

Characterization of Structural Heterogeneity of Polyurethane Coatings

M. PAOLPI,¹ C. LACABANNE²

¹ E.A.D.S., Airbus, 31060 Toulouse Cedex 03, France

² CIRIMAT/Laboratoire de Physique des Polymères, Université Paul Sabatier, 31062 Toulouse Cedex 4, France

Received 31 July 2000; accepted 10 January 2001

ABSTRACT: The thermal analysis techniques—Differential Scanning Calorimetry and ThermoStimulated Current—have been used to characterize a polyurethane high solid coating. The glass transition temperature, as determined by DSC, is 60°C. Below this glass transition temperature, an α_{sub} dielectric relaxation mode has been observed; it corresponds to cooperative movements precursor of the glass transition. The α_{ss} dielectric relaxation mode, located at $\approx T_g$ has been attributed to movements of soft sequences of the amorphous phase liberated at the glass transition temperature. The analysis of the fine structure shows that they are constituted of elementary processes characterized by relaxation times following a compensation law. Above T_g , the α_{hs} dielectric relaxation of hard sequences has been shown. It corresponds to hard sequences hydrogen bonded in polyurethane. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2786–2790, 2001

Key words: thermostimulated current; polyurethane; coating; dielectric relaxations; glass transition; physical aging

INTRODUCTION

Polyurethane topcoats are widely used to protect aircrafts from external aggressions. Now, health and environment protection oblige paint suppliers to formulate new products with low Volatil Organic Compounds (VOC).

One way to achieve this objective is to reduce the quantity of organic solvents so as to increase solid substances to obtain “High Solid Coatings.”

In this article, Differential Scanning Calorimetry (DSC) and ThermoStimulated Current (TSC) spectroscopy have been applied to the analysis of a polyurethane network based on a low VOC formulation: (a) the DSC technique has been used to determine the transition spectrum; (b) the TSC

technique, widely used to characterize polymeric materials,^{1–3} gives dielectric relaxations.

The fine structure of dielectric relaxation spectrum has been determined with the fractional polarization technique. This technique gives information on the microstructure of polymeric films: thus, a fingerprint of the coating was obtained.

From the obtained parameters, the various relaxation modes will be assigned to molecular mobility of the various entities.

MATERIALS AND METHODS

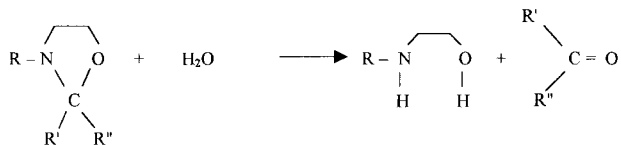
Materials

The coating is a two-component polyurethane paint. The first component is a polyester polyol mixture; the second component is constituted by an isocyanate solution.

Correspondence to: C. Lacabanne.

Journal of Applied Polymer Science, Vol. 81, 2786–2790 (2001)
© 2001 John Wiley & Sons, Inc.

A blocked catalyst increases the reaction in presence of water.



This polymeric coating is characterized by shorter and more reactive chains than nonlow-VOC polyurethane paints.

The coating was sprayed on an aluminum support to obtain a 60- μm thick layer.

Methods

Differential Scanning Calorimetry (DSC)

The thermograms were recorded on a DSC7 from Perkin-Elmer.

The sample was prepared from flakes of paint compressed and enclosed in an aluminum pan, the reference being constituted by an empty pan. The sample weight was 8.83 mg; the temperature was varied from -70 to 200°C .

The heating rate was $20^\circ\text{C}/\text{min}$. and the cooling rate $200^\circ\text{C}/\text{min}$.

All the experiments were performed under dry nitrogen.

ThermoStimulated Current (TSC)

The metallic support of the coating (a square of 1 cm^2) was used as an electrode. The sample was clamped between two capacitor plates. For recording complex TSC spectrum the sample was polarized for 2 min under a voltage of 100 V at a temperature of 63°C . Then, it was quenched down to -150°C to freeze the dipolar entities oriented by the static electric field.

