple factors, including the nature of the solvent (volatility, evaporation heat, polarity, etc.) and the polymer (molecular structure, surface tension, and molecular weight), the polymer concentration, relative humidity, and temperature.[7–12]

Although this process is influenced by many factors, the surface tension of the polymer solution is the most important factor, and it defines the coalescence, the growth, and the nucleation of water droplets on the film surface.[8–14]

Various modifiers are typically added to control the surface tension of the polymer solution and the hydrophobic or hydrophilic properties of the polymer film. In particular, organosilicon or fluoro-containing compounds are used as modifiers to increase the hydrophobicity. When accumulated on the top film layer, they decrease the surface tension. Messori et al.

found this approach to be effective for preparing porous polymer films based on polyethylene terephthalate/fluorinated block-copolymer mixtures by the *Breath Figures* method.[15–18] The "hydrophobic additive" technique is attractive for both its ability to expand the range of polymers that can be used to produce porous coatings in this way and its ability to change the surface structure of the polymer.

Over their lifetime, polymer coatings are exposed to various aggressive factors (temperature, organic solvents, humidity, etc.), leading to coating degeneration. The main requirements for porous coatings are thermal and chemical stability because of possible structural degradation during use. The polymer matrix should be crosslinked to increase the stability of the coating and its properties. In the case of porous films made by the *Breath Figures* method, the process of three-dimensional networking consists of two stages.[9,19,20] First, the porous polymer film is formed, and then, it is crosslinked under conditions that allow the surface structure to remain porous. This approach is applicable for thermoplastic polymers, but it is not possible to divide the curing process into the two stages in the case of thermoset oligomers, e.g., epoxy resins, since the film formation and crosslinking processes proceed simultaneously. Moreover, the epoxy resin curing process is accompanied by a thermal effect. The heating required during film formation prevents the cooling of the film surface and thus the condensation of water droplets and the pore formation.

Epoxy resins are characterized by high adhesion, low shrinkage, and good dielectric properties. They are widely used in various fields of science and technology such as in paints and coating materials. The surface porosity of a coating, where pores are the elements of surface roughness, can make the coating more hydrophobic.[4] In this work, we show that the use of a low-temperature curing agent and the addition of a hydrophobic modifier are the main requirements to obtain thermally stable porous coatings based on epoxy oligomers by the *Breath Figures* method.

Experimental section

Materials

D.E.R.-667 epoxy resin was used as a polymeric matrix. The content of epoxy groups was 2.7 wt%.
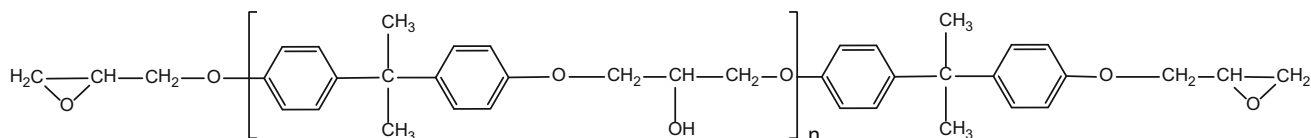
The chemical structure of the resin is as follows in Scheme 1.

The epoxy resin was cured with aminopropyltrimethoxysilane (10 wt% polymer).

A fluoro-containing organosilicon random copolymer with a molecular weight of 5 kDa was used as the hydrophobic modifier. The chemical structure of the random copolymer is as follows in Scheme 2.

This copolymer was synthesized as described in reference (21). The molecular weight was measured by means of gel-permeation chromatography using polystyrene standards.[21]

Film preparation

Chloroform was used as a solvent. All solutions were prepared at room temperature with constant stirring and successive addition of all ingredients: epoxy resin, modifier, and curing agent. The polymer concentration was 40 mg/mL. The concentration of the modifier was 0.1 and 1 wt%. Solutions were cast onto glass substrates pretreated with 3-aminopropyltriethoxysilane as a coupling agent. The films were dried in a chamber under a relative humidity of ~90% and a constant argon flow (see Fig. 1).

