Macromolecules **2002,** *35,* 5883−5890

Mechanism of Bubble Dissolution in Reactive Coatings: The Role of Benzoin

Shahab Jahromi*

DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands

Received January 22, 2002

ABSTRACT: The process of bubble dissolution in reactive coatings and the role of benzoin as a degassing agent have been investigated. The gas bubble shrinkage was monitored using a light microscope equipped with a hot stage. In the absence of benzoin, the air bubbles started to shrink very slowly as a result of a diffusion-controlled process. Because of the continuing cross-linking reaction and increase in the viscosity, the bubble shrinkage halted at elevated temperatures. Quite remarkably, we observed that in the presence of benzoin the process of bubble shrinkage was accelerated to such an extent that most air bubbles dissolved before any significant increase in the viscosity occurred. This suggests that benzoin functions by accelerating the rate of bubble shrinkage. To elucidate the mechanism of the action of benzoin in detail, we studied the coating formulations using various techniques. X-ray diffraction in combination with deuterium NMR on labeled benzoin indicated that benzoin is distributed on a molecular level in polyester resin and becomes mobile above the glass transition of the matrix. Mass spectroscopy experiments revealed that benzoin, in its oxidized form (benzil), starts to evaporate above 100 °C. As can be expected, the conversion of benzoin to benzil is halted when experiments are carried out under nitrogen. We postulated that the action of benzoin as a degassing agent is related to its ability to oxidize in situ. This claim was substantiated by the results of bubble dissolution experiments using different gases such as oxygen and nitrogen. It was found that in the presence of benzoin oxygen bubbles shrink much faster than air bubbles. On the other hand, the shrinkage of nitrogen bubbles is not affected by benzoin. On the basis of the above results, a two-step mechanism is proposed for the action of benzoin as a degassing agent.

I. Introduction

The behavior of gas bubbles in non-Newtonian fluids has been the subject of intensive research.[1] Gas bubble formation is experienced as undesirable in various industrially relevant processes and applications, such as continuous liquid film coatings,[2] polymer casting,[3] rotationally molded products,[4] and powder coatings.[5] Especially in the case of powder coatings, gas bubbles trapped during film formation, which become fixed as a result of subsequent cross-linking reactions, result in significant deterioration of the surface appearance of finished coatings. To facilitate the process of degassing, in practice a small amount of benzoin (<1% w/w) is added to the powder coating formulations.[6] Although a number of studies have focused on this issue,[7] the mechanism of the action of benzoin has so far remained a great mystery. As a result, the search for alternative degassing agents has been largely unsuccessful. Alternative degassing agents are needed especially because of the negative side effects of benzoin such as yellowing.[8]

We have studied the mechanism of the action of benzoin, and our findings are presented here. Both chemical and physical processes which take place during the degassing process in the presence and absence of benzoin have been investigated in detail using various techniques. On the basis of these results, we have postulated a mechanism for the action of benzoin as a degassing agent.

II. Experimental Section

Powder Coating Formulations and Materials. A typical formulation consists of 100 g of a Uralac polyester resin (acidity number of 82) containing 0.4% of a catalyst (triphenylmethylphosphonium bromide), 100 g of an epoxy resin (Araldite GT 7004; epoxy number = 725, Ciba), 3 g of a flow agent (resiflow-PV5, Worleé), and an appropriate amount of a degassing agent when indicated in the text. The weight percentages of benzoin are given with respect to the binder, i.e., resin plus the cross-linker. These formulations are designated in the text as clear coatings. The formulations referred to as white also contain 100 g of a titanium dioxide (TiO_2) pigment type Kronos 2310. All components were first blended in a BRAUN mixer (MX-40). The mixtures were then extruded through a PRISM TCE 16 PC at a temperature of approximately 100 °C. The extruded material was ground and classified to a particle size lower than 90 μm.

The deuterated benzoin (Benzoin-D10) was purchased from CAMPRO Scientific (Veenendaal, The Netherlands).

Optical Microscopy. These experiments were carried out using clear coating formulations and a JANA PAL microscope equipped with hot stage and videotext units of the type LIN KHN. The shrinkage of gas bubbles was recorded using this equipment at various isothermal temperatures. The isothermal temperatures were reached at a heating rate of 50 °C/min. Care was taken to ensure that all the selected air bubbles were initially of comparable sizes. The size of the gas bubbles, displayed on a TV screen, was measured using a ruler, and the data were corrected for the right magnification (±3%).

Mass Spectroscopy Experiments. The pyrolysis−gas chromatography−mass spectroscopy (Py-GC-MS) experiments were carried out using an ATAS OPTIC2 (programmable injector) coupled to a Micromass AutoSpecE mass spectrometer. The thermal desorption (TD)-GC-MS experiments were conducted with the aid of a Gerstel TDS (ThermoDesorption System) coupled to a HP5973 GC-MSD.

Rheological Experiments. These measurements were carried out using an ARES/LS instrument (Rheometric Scientific) operating at a frequency of 0.16 Hz in a temperature sweep mode (5 °C/min).

^{2}H NMR Experiments. ^{2}H NMR spectra were recorded on a Varian Inova-400 MHz wide-bore NMR spectrometer operat-

---

* E-mail: shahab.jahromi@dsm.com.