The sample was short circuited, and the depolarization current was recorded by heating the

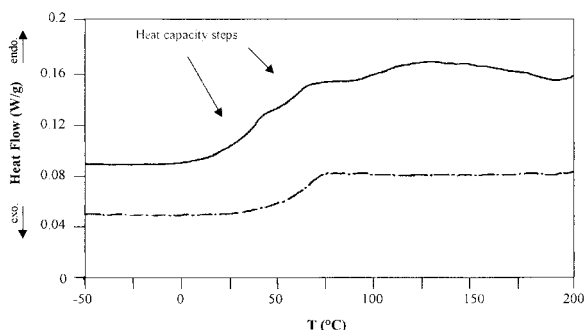


Figure 1 DSC thermograms of polyurethane.

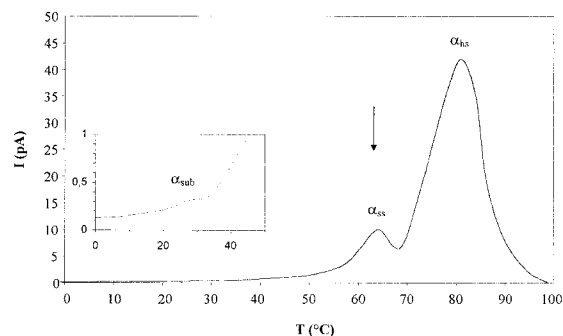


Figure 2 Complex TSC spectrum of polyurethane.

sample at a scanning rate $\beta = 7^\circ\text{C}/\text{min}$ (between 0 and 130°C).

RESULTS

Differential Scanning Calorimetry (DSC)

Thermograms obtained for the polyurethane coating are shown in Figure 1. The first temperature scan (solid line) presents two consecutive heat capacity steps. Each step of heat capacity (cf. figure) has been characterized by the temperature of its midpoint, which is respectively: $T_1 = 32^\circ\text{C}$ and $T_2 = 59^\circ\text{C}$, in the order of increasing temperature.

On the second temperature scan (dashed line), the first step has disappeared and a classical heat capacity (single step) is observed. This step is associated with the glass transition $T_g = 60^\circ\text{C}$. The first step observed during the initial scan is associated to a sub- T_g mode, and it disappears after annealing above T_g .

This phenomenon is reversible after a new annealing of a few hours below T_g , i.e., at 23°C . The sub- T_g transition has been associated with the molecular mobility of short sequences upon aging.

Complex TSC Spectrum

The polyurethane TSC spectrum is shown in Figure 2.

The polarization temperature (63°C) has been chosen to identify the fine structure of various relaxation modes.

Three relaxation modes, labeled α_{sub} , α_{ss} , and α_{hs} , are observed in the order of increasing temperature. They are respectively located at 30, 63, and 81°C .

By varying the applied voltage from the above-mentioned standard value, we have shown that all the three relaxation modes are ohmic. So, we

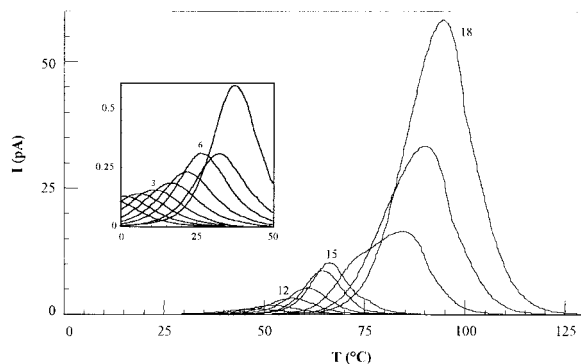


Figure 3 Elementary TSC spectra of polyurethane.

can conclude with a dipolar origin. This point is particularly important for the relaxation mode observed at higher temperature—i.e., above T_g —that might be due to a Maxwell-Wagner-Sillars effect. In our case, this hypothesis is not valid.

Note that, considering the low value of the polarization temperature, the α_{hs} mode is only partly polarized. Otherwise, it would overwhelm the other relaxation modes. The suffixes sub, ss, and hs are for, respectively, submode, soft segments, and hard segments; they will be explained in the discussion.

