

Thermooxidative stabilization of a MDI

Polyol polyisocyanate

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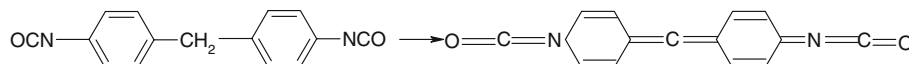
Abstract Samples of flexible PU foam were prepared from a polyol (Elastoflex W 5516/115) and an isocyanate prepolymer (Iso 145/8), both commercial Elastogram products. For the thermooxidative stabilization, two phenolic compounds were used, separately or in mixture. These compounds were: 2,6-di-*t*-butyl-4-methyl-phenol (non-reactive) (AO-1), 3,5-di-*t*-butyl-4-hydroxy-benzyl alcohol (reactive, AO-2), used in total mass% of 0.3/1.5. The TG/DTG/DTA curves were drawn up in dynamic air, with a heating rate of 10 °C min⁻¹, until 500 °C. For the unstabilized sample a single thermodegradative TG step, with a maximum rate at 268–270 °C was observed, whereas for the stabilized samples, supplementary steps at higher temperature were observed. The changes in the TG/DTG/DTA parameters are not in a single relationship with the mass% of the stabilizator, due to the following:

concentrations. But the most remarkable effect is the synergetic effect of a 1:1 mixture of AO-1 and AO-2.

Keywords Thermal stability · Thermal analysis · Stabilized polyol polyisocyanate

Introduction

The polyurethanes have a special place among the industrial polymers, due to a large variety of materials. So, flexible foams with very good physico-mechanical properties can be obtained from aromatic isocyanates and polyetheric polyols. But a major disadvantage of these polymers is a rapid degradation due to self-oxidation [1–3]. The example of methylen-diphenyl-diisocyanate (MDI) is significant:

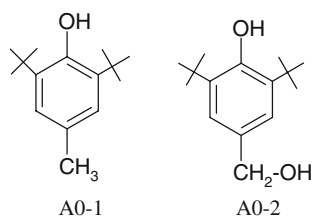


AO-1 is easily migrated out from PV, especially, at higher concentrations. AO-2 had positive effect at all studied

Therefore, the antioxidants are compulsory additives in each polyurethane composition. There are two types: reactive (which are inserted in the polymeric chain during the synthesis) and non-reactive antioxidants. The last one has the advantage of no influence on the designed properties of the polyurethane but also the major disadvantage of migration to the polymer surface due to the huge difference of the molecular mass.

In some recent paper [4–6] the kinetic analysis of thermoanalytical data (TG and/or DSC) prove its utility in estimation of the antioxidant efficiency.

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**Scheme 1**

The aim of the present paper is to perform a study on the thermal behaviour of an MDI type polyurethane stabilized with reactive and/or non-reactive additives. The effect of the concentration of added stabilizer, as well as a possible synergism by using a mixture of reactive/non-reactive stabilizers were the main objectives.

Experimental

Polyurethane synthesis

The raw materials were:

- MDI isocyanate prepolymer (ISO 145/8 from Elastogran, Hungary)
- Polyester polyol (Elastoflex W 5516/115 from Elastogran, Hungary)
- Catalyst 1,4-diazabicyclo [2,2,2] octan (Dabco from Air Products and Chemicals, USA)
- Thermooxidative stabilizers: a non-reactive type 2,6-di-*t*-butyl-4-methyl-phenol (AO-1) and a reactive type 3,5-di-*t*-butyl-4-hydroxy benzyl alcohol (AO-2), both

Table 1 Stabilizer content of the prepared samples

| Sample symbol | Stabilizer content/mass% | |
|---------------|--------------------------|-----------------|
| | AO-1/(non-reactive) | AO-2/(reactive) |
| MS | – | – |
| 2S1 | 0.3 | – |
| 2S2 | 0.6 | – |
| 2S3 | 0.9 | – |
| 2S4 | 1.2 | – |
| 2S5 | 1.5 | – |
| 3S1 | – | 0.3 |
| 3S2 | – | 0.6 |
| 3S3 | – | 0.9 |
| 3S4 | – | 1.2 |
| 3S5 | – | 1.5 |
| 4S1 | 0.15 | 0.15 |
| 4S2 | 0.30 | 0.30 |
| 4S3 | 0.45 | 0.45 |
| 4S4 | 0.60 | 0.60 |
| 4S5 | 0.75 | 0.75 |

from Fluka, Switzerland. The structural formulas are presented in Scheme 1.