10.1021/ma020115i CCC: $22.00 © 2002 American Chemical Society
Published on Web 06/13/2002

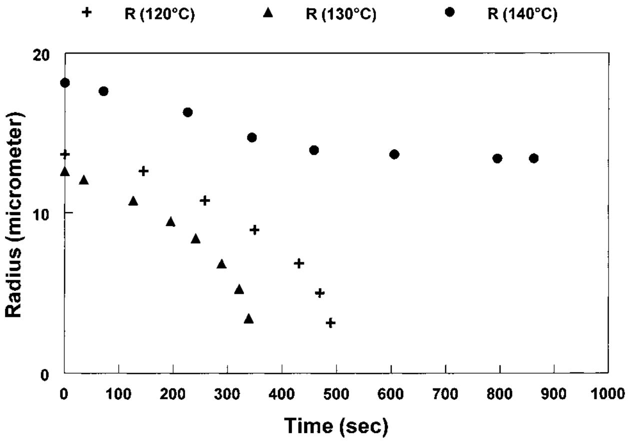


Figure 1. Diameter of air bubbles as a function of time during isothermal heating at three different temperatures. The measurements were conducted with a light microscope using a clear benzoin-free powder coating formulation.

ing at a ^{2}H frequency of 61.4 MHz, using a wide-line probe. The 90° pulse width was 2.5 μs. Wide-line ^{2}H spectra were obtained via Fourier transform of the free induction decay (FID) that was measured using the solid-echo pulse sequence with $t_{se} = 20\ \mu$s. The recycling delay time was larger than the relaxation time T_1 by a factor of 5. About 0.035 g of resin with deuterated benzoin-D10 was used for the measurements, which for each spectrum took about 2.5 days at 22−60 °C, 40 min at 80 °C, and 10 min above 80 °C.

X-ray Diffraction Experiments. These measurements were performed with the aid of powder diffractometers PW1050 and PW1820 in Bragg Brentano geometry using fixed slits (1 divergency slit; 0.2 mm entrance slit). Cu Kα radiation was used (40 kV, 50 mA) with a monochromator in the diffracted beam.

Thermogravimetric Analysis (TGA). These experiments were carried out with the aid of Perkin-Elmer TGS-2 equipment.

III. Results and Discussion

III.A. Problem Analysis. During the heating and final curing of powder particles, a series of physical and chemical processes take place, which eventually result in film formation and hardening of the coating. The following observations were made using a light microscope. Above 60−70 °C, i.e., the T_g of the polyester resin, the powder particles started to soften. Following a drastic decrease in the viscosity, the particles coalesced to form a continuous coating. During this process, which was completed below 100 °C, air bubbles became trapped. The size of the air bubbles was monitored during isothermal heating of a benzoin-free formulation at different temperatures (see Figure 1).

The size of the air bubbles decreased continuously as a function of time. The rate of bubble shrinkage increased when the temperature was raised from 120 to 130 °C, suggesting a diffusion-controlled process.[9] During heating at 140 °C, however, the process of bubble shrinkage halted after a certain time. This is related to the increase in the viscosity as a result of cross-linking (see Figure 2), which hampers and eventually stops further shrinkage of air bubbles. As can be inferred from the viscosity changes during the reaction shown in Figure 2, the addition of benzoin had no effect on the absolute value of viscosity or on its evolution during cross-linking.

Figure 3 shows the shrinkage of air bubbles as a function of time at 120 °C for powder coating formulations in the presence and absence of 0.3% w/w benzoin.

Obviously, air bubbles shrink much faster in the presence of benzoin, at 120 °C by a factor of almost 3. In fact, the rate of bubble shrinkage is accelerated to a degree that even during curing at 130 and 140 °C complete gas dissolution may occur (see Figure 4). Clearly, as a result of the accelerating effect of benzoin,

