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POLY(URETHANE METHACRYLATE) THERMOSETTING RESINS STUDIED BY THERMOGRAVIMETRY AND THERMOMECHANICAL ANALYSIS

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Abstract

Two different poly(urethane acrylate) resins (one with a trimer: PUA1, the second with a dimer: PUA2) prepared [1] by photo curing reaction are investigated by means of thermogravimetry and thermomechanical measurements. The lack of mass loss found up to 300°C for both systems shows their good thermal stability. Beyond this temperature, two mass losses occur consecutively. This mass loss already studied by TG-FTIR coupled measurements for PUA1 resin has been attributed to the degradation of carbonyl groups [1]. The extension to PUA2 and the comparison between the mass loss magnitude and the relative contain in acrylate of the resins leads to attribute the first degradation to the degradation of the acrylate fraction. The degradation of dimer based resin occurs earlier and with a faster kinetic than the trimer based resin. The variations of linear expansion and penetration coefficients measured by thermomechanical analysis (penetration probe) in the glassy state and in the glass transition temperature domain (the onset glass transition temperatures measured by DSC at 20°C min^{-1} are respectively equal to 111 and 107°C for PUA1 and PUA2, the transitions, not well defined, extending over 30°C), show that despite of a weaker compactness, the trimer based resin is more rigid than the dimer one.

Keywords: poly(urethane acrylate) resins, thermogravimetry, thermomechanical

Background

Poly(urethane acrylates) (PUA) are often used as precursors to produce three-dimensional networks leading to high performance products in term of hardness, flexibility and abrasive resistance [2]. However, changing the type of isocyanates groups as well as the length of aliphatic chains between isocyanate groups could lead to a large variety of systems. Moreover, the curing reactions which manage the final solid state

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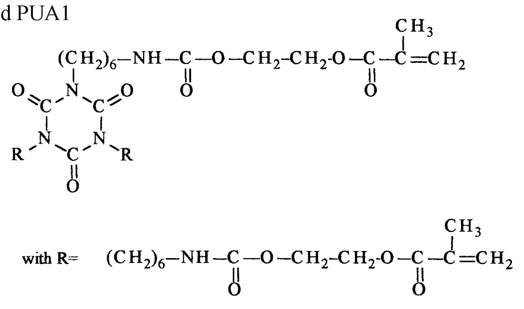
could be monitored either in a thermal way or a photochemical way [3]. The latter leads to very rapid curing kinetic and appears as a powerful industrial opportunity. This could explain the large interest of various industrial sectors like aeronautic, car industry, coating industry [4]. Recently, some of us have shown even both curing processes lead to chemically identical materials, they could differ by their physical properties, especially in their molecular relaxation behaviour [5]. In this case, the photochemically cured resin exhibits the fastest relaxation kinetic.

This work deals with experiments carried out to improve the thermal stability and the thermomechanical behaviour of two varieties of PUA differing in the nature of the branching chain. One contains a dimer and the other a trimer which is expected to act as a mechanical hardener of the resin.

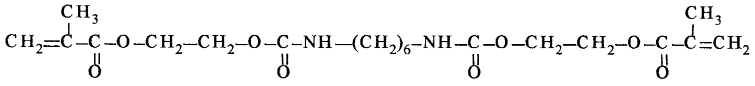
Experimental

Both resins studied in this work are obtained by photochemical curing reaction. The first, called PUA1, is synthesised from a prepolymer based on hexamethylene diisocyanate trimer (HDT) and hydroxy-2-ethyl methacrylate while the second, called PUA2, is synthesised from a prepolymer based on hexamethylene diisocyanate (HMD and hydroxy-2-ethyl methacrylate. The synthesis of the prepolymers has been already largely described elsewhere [1]. The photocuring process used to obtain these polyurethane networks has been considered without diluent reactive material, in presence of the photo-initiator 2,2-dimethyl-2-hydroxyacetophenone dissolved in the oligomer by stirring at room temperature. The radical photopolymerisation of resins was followed using a Perkin Elmer DSC7 calorimeter fitted with an irradiation unit (100 W Hg light). More details concerning this experimental process and the characterisation of the resulting crosslinked resins are given in [1] where it is particularly shown that the cure reaction has reached its maximum.