Elementary TSC Spectra

Complex TSC spectra were experimentally resolved into elementary TSC spectra that were obtained by using the fractional polarization technique.⁴ Temperature range has been restricted to 130°C to avoid irreversible changes of samples. Elementary spectra were recorded with the same polarization field as complex spectrum, with a “temperature window” of 5°C. A series of elementary spectra was obtained by shifting the polarization window along the temperature axis from 0 to 100°C. The depolarization current was recorded by using the same protocol as the complex spectrum. Thus, we obtained an elementary spectrum that can be analyzed with the hypothesis of a unique relaxation time τ .

Elementary spectra isolated in polyurethane films are shown in Figure 3.

Analysis of Elementary TSC Spectra

Each elementary peak has been analyzed and the dielectric relaxation time τ as a function of temperature T has been deduced from the following equation⁵:

$$\tau(T) = \frac{1}{\beta I(T)} \int_T^\infty I(T) dT \quad (1)$$

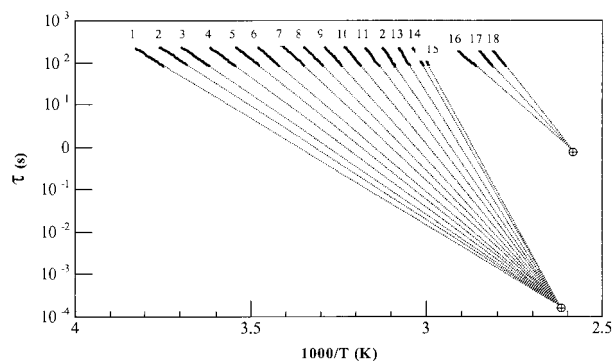


Figure 4 Arrhenius diagram of dielectric relaxation time of polyurethane.

where I is the depolarization current.

The Arrhenius diagram of the various relaxation times is shown in Figure 4.

The linear dependence of $\log \tau$ vs. T^{-1} shows that all processes obey an Arrhenius equation:

$$\tau(T) = \tau_0 \exp \frac{\Delta H}{RT} \quad (2)$$

where τ_0 is the preexponential factor, ΔH is the activation enthalpy, and R is the perfect gaz constant.

Figures 5 and 6 present, respectively, the evolutions of ΔH and τ_0 vs. the temperature of the elementary peak maximum.

The Arrhenius diagram shown in Figure 4 exhibits two series of $\tau(T)$ dependences reflected by the two groups of converging lines. The corresponding relaxation times follow a compensation equation.

$$\tau(T) = \tau c \exp \left[\frac{\Delta H}{R} (T^{-1} - T_c^{-1}) \right] \quad (3)$$

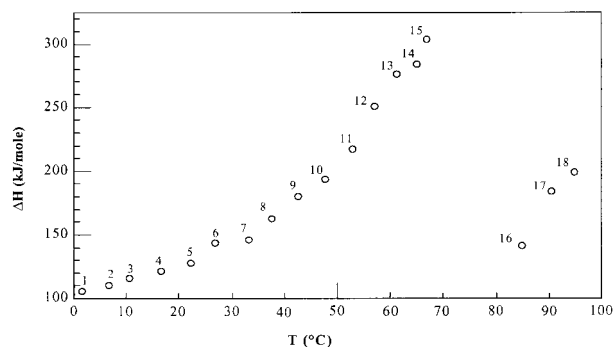


Figure 5 Activation enthalpy ΔH as a function of temperature T for polyurethane.

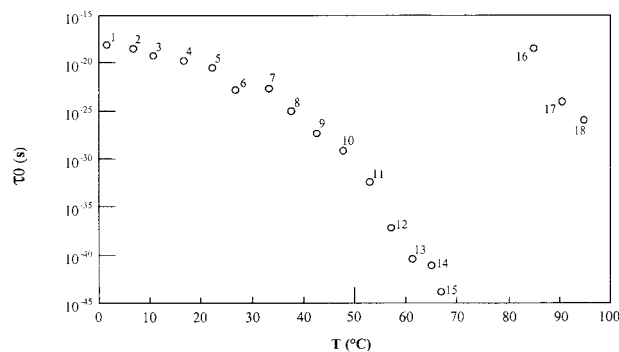


Figure 6 Preexponential factors τ_0 as a function of temperature T for polyurethane.

where τ_c is the compensation time, and T_c is the compensation temperature.