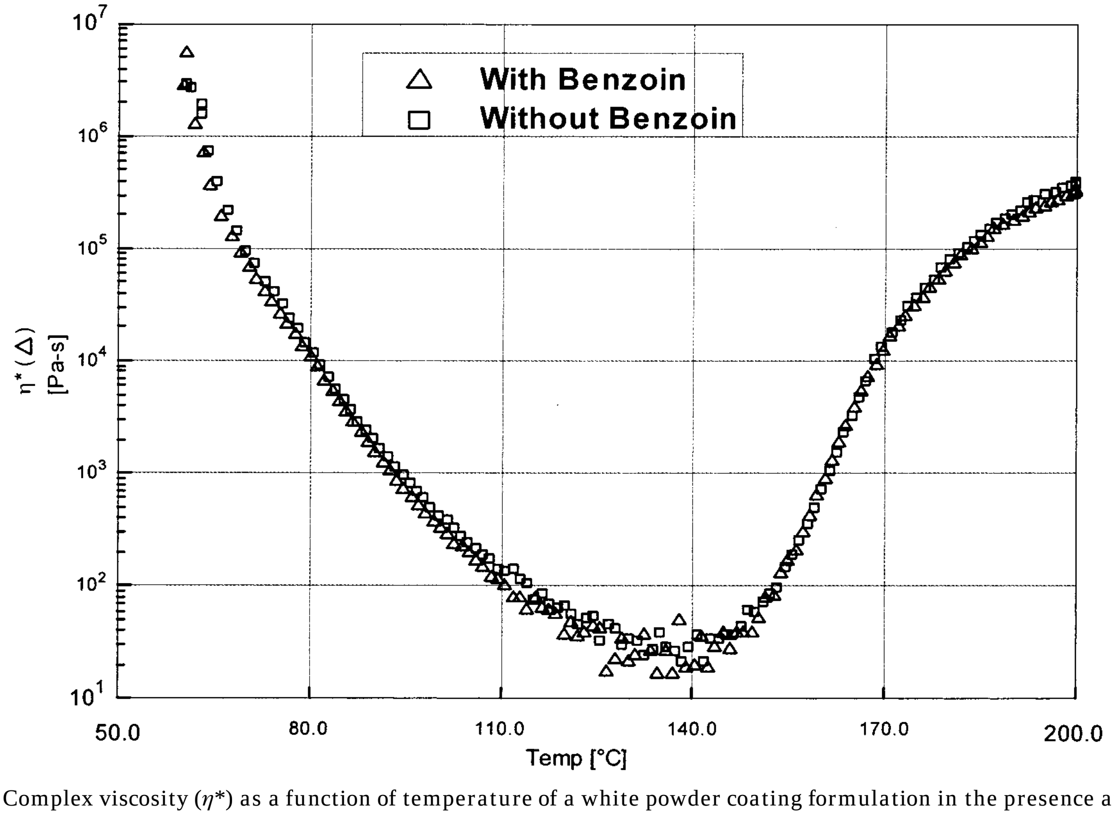


Figure 2. Complex viscosity (η^*) as a function of temperature of a white powder coating formulation in the presence and absence of 1% w/w benzoin. The viscosity initially drops because of the temperature effect and then starts to rise again at about 140 °C due to the cross-linking reaction.

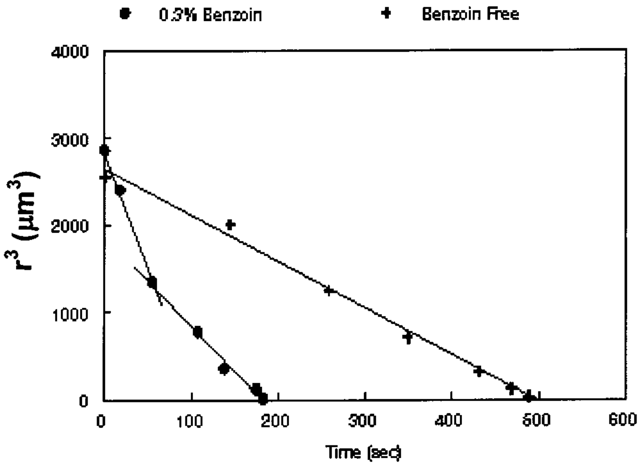


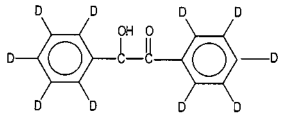
Figure 3. Diameter of air bubbles to the power three (r^3) during heating at 120 °C of a coating formulation with and without 0.3% w/w benzoin. In contrast to the coating without benzoin, bubble shrinkage in the presence of benzoin appears to proceed faster and follow a two-step process.

the bubble shrinkage may be completed before a significant rise in the viscosity has set in. Furthermore, the bubble dissolution in the presence of benzoin appears to proceed via a two-step process. We will return to this issue below.

The above results reveal the mode of action of benzoin: benzoin facilitates the degassing process by accelerating the rate of bubble dissolution. Other modes of action, such as promoting the migration of bubbles to the coating surface, can also be envisaged.[10] We have however observed that the movement of the air bubbles is highly restricted at such high medium viscosities. The main mode of action of benzoin is in our opinion the acceleration of bubble dissolution. Before discussing the mechanism according to which benzoin increases the rate of bubble shrinkage, we shall discuss the solubility of benzoin in powder coating formulations.

III.B. Solubility of Benzoin in Powder Coating Formulation As Studied by Means of X-ray Diffraction and ^{2}H NMR. With a view to elucidating the mechanism of the action of benzoin, it is important to establish whether this compound is soluble on a molecular level in the polyester formulation. Since benzoin is a crystalline compound, X-ray diffraction can be deployed to determine the amount of crystalline benzoin in the coating formulation after all the ingredients have been mixed in an extruder. Figure 5 shows the X-ray diffractograms of pure benzoin and the diffractogram of a coating formulation containing an excess of benzoin (10% w/w).

Scheme 1. Chemical Structure of Deuterated Benzoin



Even at a loading of 10% w/w, no crystalline benzoin could be detected in the coating formulation. This indicates that during the extrusion step benzoin dissolves in the polyester resin at least up to a concentration of 10% w/w, which is well above the common loading of benzoin as a degassing agent (<1% w/w).

To obtain more detailed information on the local mobility of benzoin in the polyester formulation, we carried out a series of ^{2}H NMR experiments using a powder coating formulation containing deuterated benzoin (see Scheme 1).

By conducting ^{2}H NMR experiments as a function of temperature, the mobility of deuterated benzoin (benzoin-d_{10}) molecules can be monitored especially during the particle coalescence and subsequent air bubble formation process. Figure 6 shows the ^{2}H NMR spectra of a coating formulation containing 1% w/w of benzoin-d_{10}, measured at different temperatures up to 120 °C.