The reaction components were added, under intense stirring, into a polyethylene vessel, and the reaction mass was allowed to expand for 90 min. In all samples the volume ratio of isocyanate to polyol was $\frac{1}{2}$, with 0.03 mass% of catalyst. The stabilizer content of the prepared samples is presented in Table 1.

Thermal analysis

The TG/DTG/DTA curves were drawn up on a Perkin Elmer DIAMOND devices, in dynamic air atmosphere (100 mL min^{-1}), with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ until $500 \text{ }^\circ\text{C}$.

The evolved gas analysis (EGA) was carried out by a coupled TG/FT-IR technique, using a Perkin Elmer SPECTRUM 100 devices with an IR gas chamber connected to the exit of the DIAMOND furnace. The same air flow of 100 mL min^{-1} and a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ were used. The FT-IR spectra were processed by the Sadtler Gas Vapor Library. The thermal degradation was discussed on the basis of these data and the FT-IR-UATR spectra of the initial samples.

Results and discussions

In Fig. 1 some typical thermoanalytical curves are presented.

In all samples, the thermodegradation due to an exothermic process (thermooxidation) and the maximum of the reaction rate corresponds to the maximum of the evolved reaction heat. In comparison with the unstabilized polymer, all the other samples present a more complicated thermodegradation process, first of all observed by the appearance of two or more DTG/DTA maximums.

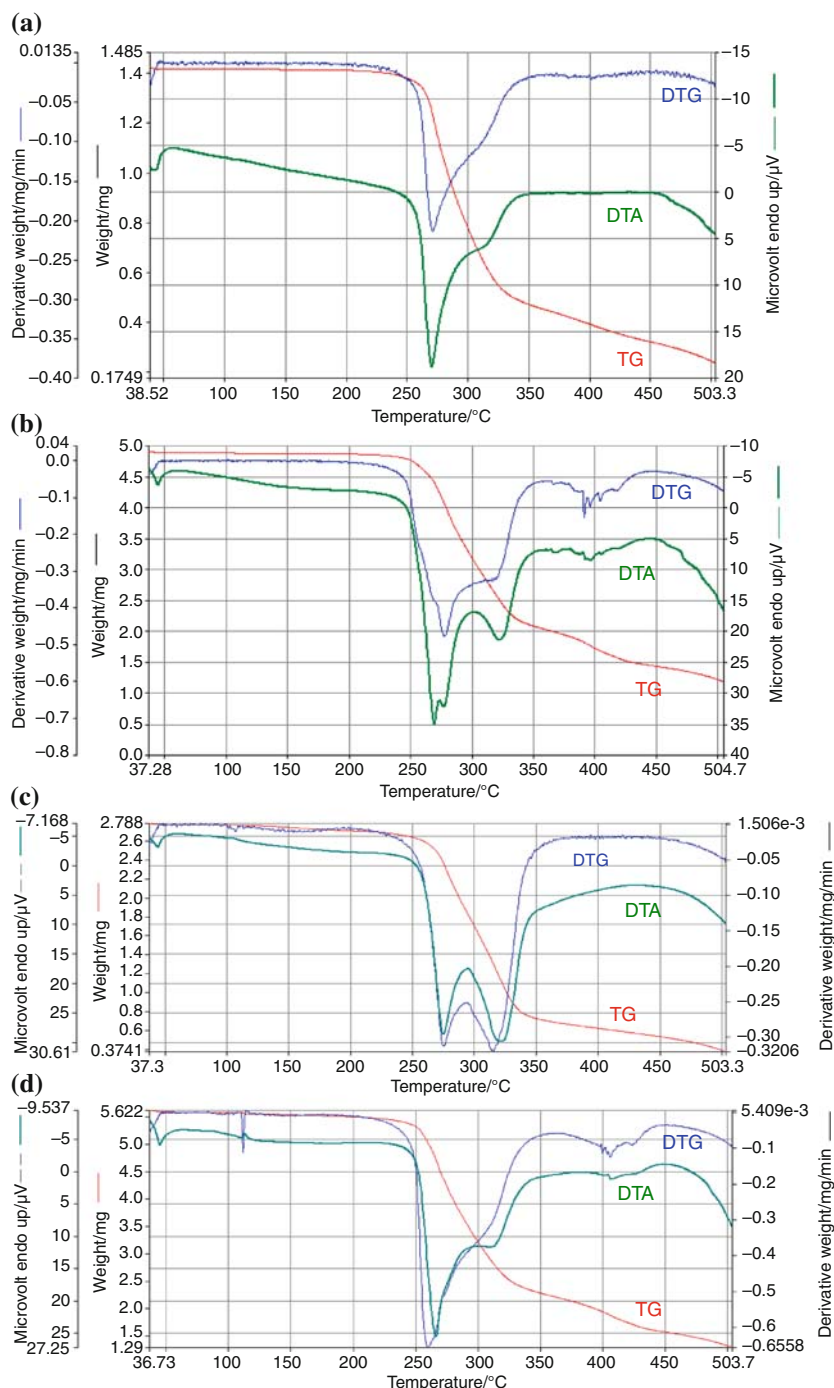
A better estimation of stabilizer's effect was possible on a comparative mass loss versus temperature diagram. For example, in Fig. 2 such diagrams for a total stabilizer concentration of 0.6 mass% are presented.

