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DSC and TSC studies of polyurethane mono- and bilayer paints [1]

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Abstract

Differential scanning calorimetry and thermally stimulated current spectroscopy have been applied to the characterization of the microstructure of polyurethane/polyurethane bilayers. The microstructure of the constituting polyurethane monolayers was used as reference. It is constituted of two phases indicating the segregation of soft and hard sequences. In bilayers, the microstructure is strongly dependent upon the recovering time. The microstructure is also modified upon ageing.

INTRODUCTION

In aeronautics, the external aircraft paint is constituted by a polymeric multilayer. The aim of this work is to characterize the outer polyurethane–polyurethane bilayer for various processing conditions. The phenomenological characteristics of the bilayer are strongly dependent upon the drying time of the inner layer before application of the outer layer. Analysis of the molecular mobility of polyurethane gives a characterization of its microstructure [1–3].

In this work, two thermo-stimulated spectroscopies were used: differential scanning calorimetry (DSC) and thermo-stimulated current (TSC) spectroscopy [4]. A preliminary study of each polyurethane monolayer will be used as reference.

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MATERIALS AND METHODS

Paint was deposited onto an aluminium support. The inner layer constituting the barrier coating (BC) was 25 μm thick. Two recovering times (RT), 0.25 and 8 h, were used for application of the outer layer, i.e. the finition (F) which was 80 μm thick. The condtions of ageing were constant at 23°C and 55% relative humidity.

For DSC experiments, flakes of paints were compressed in order to fill the aluminium pan. Experiments were carried out on a Perkin-Elmer DSC-7 with a heating rate of 20°C $\min^{-1}$ in the temperature range −60 to +250°C. For each sample, two consecutive runs were recorded. Only second-run thermograms are discussed here.

For TSC experiments, the metallic support of the bilayer was used as one electrode. An identical plate was used as the counter electrode. Experiments were carried out on a Solomat TSC-RMA spectrometer, with a heating rate of 10°C $\min^{-1}$ in the temperature range from RT to +160°C. All the samples were polarized under the same conditions, i.e. 2 min at 100°C and 200 V, quenched at −30°C.

DSC STUDY

Monolayers

Figures 1 and 2 show the glass transition temperatures T_g measured on the DSC thermograms recorded as a function of ageing time, for the two polyurethane monolayers BC and F, respectively.

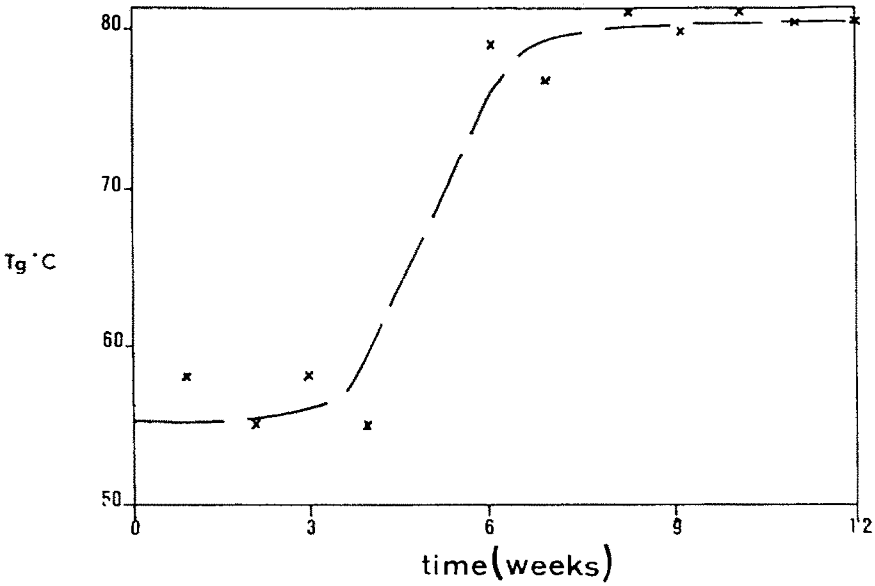

Fig. 1. Evolution of T_g as a function of ageing time for BC monolayer.