Resin called PUA1



Resin called PUA2



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-O-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_6-NH-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-O-\underset{\underset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}{=}CH_2$$

Fig. 1 Chemical formula of both PUA resins studied in this work

Thermogravimetric measurements were performed on a Setaram TG92 thermobalance under nitrogen atmosphere (flow=1 L h^{-1}). Sample pellets with a mass bounded by 10 and 20 mg, put in aluminium crucible, were heated at 5°C min^{-1} from 30 up to 800°C. Dilatometric measurements were performed using a DMA-TMA 2 Perkin Elmer modified system [6]. Disks (1 mm thick and 1 cm of diameter) were heated from 20 to 140°C with a heating rate of 5°C min^{-1} under an He flow. Three static loads 100, 1000 and 3340 mN respectively were used. Finally using an hydrostatic balance, density measurements performed on both resins did not reveal any noticeable difference between the resins: d=1.242±0.001.

Results

The good thermal stability in the classical range of temperature of use is evidenced on the typical thermogravimetric curves displayed in Fig. 2. Indeed neither of the systems shows any mass loss up to 300°C. Then a degradation is revealed by two mass losses

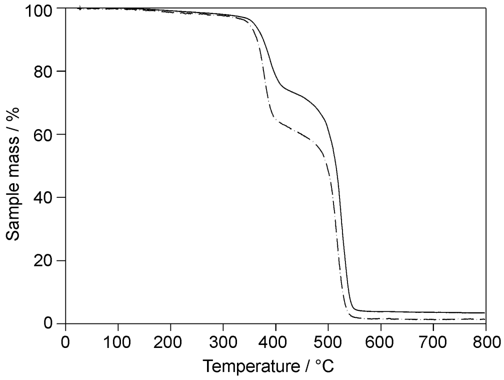


Fig. 2 Thermogravimetric curves obtained on PUA1 (full line) and PUA2 (dashed-dot line)

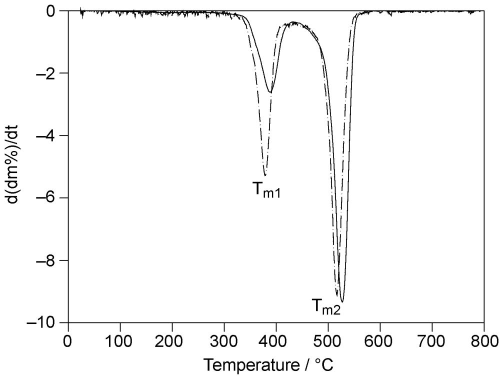


Fig. 3 Derivative thermogravimetric curves obtained on PUA1 (full line) and PUA2 (dashed-dot line)

occuring in the same temperature domain (from 350 to 550°C). This first mass loss is of the order of 40% for PUA2 while it is of 30% for PUA1. For PUA1 resin, from TG-IR coupled analysis it has recently been reported that this mass loss corresponds essentially to the liberation of CO_2 [1]. As better evidenced on the derivative loss curves displayed in Fig. 3, the resins exhibit differences in the magnitude of the first degradation stage. The temperatures characteristic of degradations, measured at the peak minima observed on the derivative curves, are equal to 388.5 and 378.5°C respectively. For both resins, a second mass loss occurs in the same range of upper temperature showing the achievement of the degradation. Observed at 527 and 517°C in Fig. 3, these peaks correspond to NCO group and attest the reversible cleavage of the urethane linkages at high temperatures [1]. Basically, all the samples are fully degraded at high temperature. The final mass, closed to zero, indicates that the products resulting from degradation processes are very volatile and the samples do not contain mineral charges.

All these thermal quantities determined are reported in Table 1.

Table 1 Thermogravimetric data measured on PUA1 and PUA2

	PUA1	PUA2
TM_1/°C	388.5	378.5
TM_2/°C	527	517
Δm/% 1	27	39
Δm/% 2	69	60
Δm/% high temperature	4	1