Some observations are noticeable:

- (i) By all sample the degradation began near $250 \text{ }^\circ\text{C}$
- (ii) The differences in thermal stability can be estimated by:
 - the mass loss at a certain temperature: the smaller the mass loss is, the more stable the sample is; according to Fig. 2, the mass loss was in the following order:

$$\text{MS} > 3\text{S} \approx 2\text{S} > 4\text{S} \quad (1)$$
 - the slope at a certain temperature $\partial m/\partial T$ is a measure of the thermo-degradation rate: also the

Fig. 1 Thermoanalytical curves for unstabilized and stabilized polyurethane. The total concentration of stabilizer was 0.9 mass%. **a** MS, **b** 2S3, **c** 3S3, **d** 4S3



smaller it is, the more stable the sample is; the order is as follows:

$$MS > 3S \approx 2S > 4S \quad (2)$$

- (iii) Both Eqs. 1 and 2 indicate the MS as the less stable sample and 4S the most stable one. By comparison with 2S and 3S, it is obvious that a synergism occurs by using a mixture of reactive and non-reactive stabilizer. The effect of concentration will be discussed. According to Fig. 3, the non-reactive stabilizer had a positive effect

only at concentrations lower than 0.6%, especially in the range of 250 to 300 °C. At higher temperatures, even if the concentration is higher, these are favourable conditions for stabilizer migration out from the polymeric mass.

In the reactive stabilizer a different behaviour is observed. According to Fig. 4, AO-2 had a positive effect at all studied concentrations. The concentration dependence of this effect is rather insignificant. However the best

Fig. 2 Comparative diagrams of mass loss versus temperature for the first decomposition step of samples without or with 0.6 mass% of stabilizers

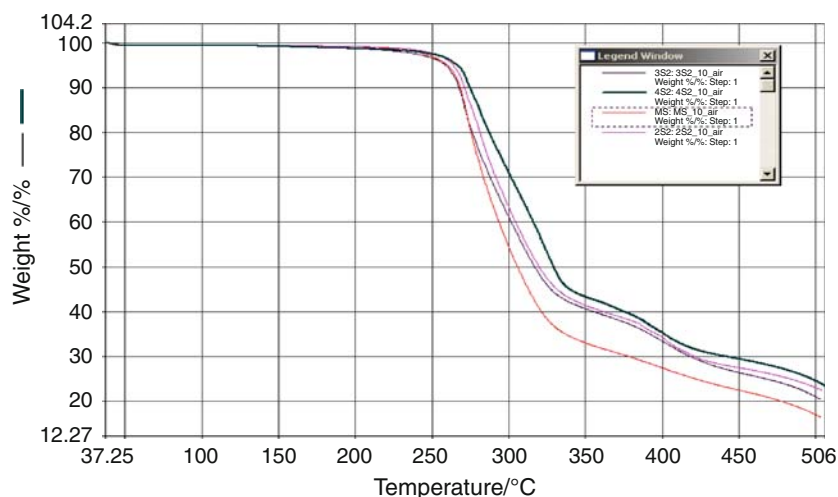


Fig. 3 Mass loss versus temperature for the AO-1 non-reactive stabilizer at different concentrations (the data corresponds to the first decomposition step)