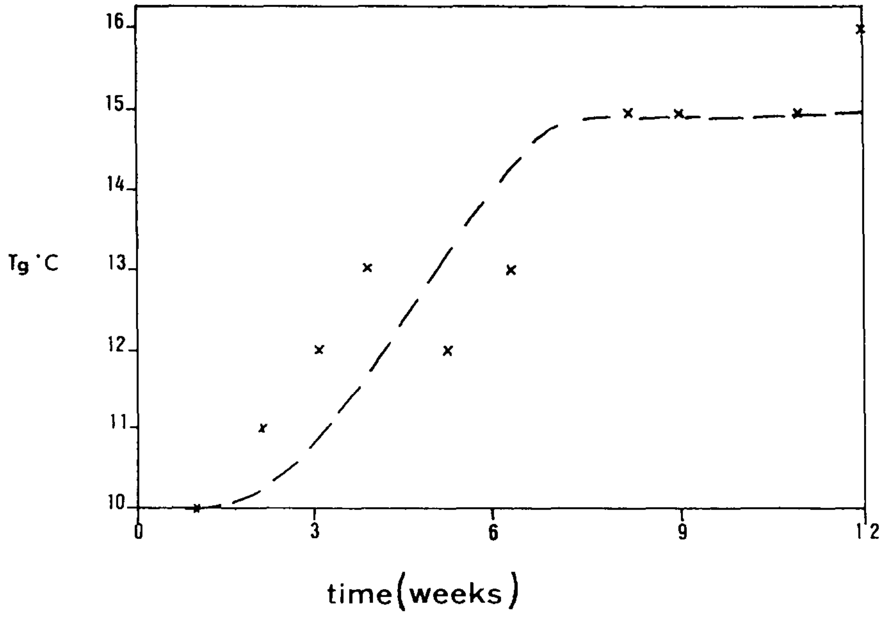

Fig. 2. Evolution of T_g as a function of ageing time for F monolayer.

BC is characterized by values of T_g that are high for a polyurethane material. The T_g values increase strongly from $T_g = 54°C$ to $T_g = 77°C$, after seven weeks of ageing time. It is important to note here that rapid kinetics are involved in the polymerization process.

F is characterized by low values of T_g (11°C) after 2 days of ageing time, and 16°C after 12 weeks of ageing time. The evolution of T_g values is less important than for BC. This result is probably related to the very low kinetics of the polymerization.

Bilayers

Figures 3 and 4 show the DSC thermograms recorded for the bilayers with recovering times RT = 0.25 and 8 h, respectively.

A single step is observed in all cases, independent of the recovering time or ageing time. The T_g values are intermediate between those of BC and F.

This phenomenological miscibility might be a result of the chemical nature of both monolayers.

The inflexion point of the step has been associated with the glass transition temperature T_g. Table 1 lists the T_g values recorded for RT = 0.25 h and RT = 8 h, as a function of ageing time. We have also indicated, as reference, the T_g values of the BC and F monolayers.

It is also interesting to note the variation in the heat capacity step at T_g,

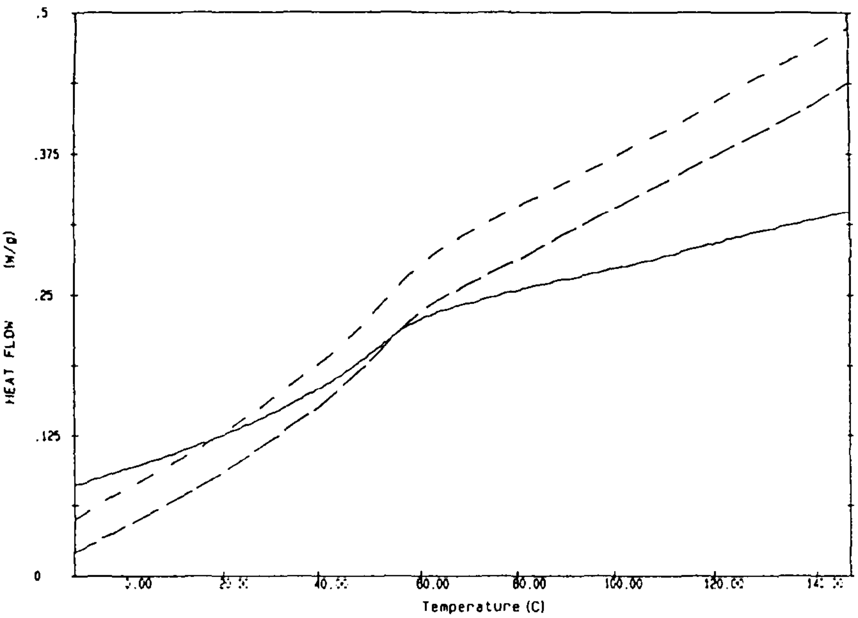

Fig. 3. DSC thermograms for BC/F bilayer with a recovering time RT of 0.25 h for various ageing times: ——, 2 days; — — —, 7 weeks; ---, 12 weeks.

