TA Instruments

Thermal Analysis & Rheology

THERMAL SOLUTION

ANALYSIS OF PHOTOCURED ADHESIVES BY DPC

PROBLEM

Photopolymerization and photocuring are popular synthetic techniques for thin film materials such as adhesives used in automotive, aerospace and computer applications. These synthetic approaches offer several benefits including rapid production of the final polymer, relatively low cost, and total monomer usage (hence no volatiles or effluents). Obtaining these benefits, however, requires a thorough knowledge of the thermodynamics and kinetics of the curing/polymerization process.

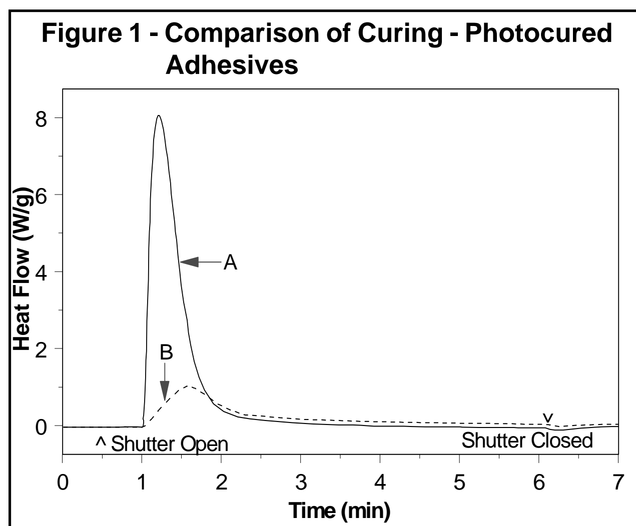
SOLUTION

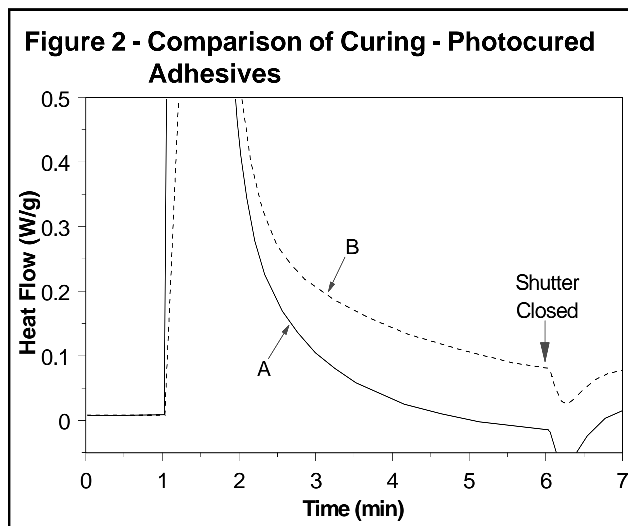
Differential photocalorimety (DPC), which measures the heat absorbed or released by a material as it is exposed to UV/visible radiation in a temperature-controlled environment, provides a convenient method for determining the properties of photocured adhesives before, during, and after exposure to radiation. Figures 1-6 illustrate the types of information which can be obtained. The materials evaluated include one that fully cures based on light exposure only (material A), one that requires heating after light exposure to complete its cure (material B), and one that is formulated to be "oxygen resistant" (material C). Figure 1 shows the photocuring of materials A and B. It is immediately obvious that these two materials are quite different. Material A (photocure only) cures much quicker (greater slope and shorter times) than material B. Figure 2 shows that material B is actually continuing to react throughout the 5 minute exposure, since the heat flow signal does not return to zero heat flow. Furthermore, material A has much greater cure enthalpy (area under the DSC curve) than B. The DPC and DSC results are shown in Table 1.

Table 1: Comparison of pre-cure, curing and post-cure for two types of photopolymers

Property	Material A	Material B
Induction time (sec)	3.4	7.6
Time to peak maximum (sec)	12.0	34.6
Enthalpy (J/g)	230	70
Tg (unexposed) (°C)	-57	-45
Tg (1st heat after exposure) (°C)	-15	3
Tg (2nd heat after exposure) (°C)	-15	28

Since these materials are elastomeric adhesives, their glass transitions should occur well below room temperature. Furthermore, to maintain constant properties (e.g., flexibility and adhesion), the glass transition temperature (Tg) should remain constant over time. Figure 3 shows the DSC scanning temperature experiments for material A. Before





photocuring (solid line), the sample shows a glass transition around -57°C. After curing (dashed line) Tg increases to -15°C. Heating of the sample (to over 200°C) does not affect the DSC thermal curve of this material, as is seen in the second heat (dash-dot curve).

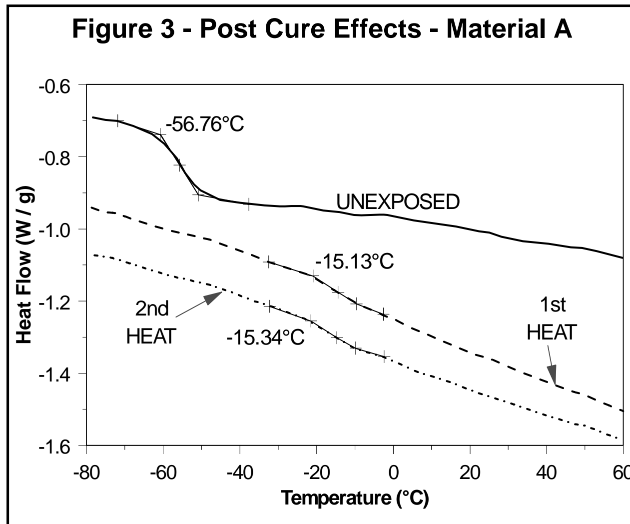


Figure 3 - Post Cure Effects - Material A

Material B, on the other hand, is affected by heat treatment (post-curing). Figure 4 shows that before curing (solid line) its Tg is around -45°C, while after curing (dashed line) the Tg increases to 3°C. The "2nd Heat" curve (dash-dot line) shows that after heating to over 200°C, the Tg increases further to 28°C. This shift is significant because it means that material B's properties such as strength, damping, and expansion coefficient, which change at the Tg, will be affected as end-use (ambient) temperature changes.