For the lower temperature processes (1 to 15) constituting the α_{sub} and α_{ss} modes:

$$\tau_{c1} = 1.8 \times 10^{-4} \text{ s}$$

and

$$T_{c1} = 108^\circ \text{C}.$$

For the higher temperature processes (16 to 18) corresponding to the α_{hs} mode:

$$\tau_{c2} = 8.2 \times 10^{-1} \text{ s}$$

and

$$T_{c2} = 114^\circ \text{C}.$$

The linear dependence between $\log \tau_0$ and the enthalpy activation ΔH is shown in the compensation diagram in Figure 7.

DISCUSSION

The transition spectrum of the low VOC polyurethane consists of two events: the glass transition at $T_g \approx 60^\circ \text{C}$, and a sub- T_g transition at $T_{\text{sub}} \approx 31^\circ \text{C}$. Both phenomena are accompanied by dielectric relaxation modes in the same temperature range: they have been designated as α_{ss} and α_{sub} , respectively. At higher temperature an additional dielectric relaxation mode, labeled α_{hs} , has been observed. The molecular origin of the various events will be discussed.

Sub- T_g Transition/Relaxation

The sub- T_g transition/relaxation have common features: (a) they are observed in the same temperature range, i.e., below T_g , and (b) they are enhanced by sub- T_g -annealing. They disappear for annealing at $T_g + 10^\circ \text{C}$. It is a perfectly reversible process, so it only involves physical bonds.

The common origin of this sub- T_g transition/relaxation might be short-range physical aging. The characteristics of the sub- T_g dielectric relaxation are the following: (a) they correspond to a series of localized movements that are cooperative, because the corresponding relaxation times obey a compensation law; (b) they appear at relatively low temperatures: this mobility is a precursor of the glass transition of soft sequences (ss); (c) they are governed by the existence of structural heterogeneity, and result from the effect of imbalances under cooling and heating.

In other words, the sub- T_g transition/relaxation corresponds to the disordering of localized domains by breaking of physical bonds responsible for physical aging of soft sequences. It probably reflects density fluctuations in the glassy state. This phenomenon is the precursor of the glass transition/relaxation of soft sequences segregated in soft domains.

Glass Transition/Relaxation of Soft Sequences

Around the glass transition temperature determined by the classical step of the heat capacity, a dielectric relaxation mode is observed. It corresponds to elementary processes with relaxation times following a compensation law with $T_c \approx T_g + 48^\circ \text{C}$. Those cooperative movements have been attributed to soft sequences. The values of activation enthalpy and entropy that increases linearly are characteristic of the length of the mobile se-

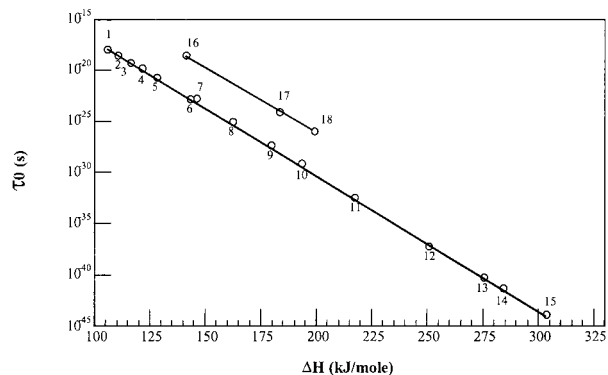


Figure 7 Compensation diagram of polyurethane.

quences according to the Hoffman-Williams-Passaglia model.⁶ The α_{ss} mode has all the typical feature of the dielectric relaxation modes liberated at the glass transition in polymeric materials.