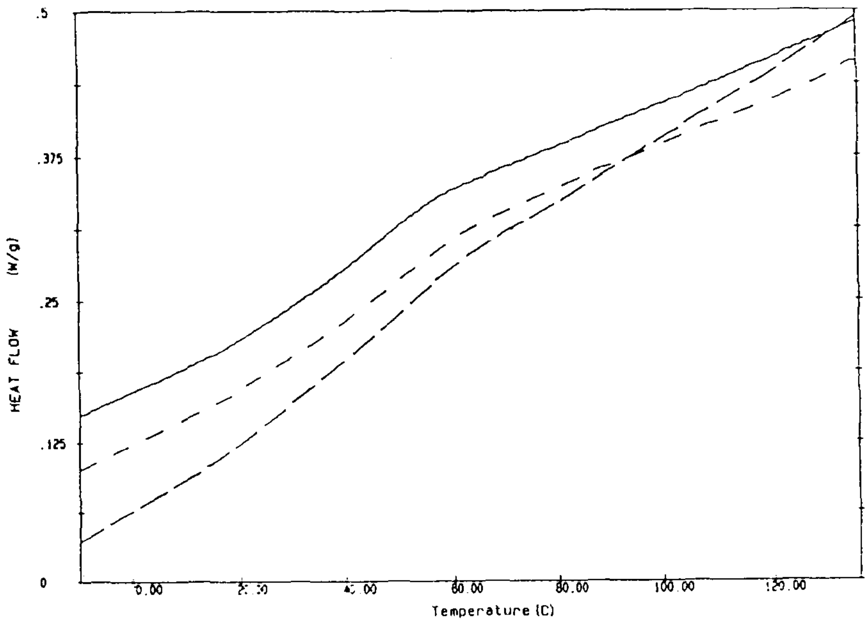

Fig. 4. DSC thermograms for BC/F bilayer with a recovering time RT of 8 h for various ageing times: ——, 2 days; — — —, 7 weeks; ---, 12 weeks.

TABLE 1

Variation of T_g from DSC experiments as a function of ageing time

Ageing time	Bilayer		Monolayer	
	RT = 0.25 h	RT = 8 h	BC	F
2 days	42.5	40.5	54	11
7 weeks	46	41	76	13
12 weeks	47	42	77	16

ΔC_p. ΔC_p is lower for RT = 0.25 h than for RT = 8 h. This evolution confirms the restriction of molecular mobility for the shorter recovering time.

TSC STUDY

Monolayers

Figures 5 and 6 show the TSC thermograms recorded for the two monolayers, BC and F, as a function of ageing time.

The TSC thermograms recorded for the BC coating show three relaxation peaks respectively situated at T_{m_l} (low), T_{m_i} (intermediate) and

