

Chemistry and characterization of some reactive polyester powder coating systems

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Rob van der Linde, Boudewijn J.R. Scholtens* and Eim G. Belder.

DSM Resins B.V., P.O. Box 615, 8000 AZ Zwolle, Netherlands.

*DSM Research B.V., P.O. Box 18, 6160 MD Geleen, Netherlands.

Introduction

Powder coating technology has developed strongly during the last decade and has proven to be very beneficial to the coating industry. Firstly, powder coatings have excellent performance in a variety of applications and a choice can be made out of several chemically different systems to meet specific requirements. Secondly, the absence of organic solvents has greatly stimulated the use of powder coatings due to environmental protection regulations.

Today the main thermosetting powder coating systems in use are:

- Pure epoxies
- Polyesters/Bisphenol A epoxies (hybrids)
- Polyesters/Triglycidyl isocyanurate (TGIC)
- Polyesters/Blocked isocyanates (polyurethanes)
- Polyacrylates.

This paper is concerned with carboxylated polyesters cured with TGIC or Bisphenol A based epoxies. A scheme of the overall curing reactions of these coating materials is given in Figures 1 and 2, respectively.

Polyester/TGIC systems provide coatings with excellent outdoor durability. Therefore these are applied, e.g., on aluminium window frames and building panels and in the automotive industry. Polyester/Bisphenol A hybrids show improved performance over pure epoxy powder coatings regarding yellowing resistance and weatherability. They find their way in domestic appliances and other indoor applications.

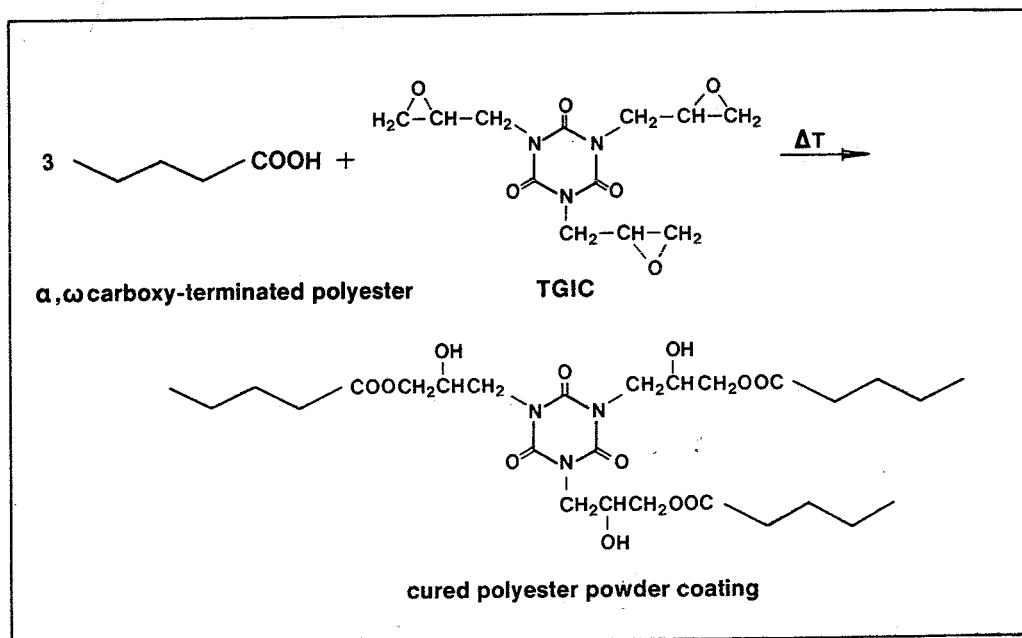


Figure 1. Curing reaction between the polyester prepolymer and TGIC.

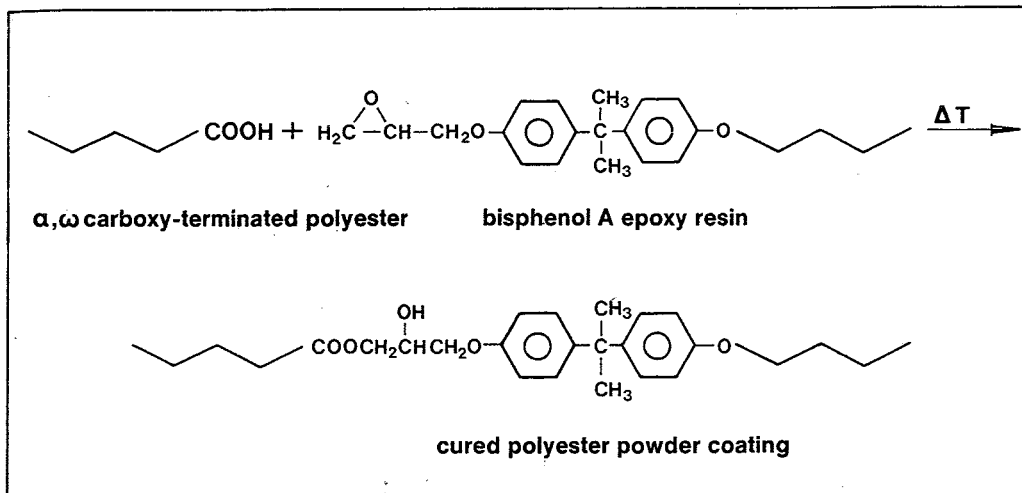


Figure 2. Curing reaction between the polyester prepolymers and a Bisphenol A based epoxy resin.