Relaxation of Hard Sequences

Regarding thermal history, this relaxation mode has the same behavior as α_{sub} : its magnitude increases upon aging below T_g , and it disappears after annealing in the liquid state. Because this mode is at a higher temperature than the preceding one, it has been associated with more cohesive domains. Because the studied polyurethane is completely amorphous, as shown by DSC thermograms, we are dealing with ordered domains at nanometric scale.

Considering the ohmic character of this relaxation mode, a Maxwell-Wagner-Sillars effect due to charges trapped at the soft-hard interface cannot be invoked.

The time constant of this mode is coherent with the low kinetic of hydrogen bonds. The hard sequences hydrogen bonded between each other have been proposed for explaining this relaxation mode. Moreover, the segregation of hard sequences in hard domains has been extensively discussed in the literature concerning polyurethanes.⁷⁻⁹ This might explain the existence of a compensation effect characteristic of a morphological entity. One of the features of the compensation line associated with this hard sequence phase is that for a given activation enthalpy, τ_0 is always larger than for the α_{ss} mode. According to the Eyring equation, τ_0 is related to the activation entropy ΔS :

$$\tau_0 = \frac{h}{kT} \exp - \frac{\Delta S}{R} \quad (4)$$

where h is the Plank constant, and k is the Boltzmann constant.

Then, the α_{hs} mode has lower activation entropies than the α_{ss} one. Considering the Boltzmann equation $\Delta S = R \ln \Omega$, where Ω is the number of accessible sites; the lower Ω , the higher the local order. In other words, hard sequences constitute domains where local order is higher than in soft sequences domains.

Structural Heterogeneity

The presence of the sub- T_g mode reflects a structural heterogeneity due to the effects of imbalances in the heating and cooling rates over T_g .

The existence of two components for the α mode is a dynamic manifestation of the well-

known biphasic structure of polyurethane. The lower temperature component reflects the existence of the soft sequence phase: it is due to the breaking of Van der Waals bonds stabilizing apolar sequences in the glassy state. The higher temperature component of the α mode corresponds to the hard segment phase: it is due to the breaking of the hydrogen bonds stabilizing polar sequences in the glassy state. The higher cohesion of those harder domains is coherent with the higher temperature position of α_{hs} regarding the α_{ss} mode. It is accompanied by a higher level of local order than in the soft phase.

CONCLUSION

The analysis by Differential Scanning Calorimetry and ThermoStimulated Current of a low VOC polyurethane has allowed us to characterize its microstructure. If local instabilities and the soft sequences phase is observed by both techniques, the hard sequences phase is only seen by TSC. The biphasic structure is exhibited on the compensation diagram by two compensation lines. The one with higher activation entropies corresponds to the soft sequences phase; the one with lower activation entropies corresponds to the hard sequences phase.

The set of activation parameters constitutes a fingerprint of the polymeric coating.

REFERENCES

1. Dufresne, A.; Lacabanne, C. *Polymer* 1995, 36, 441.
2. Schönhals, A.; Schlosser, E. *Colloid Polym Sci* 1988, 78, 24.
3. Boiteux, G.; Seytre, G. *J Non-Cryst Solids* 1991, 131, 1131.
4. Fois, M.; Lamure, A.; Lacabanne, C. *J Appl Polym Sci* 1997, 66, 135.
5. Teyssedre, G.; Mezghani, S.; Bernes, A.; Lacabanne, C. In *Dielectric Spectroscopy of Polymeric Materials*; Runt, J. P.; Fitzgerald, J. J., Eds.; ACS 227; American Chemical Society; Washington, DC, 1997.
6. Hoffmann, J. D.; Williams, G.; Passaglia, E. *J Polym Sci* 1966, 14, 173.
7. Cooper, S. L.; Tobolsky, A. V. *J Polym Sci* 1967, 11, 1361.
8. Vallance, M. A.; Yeung, A. S.; Cooper, S. L. *Colloid Polym Sci* 1983, 261, 541.
9. Tao, H. J.; Fan, C. F.; MacKnight, W. J.; Hsu, S. L. *Macromolecules* 1994, 27, 1720.