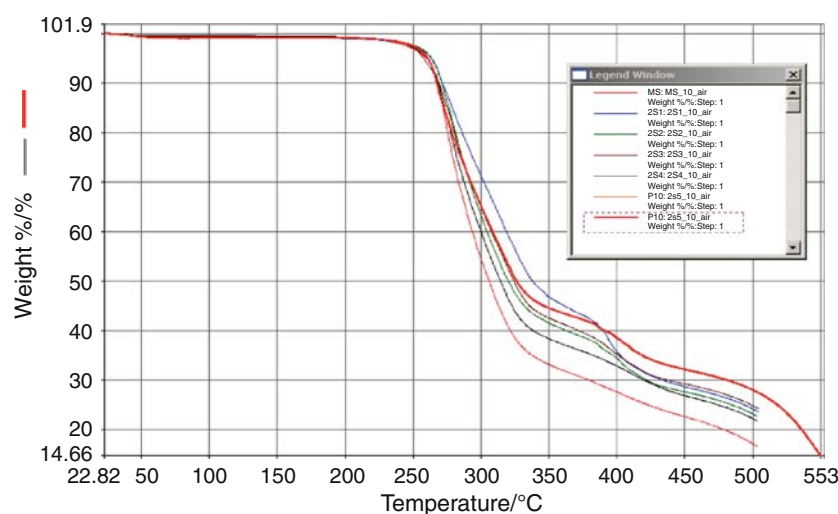
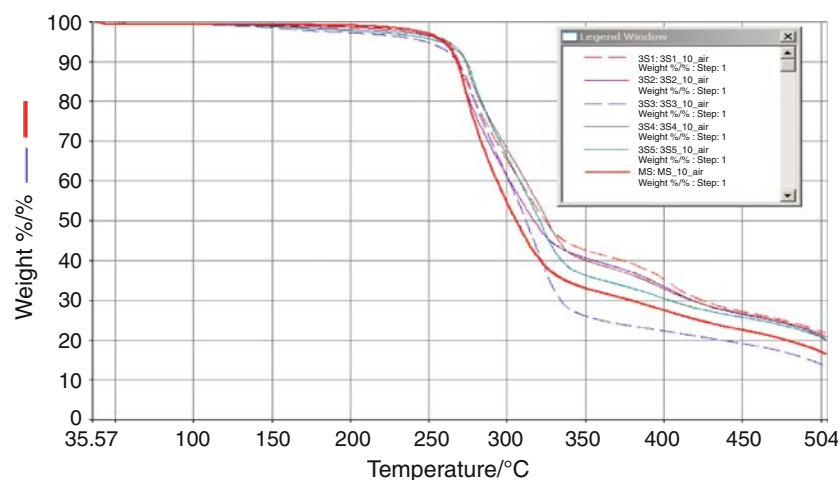


Fig. 4 Mass loss versus temperature for AO-2 reactive stabilizer at different concentrations



behaviour in the range of 250 to 320 °C was obtained at concentrations of 1.2–1.5 mass%.

The thermal behaviour of the polyurethane stabilized with a 1/1 mixture of AO-1 and AO-2 proved the synergism,

especially at low concentrations (see Fig. 5). Probably the decreasing of the stabilization effect at higher concentrations is in connection with the mentioned tendency of AO-1 for migration out from the polymeric mass.

Fig. 5 Mass loss versus temperature for a 1/1 mixture of AO-1 and AO-2, at different total concentration of stabilizer