Suitable powder coating formulations meet with various conflicting requirements. Firstly, the powder coating composition should possess a good physical and chemical stability. This sets limits to the glass transition temperature and reactivity of the system. Secondly, good levelling and crosslinking at the lowest possible temperature requires a.o. low melt viscosity and high reactivity. Essential properties of powder coatings are: viscosity above the glass transition temperature, reaction kinetics, gelpoint and network structure.

In this study we will concentrate on two important subjects, namely the effects of catalyst concentration on the reaction kinetics and of molecular structure of the resin and crosslinker (functionality and molecular mass) on the network formation and network structure. These effects are studied experimentally with differential scanning calorimetry (DSC) and thermoviscoelastic analysis (TVA), respectively.

Experimental

The carboxy-terminated polyester prepolymers used in this study were based on terephthalic acid and 2,2-dimethylpropanediol-1,3. The number average molecular mass, \bar{M}_n , ranged between 2.5 and 5.6 kg/mol and the number average functionality, ϕ_n , between 2.0 and 3.0. These polyesters were mixed in the molten state with a stoichiometric amount of TGIC (epoxy equivalent mass 0.10 kg/mol) or a Bisphenol A based epoxy resin (epoxy equivalent mass 0.73 kg/mol) and are designated by a number referring to the prepolymer followed by T, respectively E. Dimethylbenzylamine (DMBA) was used as the catalyst in amounts ranging from 0-1% based on the total mass of the composition.

DSC measurements were performed with a Mettler TA 3000 apparatus using a heating rate of 20 °C/min. TVA measurements were carried out with a Rheometrics mechanical spectrometer with the parallel plate geometry. Both isothermal and heating runs (with 20 °C/min) were performed using an oven with N₂ atmosphere. The isothermal measurements were run as a function of frequency (-1.0 < log ω < +2.0). From these data the Newtonian viscosity of the uncured mixture and the equilibrium modulus of the network formed subsequently can be estimated. During the

heating run measurements were performed intermittently at constant frequency. More details on the materials and methods were published recently (1).

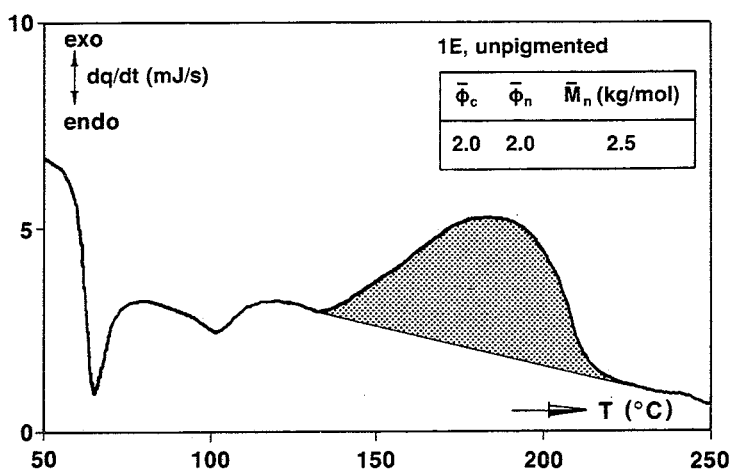


Figure 3. Heat flux DSC-curve for formulation 1E obtained with a scanspeed of 20 °C/min.

Results

A typical DSC curve is given in Figure 3. The shaded area represents the exothermic reaction enthalpy, Δq . With some data manipulation it is possible to calculate a.o. the reaction rate constant, k , at various temperatures (1, 2). Previously (1) we found no effect of molecular mass or functionality of the prepolymers on the reaction kinetics at a constant catalyst level. This was ascribed to the fact that the same reaction takes place in all compositions, viz. the carboxylic acid-epoxy reaction.

Obviously, the reaction rate constant, k , is much dependent on the catalyst concentration. Some typical results are collected in Table 1. From these data it can be concluded that DSC measurements provide valuable information on the rate of the polyester-epoxy reaction, but do not differentiate between molecular mass or functionality of the prepolymer. As a consequence these data do not provide information on the gelpoint of the system or the resulting network structure.