The spectrum of crystalline benzoin shows a typical quadrupolar splitting of deuterium in a rigid environment, i.e., a crystalline phase. The spectrum of benzoin-d_{10} in the coating formulation at 22 °C is quite broad, indicating that the mobility of benzoin is still highly restricted. The restriction of the mobility may be due either to the crystalline nature of benzoin or to the fact that benzoin resides in the glassy regions of polyester resin. Which is the case is difficult to infer from this spectrum. The results of the temperature-dependent

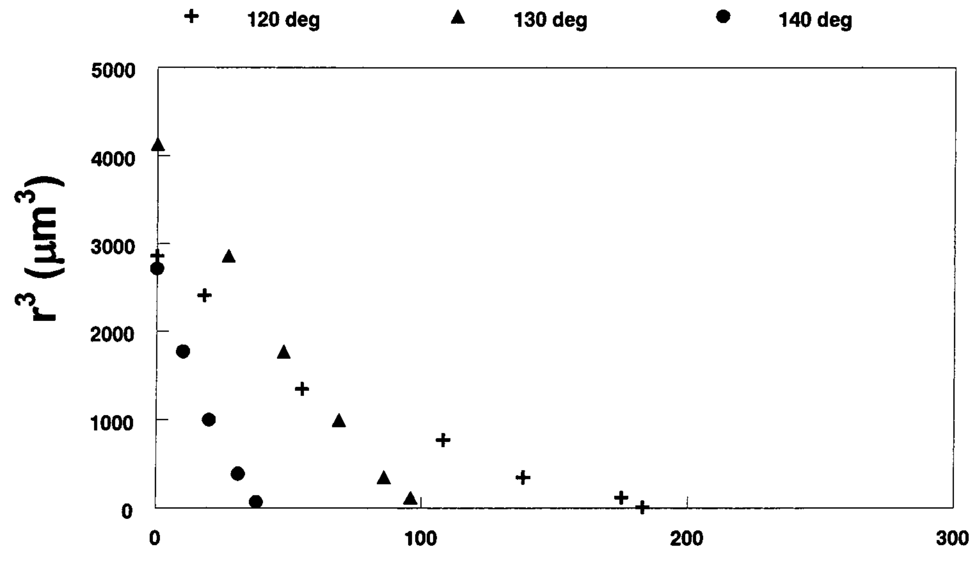


Figure 4. Diameter of air bubbles to the power of three (r^3) as a function of time at 120, 130, and 140 °C of clear powder coating formulations containing 0.3% w/w benzoin.

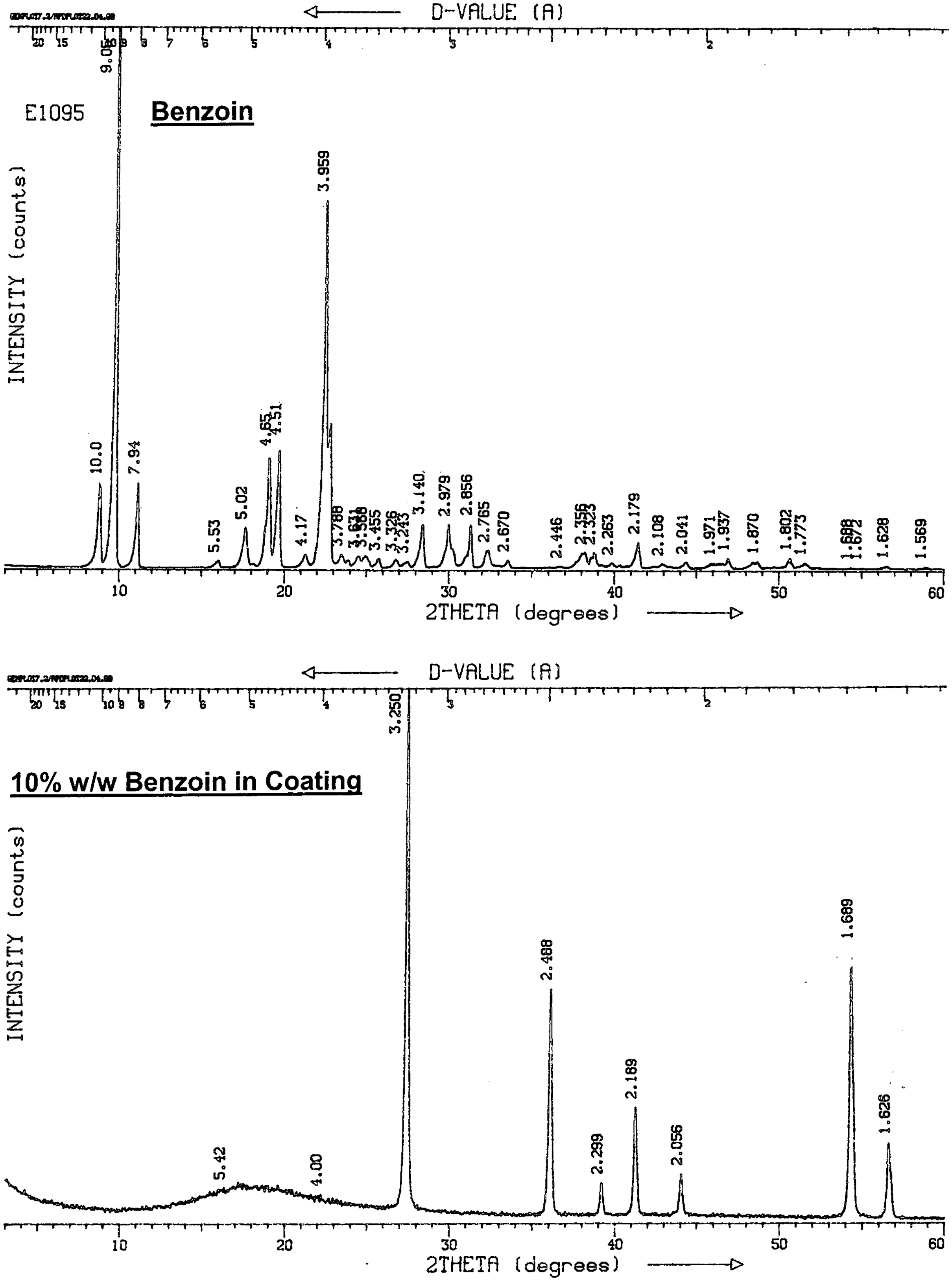


Figure 5. X-ray diffraction of pure benzoin and a powder coating formulation containing 10% w/w benzoin. The diffraction peaks that can be observed in the powder coating formulation derive from the pigment, i.e., TiO_2.

experiments however reveal a drastic line narrowing especially upon heating above the glass transition temperature of the polyester resin, i.e., 60 °C. This proves that the mobility of the benzoin is closely coupled to the mobility of polyester resin, indicating that benzoin is indeed dissolved on a molecular scale in the polyester resin.