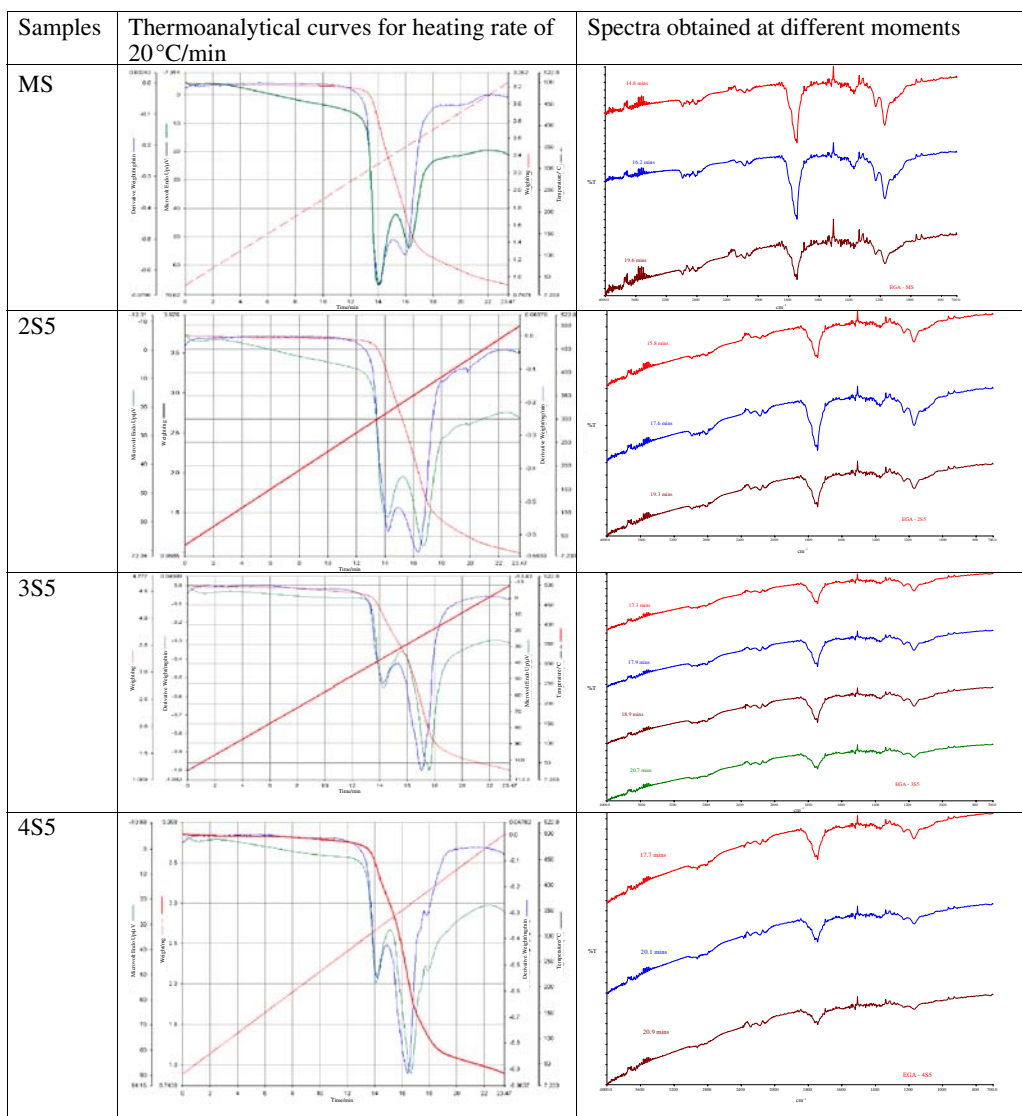
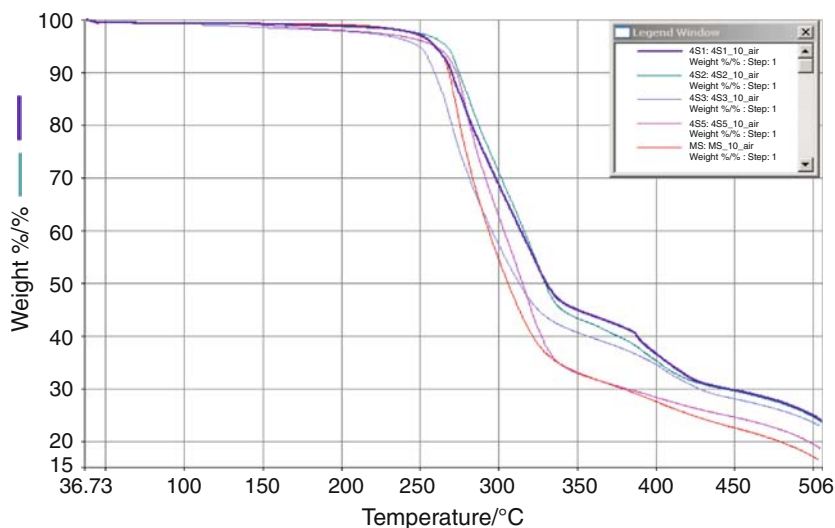


Fig. 6 Thermoanalytical curves for heating rate of 20 °C/min and spectra obtained at different moments for unstabilized polymer and for stabilized polymers with 1.5 total mass% of stabilizers