For calorimetric analysis, the films were prepared by casting a polymer solution onto cellophane films followed by drying at room temperature for 8 h.

Characterization

The phase behavior of the epoxy resin-modifier system was studied by optical interferometry in the interval from 80 to 130°C with stepwise variation of the temperature.[22] A helium–neon laser with a 630-nm wavelength was used as the light source. In this method, the epoxy resin and modifier are brought into contact "side-by-side" in the wedge gap between the two, optical glass-coated reflective layers on the inner surface. Each component is characterized by a set of interference fringes, and the distance between them is inversely proportional to the refractive index of the components. At the initial moment of contact, a phase boundary exists between the two substances at a given temperature. Due to the interdiffusion interference, the fringes near the boundary are distorted, and if the components are compatible, the border disappears completely. Fringe pattern registration and processing
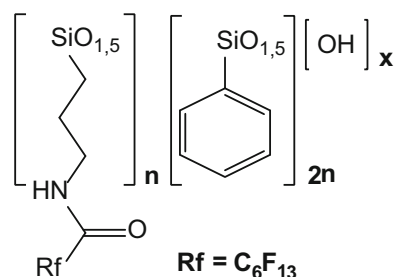

Scheme 1: Chemical structure of the epoxy resin

were carried out in accordance with standard methods using an optical interferometer.[23]

The glass transition temperature (T_g) of the modifier was determined by differential scanning calorimetry (DSC) using a DSC-822e thermoanalyzer (Mettler-Toledo, Switzerland) in argon at a heating rate of 10°C/min from −20 to 120°C.

The glass transition temperatures of epoxy films were determined by DSC using a DTAS-1300 thermoanalyzer (Russia) at a heating rate of 16°C/min from 25 to 150°C.

The water contact angles were measured with a KRÜSS EasyDrop Standard device (Germany). Data were processed with DSA v 1.90.0.14 software. The droplet volume was 2 μL.

The porous morphology of the films was studied with an Axioskop 40 Pol optical microscope (Zeiss, Germany). Atomic force images (AFM) were obtained using a Solver-Next scanning-probe microscope (NT-MDT, Russia) in semicontact mode. AFM images were analyzed with Gwyddion 2.41 software.

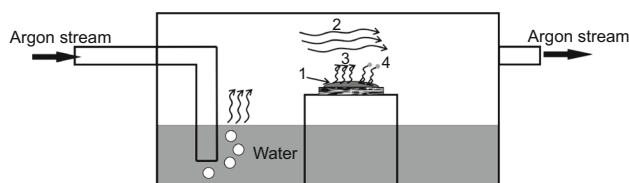**Scheme 2: Chemical structure of the fluoro-containing organosilicon modifier**

Fig. 1: Schematic illustration of the device for the preparation of porous coatings. 1-Polymer solution; 2-Humid argon stream; 3-Solvent evaporation; and 4-Water droplet condensation

To study the thermal stability of polymer films, the films were placed onto a warm stage with a heating rate of 5°C/min. The films were held for 20 min at temperatures of 75, 100, and 120°C.

Results and discussion

The initial epoxy resin properties are presented in Table 1. The film has a water contact angle of 67° due to surface hydrophilicity. 3-Aminopropyltrimethoxysilane was shown to be an effective curing agent at room temperature. The T_g of the cured resin is higher than that of the initial one at 20°C.

Optical and AFM images of a film based on the cured epoxy resin and prepared via the *Breath Figures* method are shown in Figs. 2a and 2b. The film is characterized by a bimodal distribution of pore sizes (see Fig. 2c). There are small pores with 1–2.5 μm diameters and larger pores with 4–7 μm diameters. Preparation of porous films based on the epoxy resin is possible and that the curing process does not prevent formation of a porous structure of coatings, i.e., it does not interfere with the nucleation and growth of water droplets on the surface. Hence, the *Breath Figures* method is indeed promising for preparing porous coating based on thermoset polymers when a low-temperature curing agent is used.