III.C. Chemical Transformation of Benzoin during the Dissolution Process. Benzoin is a volatile compound, which starts to sublime above 120 °C, i.e., its melting point. This can be clearly inferred from the TGA trace of benzoin shown in Figure 7.

Some data in the literature suggest that benzoin can evaporate from coatings in significant amounts during

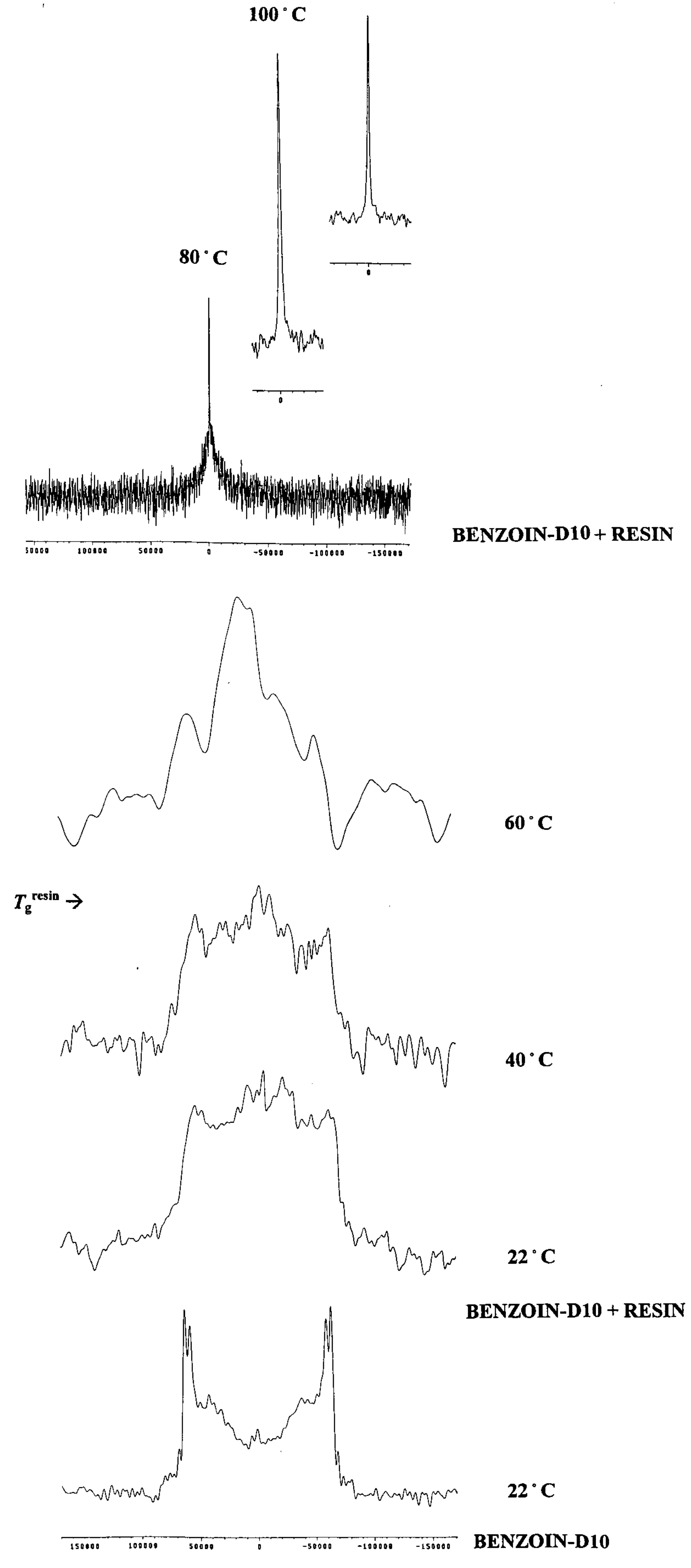


Figure 6. ^{2}H NMR spectra of a coating formulation containing 1% w/w deuterated benzoin (benzoin-d_{10}) at different temperatures. For comparison, the ^{2}H NMR spectrum of crystalline benzoin-d_{10} is also shown.