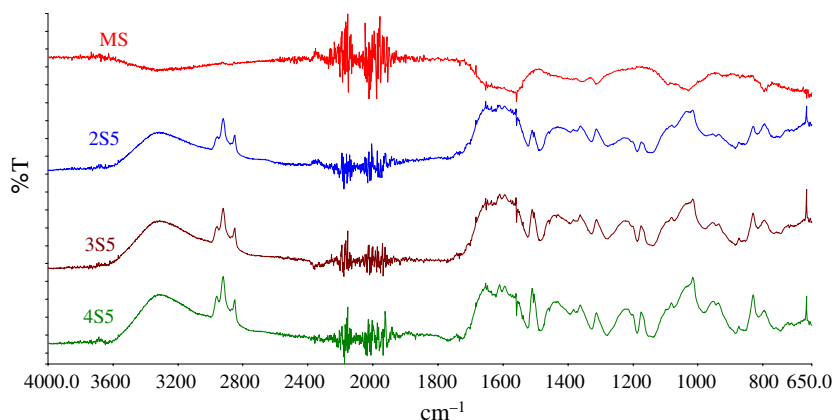
Table 2 Assignment of peaks of evolved gases

| Wave number | Assignment |
|-------------|--------------------|
| 1745,71 i | $\nu_{C=O}$ esters |
| 1171,74 i | Formates |
| 1230,44 i | Acetates |
| 1693,59 m | Aldehydes alif. |
| 1230,44 m | Ketones alif. |

Spectroscopic analysis

EGA

The FT-IR spectra (see Fig. 6 and Table 2) confirmed that more than 80% of the evolved gases are the same by the non-stabilized as well as by the stabilized samples. This is an argument that the stabilizers are included in the

Fig. 7 UATR-FT-IR spectra of the samples remaining char**Table 3** Assignment of peaks for MS

| Wave number | Assignment |
|-------------|---|
| 798,29 i | γ_{CH} benzene disubstituted in positions 1, 4 |
| 1029 i | $\nu_{C=O}$ sim esters |
| 1314,35 i | ν_{C-O} as esters |
| 1560 i | δ_{NH_2} amides |
| 1653,58 i | δ_{NH_2} amines, |
| 1688,48 i | $\nu_{C=O}$ characteristic bands for urethanes unsubstituted or monosubstituted which have amidic bands by 1560 i |
| 1734 s | |
| 3329,60 m | ν_{OH} large bands specific to $\bar{O}H$ from polymers (hydrogen intermolecular bond) |
| 3450,57 s | |
| 3626,06 s | |

Table 4 Assignment of peaks for 2S5

| Wave number | Assignment | Obs. |
|-------------|--|--|
| 1146,97 i | ν_{C-OH} characteristic bands for phenolic OH | Phenolic $-OH$ from AO-1 |
| 1187,46 i | | |
| 2880,88 i | ν_{-OH} large bands (hydrogen intermolecular bond $>C=O$) | Hydrogen intermolecular bond under $-OH$ and $>C=O$ from COO^- |
| 3000,43 i | ν_{CH_3} as bands specific to CH_3 | CH_3 from AO-1 |

Table 5 Assignment of peaks for 3S5

| Wave number | Assignment | Obs. |
|-------------|--|--------------------------|
| 3666,21 i | ν_{-OH} characteristic bands for OH unassociated | $-OH$ alcohols from AO-2 |
| 2900,77 i | ν_{CH_2} as specific bands CH_2 | CH_2 from AO-2 |

polymer structure playing the role of stabilization and not of chain extender.

UATR

The UATR-FT-IR spectra of the initial samples (Fig. 7.) confirmed (see Table 3) that the polymer was obtained from a polyesteric polyol and aromatic diisocyanate using an aminic catalyst. It was confirmed that the polyurethane contains –OH as the end chain.

Bands presented in Tables 4 and 5 show the differences between AO-2 bifunctional (contains one phenolic –OH blocked non-reactive, implied in process of stabilization, and one reactive alcoholic –OH binding with polyurethane in reactive stabilization process) and AO-1 that contain only phenolic –OH blocked and non-reactive. For mixed stabilization all characteristic bands appear.

Conclusions

A versatile way for obtaining and processing data regarding the thermooxidative stabilization of polyurethane foams was suggested.

The best results were obtained by the mixed reactive non-reactive stabilization, which allowed low concentrations of stabilizer. This low quantity avoided a significant

migration (by the non-reactive) or an important influence on the polymeric chain.

The obtained results will be useful by designing practical recipes for thermostable elastic polyurethane foams.

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