The surface tension of a polymer solution is one of the key factors for controlling the porosity of a formed coating.[8–14] The fluorinated copolymer used in this work is an effective hydrophobic agent for epoxy resins.[21] The organosiloxane moiety of this copolymer increases its solubility in organic solvents and its compatibility with organic polymeric matrices; the fluorinated moiety accumulates at the surface,[24] thus decreasing the surface tension and the wettability.

To determine the optimal concentration of the modifier in the mixture, we investigated its compatibility with the uncured epoxy resin from 80 to 130°C at increments of 20°C. The starting temperature was higher than the glass transition temperatures of both the epoxy resin (65°C) and the modifier (62°C).

The concentration profiles in the diffusion region were generated based on optical interferometry data, and the critical concentrations at various temperatures were determined, which correspond to the bimodal curve shown in Fig. 3. The curve represents mixtures

Table 1: Properties of films based on epoxy resin

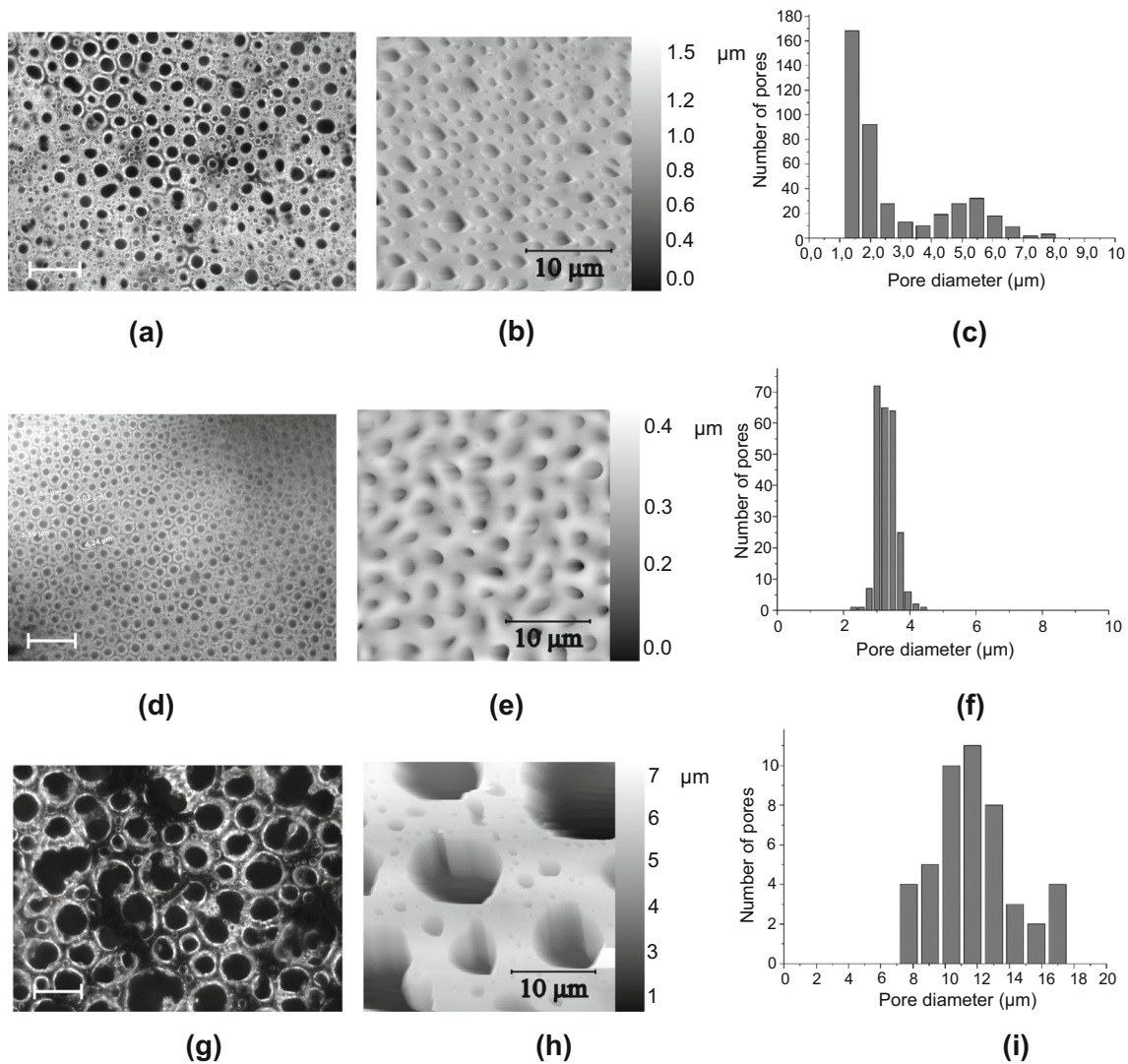| Sample	Content of modifier (wt%)	T_g (°C)	Water contact angle (°)	
			Smooth film	Porous film
Uncured resin	−	65	−	−
Cured resin	−	85	67 ± 1	98 ± 2
	0.1	86	109 ± 2	122 ± 2
	1	86	108 ± 2	120 ± 3