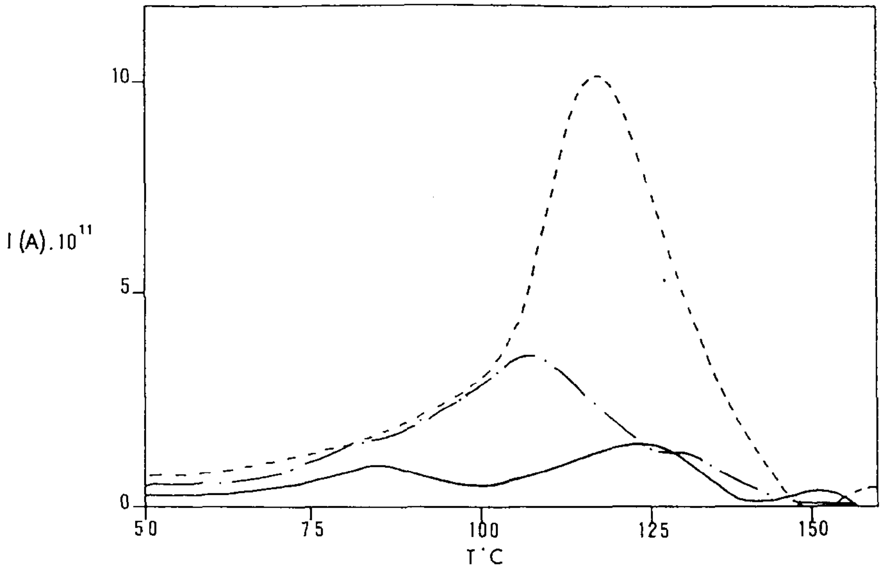

Fig. 5. TSC thermograms for BC monolayer as a function of ageing time: ——, 4 days; — · —, 4 weeks; – – –, 13 weeks.

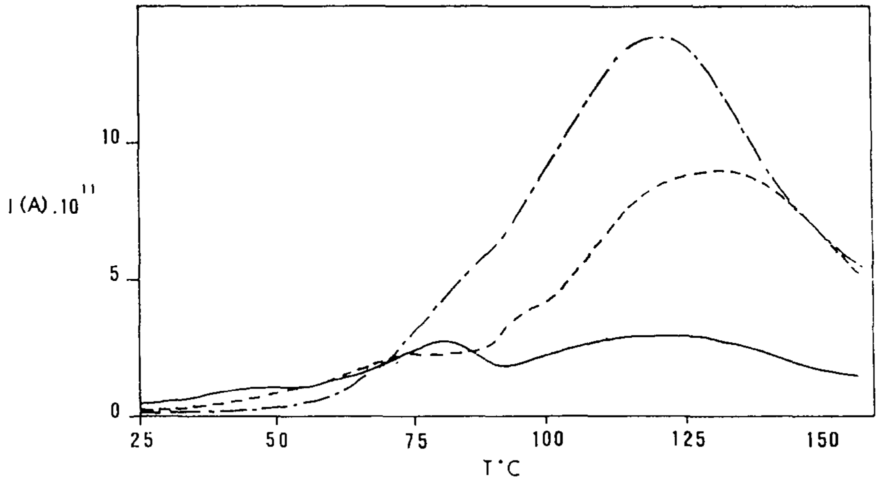

Fig. 6. TSC thermograms for F monolayer as a function of ageing time: ——, 4 days; — · —, 4 weeks; ---, 13 weeks.

T_{m_h} (high) in order of increasing temperature. The first peak is shifted from 81 to 121°C, with a decrease in intensity with ageing time. It probably corresponds to the dielectric relaxation of the soft sequences of the polyurethane. The second peak is shifted from 126 to 138°C and increases in intensity with ageing time. This relaxation mode is assigned to the molecular mobility of the hard polyurethane sequences that are strongly involved in the polymerization process of the inner coating BC. The third peak is probably the consequence of free charge movements.

The TSC thermograms recorded for the F outer layer also show three peaks. The first, associated with the dielectric relaxation of the soft sequences, increases in temperature and in intensity. It is interesting to note the influence of soft segments in the polymerization of the outer layer. All values measured on the different thermograms for the three peaks are lower than those measured for BC. The second peak increases in temperature, but decreases in intensity. It corresponds to the relaxation of the hard sequences. The third peak is characterized by a higher intensity than for BC. A more important mobility of the polyurethane sequences is involved in the polymerization process. It might facilitate charge transport.

Bilayers

Figures 7 and 8 show the TSC thermograms recorded for the bilayers with recovering times of 0.25 and 8 h, respectively.