Table 1. Variation of reaction rate at 160 °C with DMBA concentration for two polyester prepolymers with different ϕ_n and \bar{M}_n .

wt. % DMBA	ln k at 160 °C (k in s ⁻¹)	
	$\phi_n=2.0, \bar{M}_n=2.5$ kg/mol	$\phi_n=3.0, \bar{M}_n=4.5$ kg/mol
0.00	- 8.4	- 9.5
0.25	- 5.7	- 5.8
0.50	- 4.9	- 4.9
1.00	- 4.5	- 4.4

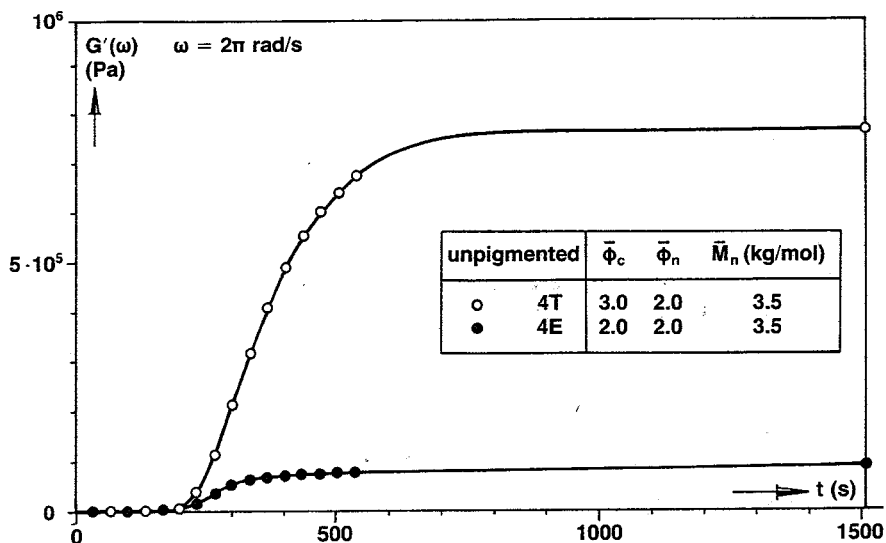


Figure 4. Variation of storage modulus with time for two formulations which differ in the functionality of the crosslinker, ϕ_c .

TVA measurements do give information on the network structure and crosslinking efficiency (1). Some typical results are shown in Figures 4 and 5, which give the storage modulus, G' , as a function of time. Although the frequency applied is too high to interpret these moduli as equilibrium moduli, their value is roughly proportional to the concentration of crosslinks (1).

The results of Figure 4 show the importance of the functionality of the crosslinking agent, ϕ_c , for a linear polyester prepolymer. Equilibrium moduli estimated from oscillation measurements at 200 °C after completion of the reaction show that 4T forms a permanent network whereas 4E does not. Figure 5 demonstrates the effect of differences in the molecular mass of the prepolymer on the crosslink density. As predicted by theory the crosslink density is proportional to \bar{M}_n^{-1} . From our results we conclude that the network structure of polyester powder coatings can be influenced deliberately by variations in the functionality and molecular mass of the prepolymer and crosslinker.

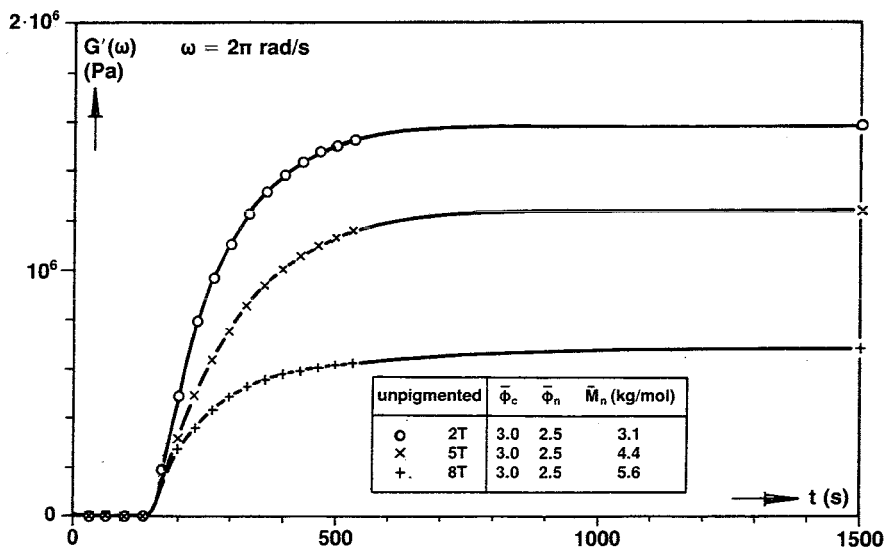


Figure 5. Variation of storage modulus with time for three formulations which differ in the molecular mass of the prepolymer, \bar{M}_n .

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