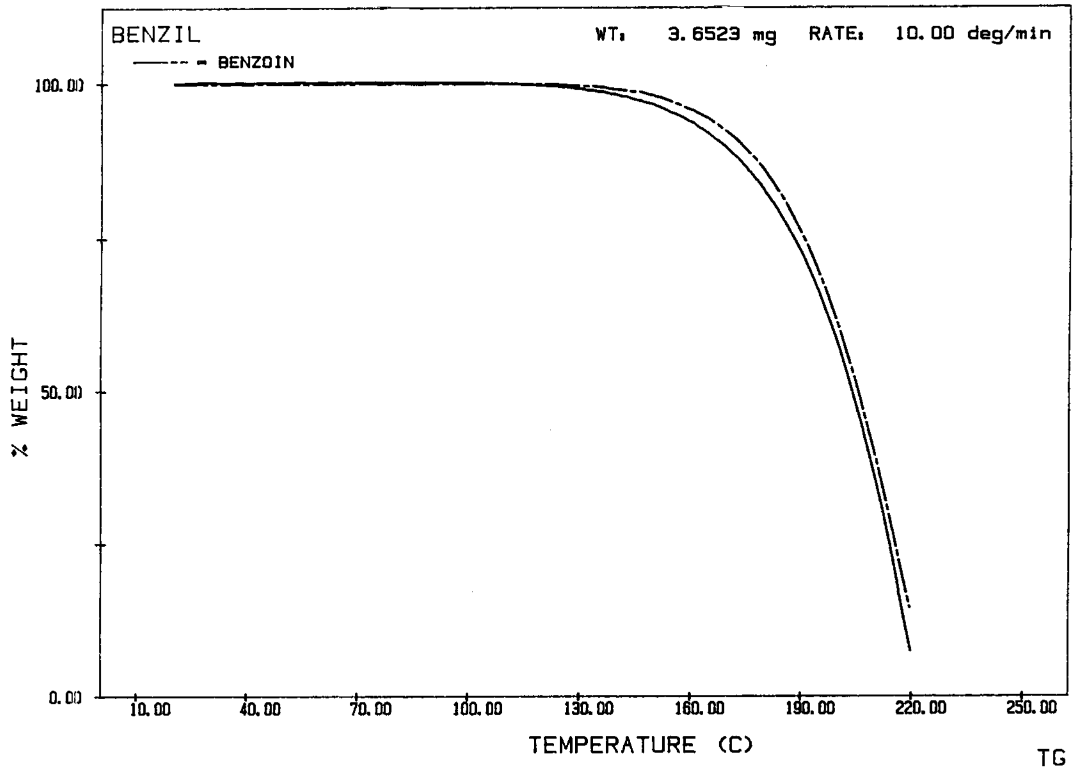


Figure 7. TGA trace of benzoin and its oxidation product, i.e., benzil.

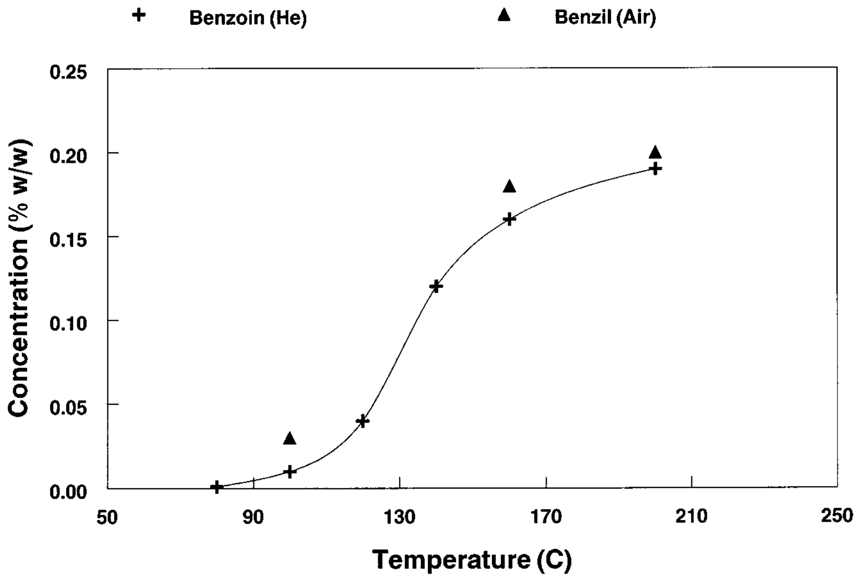


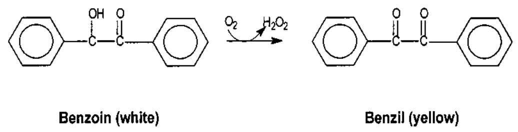
Figure 8. Characterization of volatile compounds released during isothermal curing of white powder coating formulations at different temperatures in air and in a helium atmosphere. The data were obtained by means of GC-MS. The concentration values are given as mass ratio relative to each formulation's total weight, i.e., including pigment. The loading of benzoin in the formulations was 0.3% w/w with respect to the binder (resin + cross-linker) and 0.2% w/w relative to the total mass including pigment.

curing of different types of powder formulations.[11] To study this phenomenon in some detail using the above formulations, we conducted a series of gas chromatography–mass spectrometry (GC-MS) experiments using coatings cured in an inert atmosphere, i.e., helium, and in air. The samples were isothermally heated for 60 min at different temperatures, and the volatile compounds were collected in a cold trap. After a desorption step, the evaporated compounds were then characterized by means of GC-MS. The results are shown in Figure 8.

During the curing in the inert atmosphere, benzoin started to evaporate above 100 °C. After heating at 200 °C, 0.2% w/w of benzoin was released, which corresponds to the initial loading of benzoin.[12] Similar trends, though seemingly in somewhat lower concentrations, were observed when the curing was carried out in air. But in this case not benzoin, but its oxidation product, i.e., benzil, was obtained (see Scheme 2).

Oxidation of benzoin to benzil is a very common reaction in organic chemistry,[13] which has been carried out using different types of catalysts.[14] As far as the chemical transformation in the coating is concerned, it is difficult to determine whether benzoin is formed in the condensed phase, i.e., before evaporation, and/or in

Scheme 2. Oxidation of Benzoin to Benzil[a]



[a] Benzoin forms white crystals, whereas benzil is a yellow crystalline compound.