Figure 4 shows a typical probe displacement as a function of temperature. In this figure the significant probe penetration (negative displacement) reveals the change from a highly viscous state to a like liquid state characterising the glass transition. Thus, different thermal parameters can be measured on this curve as T_{g1} (temperature at the beginning of the glass transition), T_{g2} (temperature at the end of the glass transition), ΔL the magnitude of the penetration observed between glassy and like liquid states and α_L the linear expansion coefficient in the glassy state due to temperature. However, we have to point out that the values of these thermal parameters depend on the applied static load F. Figures 5 and 6, show the results obtained for both resins. On the opposite from ΔL, data reported in Table 2 show that T_{g1}, T_{g2} and α_L decrease as the load increases. So, thermal expansion coefficients in the glassy state given by $\alpha_g=3\ \alpha_L\approx2\cdot10^{-4}\ K^{-1}$ for PUA1 and $1.5\cdot10^{-4}\ K^{-1}$ for PUA2 are obtained by extrapolation at nil load. These values are in good agreement with various data collected in the literature for polymeric materials [7–8] (for example α_g varies between 1.9 and $2.4\cdot10^{-4}\ K^{-1}$ for poly(vinyl acetate)). In agreement with the differential scanning calorimetric data obtained on these resins [9] (the onset glass transition temperatures measured by DSC at 20°C min^{-1} are respectively equal to 111 and 107°C for PUA1 and PUA2), the mechanical glass transition temperature of PUA2 is lower than the PUA1 one.

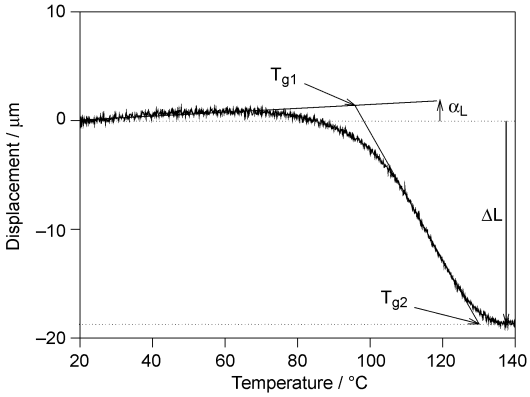


Fig. 4 Thermomechanical curve obtained on PUA2, illustrating the definition of the different thermal parameters measured with this technique

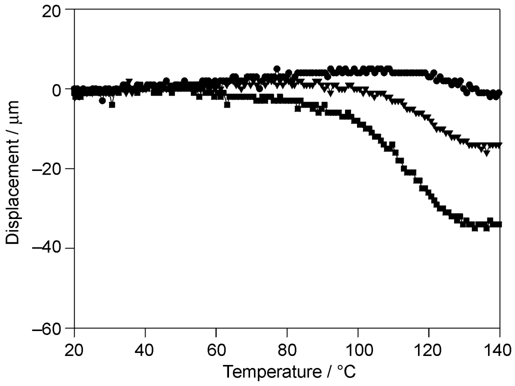


Fig. 5 Thermomechanical behaviours measured in penetration on PUA1 resin for different values of the static load: ● – F=100 mN, ▼– F=1000 mN, ■– F=3340 mN

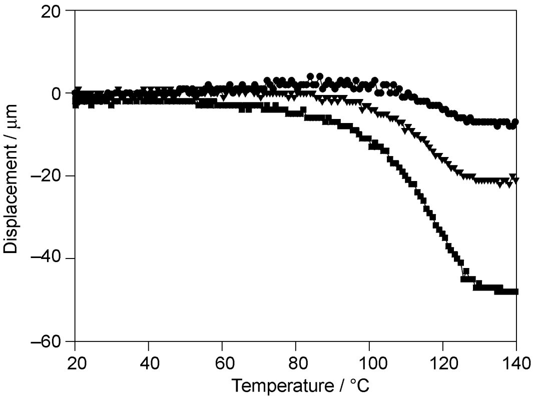


Fig. 6 Thermomechanical behaviours measured in penetration on PUA2 resin for different values of the static load: ● – F=100 mN, ▼ – F=1000 mN, ■ – F=3340 mN

Table 2 Thermomechanical data measured on PUA1 and PUA2

	PUA1			PUA2		
Load *F*/mN	100	1000	3340	1000	1000	3340
T_{g1}/°C	115	101	96	105.5	99	100
T_{g2}/°C	132	131	127	126	126	129
T_g/°C	124	117	115	115	112	114
ΔL/µm	1	14	34	8	20	48
$10^5\ \alpha_L$/K^{-1} in glassy state	6.5	3.5	1	5	2.5	0