Fig. 2: Optical images (a, d, g), AFM images (b, e, h) and pore size distributions (c, f, i) of epoxy films prepared from chloroform solutions via the *Breath Figures* method. Content of modifier—0 (a, b, c), 0.1 wt% (d, e, f), and 1 wt% (g, h, i). The scale bar of optical images is 20 μm
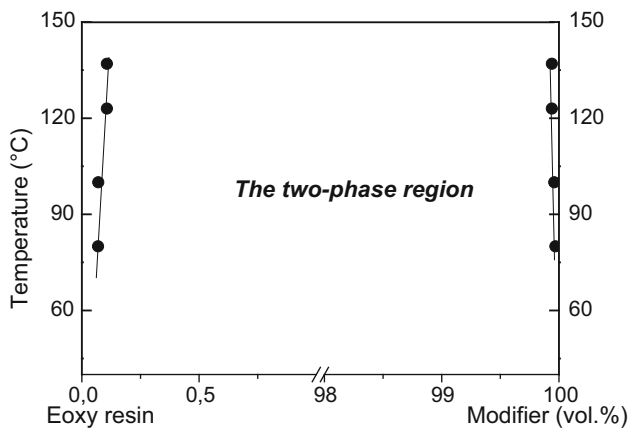

Fig. 3: Phase diagram of an epoxy resin/modifier system

with an upper critical mixing temperature higher than the destruction temperature of mixture components. Based on analysis of concentration profiles in the diffusion area, no more than 0.07–0.1 vol% (or approximately 0.07–0.1 wt%) of modifier could be dissolved in the epoxy resin. When the modifier concentration is higher than 0.1 wt%, phase separation occurs.

Some properties of the modified films prepared without the use of a humid chamber are shown in Table 1. By adding the fluoro-containing organosilicon random copolymer, one can obtain hydrophobic coatings with contact angles of 108°–109°. The modifier does not influence the Tg of the cured resin.