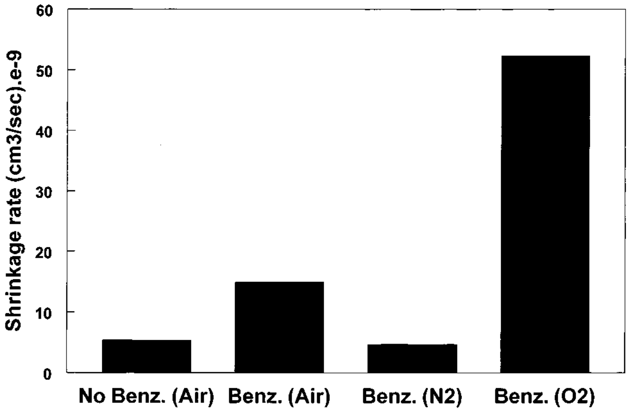


Figure 9. Rate of shrinkage of different gas bubbles formed during isothermal heating of clear coating formulations (0.3% w/w benzoin) at 120 °C in a corresponding gas atmosphere. For comparison, the rate of air bubble shrinkage of a benzoin-free formulation at 120 °C is also shown. The shrinkage rates were determined via a linear fit through all the data points. The nature of the gases is indicated between brackets.

the gas phase. This most certainly depends on various factors such as the curing temperature and the oxidation/sublimation rate of both benzoin and benzil. As can be seen in Figure 7, TGA traces of benzil and bezoin are quite comparable, suggesting that benzil evaporates from the coating in a similar manner as benzoin. It should be also noted that, because of its conjugated structure, benzil is a yellow compound. Therefore, the yellowing side effects of benzoin on powder coatings may be related to the formation of benzil.

In short, we have demonstrated that during curing of powder coating formulations under atmospheric conditions, benzoin transforms to benzil, which oxidation product evaporates from the coating. Interestingly, both the oxidation and the evaporation process occurs at the temperatures at which benzoin becomes active as a degassing agent, i.e., 100−120 °C. The bubble dissolution rates of different gas bubbles, which will be discussed in the next section, provide more insight into the action of benzoin.

III.D. Bubble Dissolution Experiments under Various Conditions. We now have some indications that oxidation of benzoin may indeed play a role in the degassing process. To study this in more detail, we determined the rate of shrinkage of bubbles consisting of various types of gases. The experiments were carried out by simply curing the clear coating formulations in the presence of different gases so that the bubbles formed during the film formation would consist of the corresponding gases. Figure 9 shows the rate of shrinkage of different gas bubbles formed during isothermal heating of clear coating formulations at 120 °C.

In the presence of benzoin, oxygen bubbles shrink much faster than air bubbles. The rate of shrinkage of nitrogen bubbles is low and comparable with the dissolution rate of air bubbles in benzoin-free formulations. In fact, in the absence of benzoin, the shrinkage of all three gases in the polyester resin was roughly the same (data are not shown). This is logical in view of the fact that the van der Waals volumes of O_2 and N_2 are similar.[15]

On the basis of the above results, we can conclude that benzoin is apparently inactive with respect to the removal of nitrogen bubbles, i.e., when the curing is carried out in N_2. In the presence of air, benzoin becomes active, reaching its highest activity when pure O_2 is used. This is a very important conclusion, again pointing to the fact that the oxidation of benzoin to benzil indeed plays a crucial role in the degassing process. On the basis of the results presented here, we propose the following mechanism for the action of benzoin.

III.E. Proposed Mechanism for the Action of Benzoin. We know that air consists primarily of nitrogen (mass percentage of dry air at sea level: 75.5% N_2, 23.2% O_2, and 1.3% Ar).[16] Therefore, the decrease in the volume of air bubbles should not exceed 25% solely as a result of the consumption of oxygen during the formation of benzil. It is possible that degassing under the influence of benzoin occurs in two steps. The first process is controlled by the oxidation of benzoin, and the second is dominated by the diffusion of N_2 in the matrix. After careful analysis of all the shrinkage data it seems that the dissolution of air bubbles under the influence of benzoin indeed occurs in two steps (see for example Figure 3). The first process is fast and accounts for 20−25% of the total volume shrinkage. This value agrees well with the mass percentage of O_2 in air. The second process is somewhat slower, but the shrinkage rate is still high when compared with dissolution rates of pure N_2 in polyester resin; at 120 °C the shrinkage rate was almost 3 times higher. The chemical scavenging of O_2 by benzoin leads to a reduction of bubble diameter, which in turn results in an increase in the Laplace pressure inside the bubble, as dictated by the laws of surface tension. The increase in pressure forces nitrogen to dissolve faster in the polymer, thus further reducing the size of the bubbles. The removal of air bubbles mediated by chemical reactions has been proposed before, but never proven, for example for the degassing processes in the glass melt and refining.[17]

Because of the detrimental role of oxidation of benzoin, it is important to establish whether the degassing process benefits most from reaction in the condensed phase or in the gas phase, i.e., in the bubble. In other words, *is the volatilization of benzoin important for its action as a degassing agent?* To answer this question, we chemically attached benzoin molecules to end groups of poly(ethylene glycol). As a result, benzoin moieties became immobilized without their ability to oxidize being affected. These benzoin-functionalized poly(ethylene glycol) molecules were tested in powder coating formulations. The molecules appeared to be inactive as a degassing agent, indicating that volatilization of benzoin is also an important feature (data are not shown here).

On the basis of the proposed mechanism of action, we can formulate a set of conditions with which potential degassing agents must comply:

(1) To ensure a homogeneous distribution, the degassing agent must be soluble (compatible) in the resin formulations.