For short recovering times, at 1 week of ageing, three relaxation peaks are observed. The lower temperature peak is situated at 70°C. It corresponds to the step recorded on the DSC thermograms and therefore it

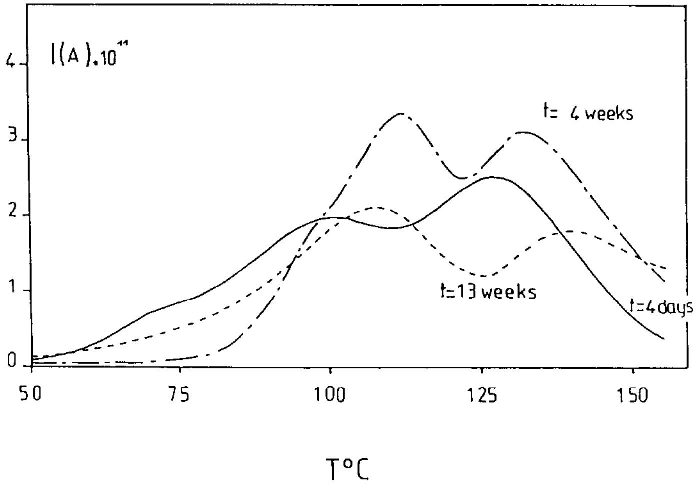

Fig. 7. TSC thermograms for BC/F bilayers for a recovering time RT of 0.25 h.

has been attributed to the dielectric manifestation of the glass transition of the bilayer. The soft polyurethane sequences might be involved in this mode. The intermediate peak is situated at 100°C. According to previous data, this relaxation mode has been assigned to the molecular mobility of the hard sequences. The high temperature peak is located at 128°C. Free charge movements are probably involved in this process. Table 2 lists the T_m values corresponding to the maximum of the TSC peak for RT = 0.25 h and 8 h, as a function of ageing time.

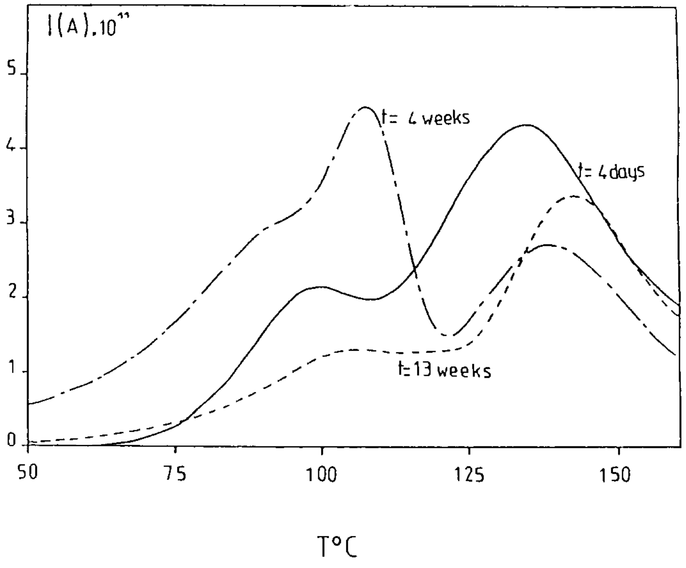

Fig. 8. TSC thermograms for BC/F bilayers for a recovering time RT of 8 h.

TABLE 2

Variation of T_m from TSC experiments as a function of ageing time

Ageing time	Bilayer BC/F						Monolayer					
	RT = 0.25 h			RT = 8 h			BC			F		
	T_{m_l}	T_{m_i}	T_{m_h}	T_{m_l}	T_{m_i}	T_{m_h}	T_{m_l}	T_{m_i}	T_{m_h}	T_{m_l}	T_{m_i}	T_{m_h}
4 days	70	100	127	75	100	134	81	126		50	80	120
4 weeks	95	112	133	91	108	139	97	123		55	85	129
13 weeks		108	140	107	120	142	121	138	160	72.5	95	131

It is interesting to note that upon ageing, the contribution of the low temperature peak is strongly decreased [5]. This confirms the hypothesis proposed for explaining previous DSC data. For long recovering times, the intensity of the low temperature peak is smaller so that it is not well-resolved on the TSC spectrum for 1 week of ageing. It can only be distinguished after 3 weeks. This indicates a softening of this bilayer by comparison with the previous case.

CONCLUSION

Differential scanning calorimetry and thermally stimulated current spectroscopy are well adapted to the investigation of molecular mobility in polyurethane coatings.

Charactersitic parameters of the monolayers are proposed, and the contributions of the hard and soft sequences have been identified.

The study of the bilayers has shown the existence of a phenomenological miscibility of the hard and soft sequences. This pseudo-miscibility is strongly dependent upon the recovering time.

This methodology is well adapted to the study of ageing procedures in polymeric coatings.

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