The images of a film prepared by the *Breath Figures* method from the cured modified epoxy resin are presented in Figs. 2d and 2e. The addition of
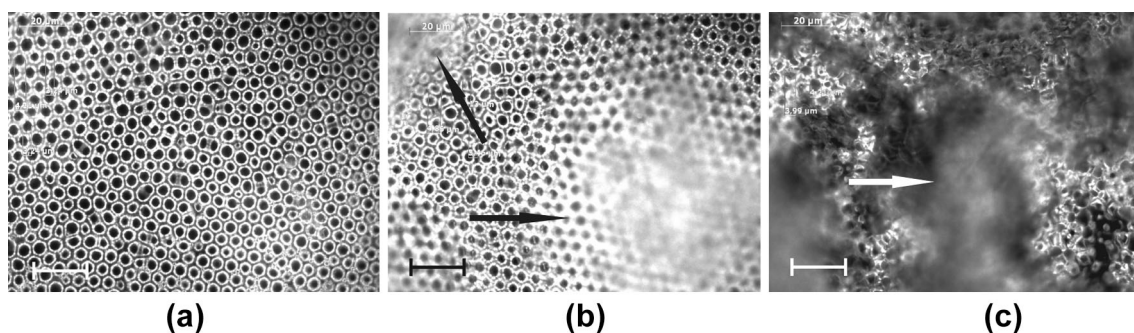
Fig. 4: Porous morphology of cured epoxy film with 0.1 wt% modifier at various temperatures—75 (a), 100 (b), and 120°C (c). The regions of local destruction are indicated by arrows. The scale bar is 20 μm

0.1 wt% copolymer leads to the formation of an ordered porous film structure with 3- to 4-μm-diameter pores and a monomodal pore size distribution (see Fig. 2f).

At 1 wt% modifier, the size of pores increases to 7–18 μm (see Figs. 2g, 2h, 2i). Pore enlargement continues due to the formation of cavities and the coalescence of several pores. According to AFM images of this film, small pores with diameters of 1–1.5 μm are also present.

The influence of the modifier concentration on the porous structure of the epoxy coating is likely related to the phase structure of the epoxy resin/modifier mixture. This assumption is based on previous work,[15,16,25–27] where it was shown that the defective porous film forms with phase separation of the polymer mixture. As previously detailed, at a modifier content less than 0.1 wt%, the mixture is homogenous (see Fig. 3). In this case, the polymer modifier prevents coalescence of water droplets and leads to formation of the monomodal porous structure.[26] At higher modifier concentrations, the mixture becomes heterogeneous, which leads to an uneven distribution of the modifier both in the bulk and on the surface of the coating.[25,27] The positive influence of the added modifier is lost as a result of local coalescence of water droplets followed by formation of large and nonordered pores.

Water contact angles for the modified porous films are presented in Table 1. The porous structure promotes the realization of heterogeneous wetting, and as a result, the water contact angles increase. It should be noted that 1 wt% modifier does not affect the contact angle with the observed pore enlargement. This is partly because the ratio between areas of porous roughness and occupied with water droplets. The simple calculation shows that the latter is several orders of magnitude greater than the former and that it does not influence the contact angle. Perhaps the influence of surface defects, caused by the merging of pores, can be seen upon measurement of the dynamic water contact angle, which demands more research.

The coating with 0.1% modifier was used to study the thermal stability of the porous structure. Images of this film at various temperatures are shown in Fig. 4. As seen, the porous structure remains undamaged up to 100°C. At 100°C, the film starts to deform and further increases in temperature lead to the total destruction of the porous structure. It is clear that the destruction of the initial porous morphology is caused by polymer devitrification and softening. At temperatures below 100°C, the coatings maintain their porous structure.

Conclusions

We conclude that the *Breath Figures* method is promising in terms of the preparation of porous structures based on crosslinked epoxy resin. The use of low-temperature curing agents (3-aminopropyltri-ethoxysilane) and compatible epoxy resin fluoro-containing organosilicon random copolymers makes it possible to obtain porous, thermostable, and highly hydrophobic coatings. The influence of the fluorinated copolymer on the porous structure of the coating is dependent on its concentration. If the epoxy resin/modifier mixture is homogenous, the modifier prevents water droplet coalescence and leads to formation of an ordered porous structure with a pore diameter of 3–4 μm; otherwise, the mixture becomes heterogeneous, and the positive influence of the modifier is lost. The simplicity of the *Breath Figures* method has the potential to make water-repellent paint coatings based on epoxy resin a widely applicable technology.

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