Discussion

Thermogravimetric measurements have shown that if the resins exhibit similar responses in the same temperature domain, they differ in the magnitude of the degradation. Moreover, it can be expected that the same produces are degraded in both resins. Now, for PUA1, it was already mentioned that CO_2 and CO vapours are mainly produced [1] during the first step of decomposition which proceeds successively by chain breaking of the carbonyl groups located in the surrounding of the crosslinking points and by decomposition of the acrylate groups. In regard to the composition of each resin, the acrylate part concerns 40% and 30% mass/mass of the total resin mass for PUA2 and PUA1 respectively. At this point it is remarkable to notice that these ratios are exactly those experimentally found for the mass loss on the thermogravimetric curves. In other words, if we normalise the curves of mass loss to the mass of acrylate contain instead of the whole mass of sample, these curves must have the same magnitude for both resins. The kinetic aspect of this first degradation stage, as evidenced in Fig. 7, shows that the kinetic is faster for PUA2 than for PUA1. This difference in the kinetic of degradation is also revealed by the small shift toward the lowest temperature of the minimum observed in Fig. 2 for PUA2 resin. Another argu-

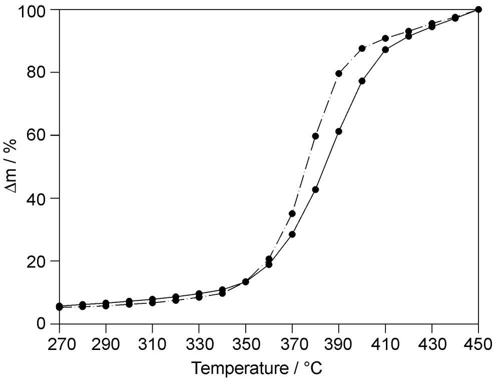


Fig. 7 Kinetic of the first stage degradation for PUA1 (full line) and PUA2 (dashed-dot line) as a function of temperature

ment to observe two different kinetics for the degradation of the resins consists in their own structures: indeed (Fig. 8 [10]), for PUA1 the linking between the main chains is performed by the trimers while only the connection of linear chains leads to the network of PUA2. It follows differences in the rigidity of the resins. This is clearly observed with the mechanical probe acting as an identator for which, at a given load value, the penetration depth ΔL in the glassy state is always greater for PUA2 than for PUA1 (Table 2). Moreover. these results, which tend to prove better mechanical qualities of PUA1, hold in spite of a lower compactness of PUA1. Indeed for equivalent densities, the molecular mass of PUA1 is about twice the PUA2 one (894 and 428 g mol^{-1} respectively).

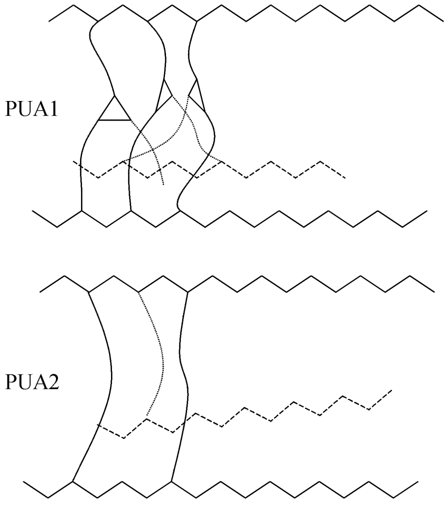


Fig. 8 Structures expected for PUA1 and PUA2

Conclusions

Combination of thermogravimetrical and thermomechanical measurements performed on two poly(urethane acrylate) resins prepared one with a dimer and the other with a trimer cross linkers, has shown that the network rigidity is enhanced when the trimer is used in spite of the dicrease of the compactness. In both cases, it was also shown that the first stage of the degradation process is due to the decomposition of the acrylate fraction of the resin.

References

1 F. Burel, L. Lecamp, B. Youssef, C. Bunel and J. M. Saiter, Thermochim. Acta, 326 (1999) 133.

2 X. Yu, G. P. Grady, R. S. Reiner and S. L. Cooper, J. Appl. Polym. Sci., 49 (1993) 1943.

3 C. Decker, in UV Curing Chemistry: Past, Present and Future, Sup. to Polymers Paint Colour, 1988.

4 S. Oprea, S. Vlad and A. Stanciu, Polymer, 42 (2001) 7257.

5 J. Ledru, J. M. Saiter, J. Grenet, B. Youssef, F. Burel and C. Bunel, J. Therm. Anal. Cal., 58 (1999) 13.

6 T. Philippe, Thesis CNAM, Rouen, France 1997.

7 A. J. Kovacs, J. Polym. Phys., 30 (1958) 131.

8 A. J. Kovacs, Fortschr. Hochpolym-Forsch, 3 (1963) 394.

9 J. Ledru, PhD Thesis, Rouen, France 2000.

10 W. Oraby and W. K. Walsh, J. Appl. Polym. Sci., 23 (1979) 3227.