(2) The degassing agent must be volatile and start to evaporate preferably just above the temperature at which film formation is complete and air bubbles start to form, i.e., 90−110 °C.

(3) The volatilization should be accompanied by oxidation of the degassing agent in a temperature range similar to that specified above.

Benzoin satisfies all the above conditions. The obtained knowledge on the action of benzoin can be used to develop more efficient degassing agents with less severe yellowing side effects. By taking advantage of the fact that the oxidation of benzoin can be accelerated by attaching various groups to the aromatic rings,[18] we have already developed more efficient degassing agents through "smart" derivatization of benzoin. And by using the above criteria, we have succeeded in finding effective degassing agents with chemical structures completely different from that of benzoin.[19]

IV. Conclusions

The results presented here indicate that benzoin facilitates the removal of gas bubbles by accelerating the rate of bubble shrinkage. During the degassing process, benzoin evaporates (into the gas bubbles) and oxidizes to form benzil. The size of the air bubble rapidly shrinks 20−25% because of the resulting oxygen depletion. The decrease in bubble diameter leads to an increase in the pressure inside the bubble (as dictated by the laws of surface tension) and forces the nitrogen to dissolve in the system. Besides the development of a new generation of degassing agents for reactive coatings, this new knowledge can in our opinion also be used for gaining an understanding of problems associated with bubble formation and removal in other areas of polymer science and beyond.

Acknowledgment. The author thanks the management of DSM Coating Resins for granting permission to publish the present work. The discussions with F. Koldijk and the valuable help of A. Derks (both from DSM Coating Resins) are gratefully acknowledged. V. Litvinov and G. Kwakkenbos carried out NMR and mass spectroscopy experiments, respectively. B. Mostert has conducted some of the experimental work.

References and Notes

(1) (a) Chhabra, R. P. *Bubbles, Drops, and Particles in Non-Newtonian Fluids*; CRC Press: Boca Raton, FL, 1993.

(2) (a) Simpkins, P. G.; Kuck, V. J. *Nature (London)* **2000**, *403*, 641. (b) Debrégeas, G.; Gennes de, P.-G.; Brochard-Wyart, F. *Science* **1998**, *279*, 1704.

(3) Schruben, D. L.; Kumble, D. *Polym. Eng. Sci.* **1996**, *36*, 2494.

(4) (a) Spence, A. G.; Crawford, R. J. *Polym. Eng. Sci.* **1996**, *36*, 993. (b) Kontopoulou, M.; Vlachopoulos, J. *Polym. Eng. Sci.* **1999**, *39*, 1189; **2001**, *41*, 155.

(5) Lange de, P. G. *J. Coat. Technol.* **1984**, *56*, 23.

(6) (a) Grolitzer, M. A.; Erickson, D. E. *J. Coat. Technol.* **1995**, *67*, 89. (b) Bodnar, E. *Eur. Coat. J.* **1997**, *97*, 248.

(7) See for example: (a) Uhlmann, P.; Grunfke, K. *Farbe Lack* **1996**, *102*, 48. (b) Uhlmann, P.; Grundke, K.; Wulf, M.; Jacobasch, H.-J. *FATIPEC Congr.* **1998**, A-131. The reliability of the results regarding the effect of benzoin on surface tension reported by Uhlmann et al. is doubtful. This is related to the fact that surface tension measurements in the presence of benzoin have been carried out above the volatilization temperature of benzoin, i.e., 120 °C. Therefore, it is to be expected that during long-term surface tension measurements benzoin evaporates from the resin solution, which negatively influences the experiments.

(8) Bate, D. A. *The Science of Powder Coatings: Chemistry, Formulation and Application*; SITA Technol.: London, 1990; Vol. 1.

(9) (a) Hoeflaak, M.; Selier, P. *Farbe Lack* **1973**, *79*, 960. (b) Zorll, U. *Farbe Lack* **1974**, *80*, 1123.

(10) (a) Maceto, C.; Yang, W.-J. *Jpn. J. Appl. Phys.* **1974**, *13*, 529. (b) Zieminski, S. A.; Raymond, D. R. *Chem. Eng. Sci.* **1968**, *23*, 17. (c) Rodrigue, D.; De Kee, D.; Chan Man Fong, C. F. *J. Non-Newtonian Fluid Mech.* **1996**, *66*, 213.

(11) Randoux, T.; Vanderhorst, D.; Loutz, J.-M.; Robijns, G. *Eur. Coat. J.* **1995**, *11*, 799.

(12) In practice, the polyester/epoxy based powder coating formulations are often cured at 180−200 °C.

(13) Trahnovsky, W. S. *Oxidation in Organic Chemistry,* Part B; Academic Press: New York, 1973.

(14) See for example: (a) Weiss, M.; Appel, M. *J. Am. Chem. Soc.* **1948**, *70*, 3666. (b) Kinoshita, K. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 783.

(15) Comyn, J. *Polymer Permeability*; Elsevier: London, 1985.

(16) Atkins, P. W. *Physical Chemistry*; Oxford University Press: Oxford, 1978.

(17) See for example: (a) Itoh, E.; Yoshikawa, H.; Miura, H.; Kawase, Y. *Class Technol.* **1997**, *38*, 134−140. (b) Takemura, F.; Matsumoto, Y. *Chem. Eng. Sci.* **2000**, *55*, 3907−3917.

(18) Weissberger, A.; Schwarze, W.; Mainz, H. *Justus Leibzigs Ann. Chem.* **1930**, *68*, 481.

(19) Jahromi et al. Manuscript in preparation.

MA020115I