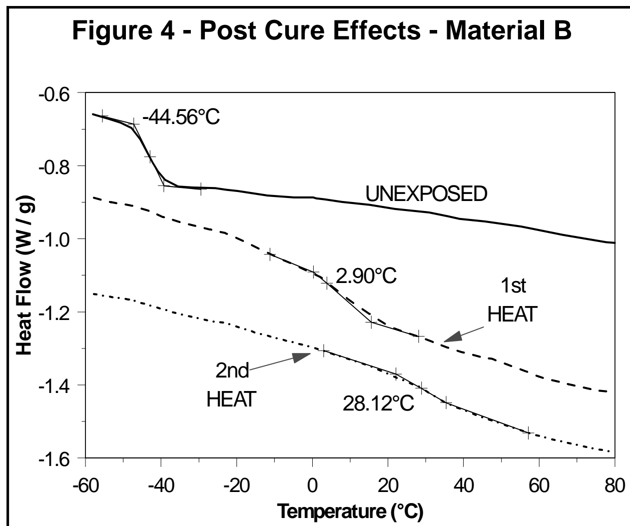


Figure 4 - Post Cure Effects - Material B

Most photocure production lines are not operated under an inert atmosphere. Rather, photocuring usually takes place in an air environment. Figure 5, however, shows that the curing process of (non-oxygen resistant) material A is slowed by the presence of oxygen.. All measures of the kinetics of curing (induction time, peak time and end of

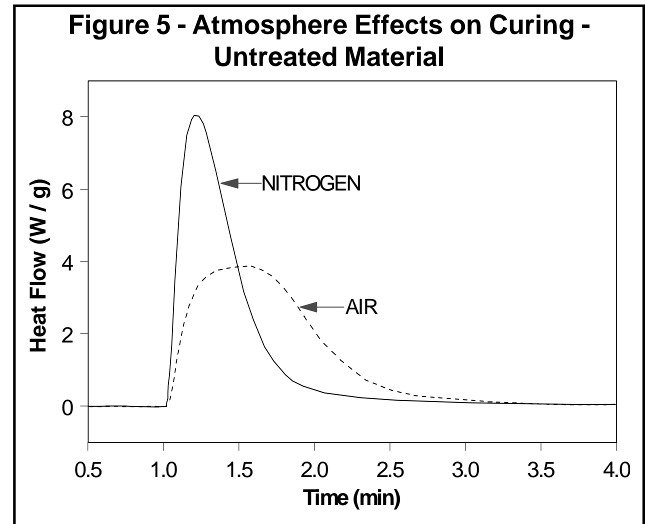


Figure 5 - Atmosphere Effects on Curing - Untreated Material

cure) are pushed to longer times. The enthalpy of curing, on the other hand, is not significantly affected, indicating that similar cure levels are achieved independent of the atmosphere. Because curing can go to completion, the slower cure kinetics are usually accommodated in production either by slowing the production line (less throughput) or by increasing the light intensity (higher utility expense). Oxygen resistant adhesives may help avoid these problems. Figure 6 shows that there is almost no

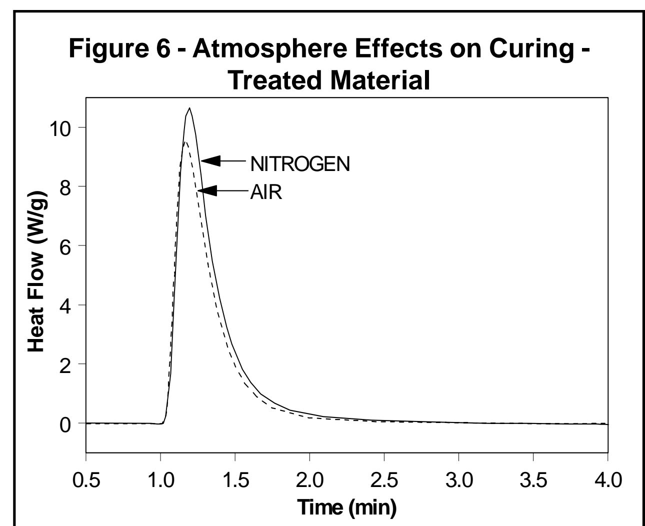


Figure 6 - Atmosphere Effects on Curing - Treated Material

kinetic (time) effect when using oxygen-resistant material C, though there appears to be a slight reduction in cure enthalpy. (See Table 2) Further testing is necessary to compare the physical properties of the cured oxygen-resistant adhesive to the standard material and to ultimately determine which is the best economic alternative.

Table 2: Comparison of cure properties for Standard and "Oxygen resistant" materials.

Property	[Standard]		[Oxygen-Resistant]	
	N_2 Purge	Air Purge	N_2 Purge	Air Purge
Induction time (sec)	3.4	5.2	4.0	4.5
Time to peak maximum (sec)	12.0	33.4	11.4	11.2
Enthalpy (J/g)	230	236	204	175

Acknowledgment

Acknowledgment: This brief is based on studies by Jon Foreman (U.S. Applications Laboratory).

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