CHARACTERIZATION OF PHASE STRUCTURES OF NOVEL METALLO-POLYURETHANES

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Abstract

Polyurethanes (PUs) are widespread used in chemical and building industries due to the fact that a large variety of starting materials with specific properties can be used for their formation. In other advanced applications, such as in the aerospace field, they are used as polymeric matrix of energetic composite materials. Butacene is a functional polyol, with a ferrocene group grafted onto the main chains of an OH-terminated polybutadiene (HTPB). Thus, new organometallic PUs with relevant catalytic properties can be obtained from this prepolymer.

It is well-known that segmented PUs have phase-separated morphology giving rise to nanodomains. The physico-chemical differences between two families of PUs, one synthesized with HTPB and the other one obtained from Butacene (soft segments, SS) are studied in this contribution. Different diisocyanates have been used at a given family forming the hard segments (HS), either aliphatic (isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HMDI)) or aromatic (toluene-2,4-diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI)). The chemical structures of diisocyanates greatly affect the final micro-structure as well as the nanodomains formation and their ordering through hydrogen bonds between urethane groups dispersed within an amorphous matrix of flexible segments of polybutadiene. The presence of hydrogen bonds has been evaluated by Fourier transform infrared (FTIR) spectroscopy, while the existence of phase separation either by Differential Scanning Calorimetry (DSC) or Dynamic Mechanical Analysis (DMA) and the organization of those domains by X-ray diffraction.

Materials

Results and discussion

DMA

DMA analysis shows the existence of phase separation and, then, two different glass transitions regions: the related to cooperative motions of the soft and hard segments, respectively. At a given family, the relaxation of soft segments takes place at similar temperatures (T_{max} at around -75 °C for HTPB samples and at about -50 °C for Butacene specimens, at 1 Hz in E" basis). The storage modulus is about 1000 MPa for all of them at the lowest temperatures.

The relaxation of soft segments exhibits in the Butacene systems an intensity in $\tan \delta$ much higher than in the HTPB samples, implying a greater energy dissipation capacity at this temperature range in the former specimens. The relaxation time distributions associated with the SS mechanism and, consequently, its width, are narrower than those involved in the relaxation of the rigid segments.

DSC

HTPB	Tg o	Tg f	ΔCp	Tg m	ΔCp	Tg m	ΔCp	Tg m	ΔCp	Tg m	ΔCp
	SS1	SS1	SS1	SS1	SS2	SS2	HS1	HS1	HS2	HS2	HS2
	(°C)	(°C)	(J/g°C)	(°C)	(J/g°C)	(°C)	(J/g°C)	(°C)	(J/g°C)	(°C)	(°C)
IPDI	-77	-70	0,55	-73	<0,1	-43	<0,1	-12	-	-	-
HMDI	-76	-70	0,40	-72	<0,1	-57	<0,1	-10	<0,1	49	-
TDI	-74	-68	0,45	-71	<0,1	-40	<0,1	-11	-	-	-
MDI	-75	-68	0,41	-72	<0,1	-56	<0,1	-8	-	-	-

BUTACENE	Tg o	Tg f	ΔCp	Tg m	ΔCp	Tg m	Tg o	Tg f	ΔCp	Tg m	ΔCp	Tg m
	SS1	SS1	SS1	SS1	SS2	SS2	HS1	HS1	HS1	HS2	HS2	HS2
	(°C)	(°C)	(J/g°C)	(°C)	(J/g°C)	(°C)	(°C)	(°C)	(J/g°C)	(°C)	(J/g°C)	(°C)
IPDI	-50	-44	0,24	-47	-	-	-14	-4	0,17	-9	-	-
HMDI	-54	-46	0,34	-50	<0,1	-38	-	-	<0,1	54	-	-
TDI	-55	-47	0,34	-51	-	-	-	-	<0,1	-28	-	-
MDI	-53	-43	0,33	-48	-	-	-	-	<0,1	-21	<0,1	2

DSC results are in a good agreement with those obtained by DMA analysis. Phase separation is observed and, then, two different glass transitions regions appears: the ascribed to generalized motions of the soft and hard segments, respectively. It should be commented that only the glass transition located at the lowest temperatures and related to SS is possible to be accurately determined since the one ascribed to HS involves a very small specific heat increment (lower than 0,1 J/g °C).

FTIR

Quantitative information regarding the relative amounts of non-hydrogen bonded (1738-1725 cm⁻¹), loosely hydrogen bonded (1715-1700 cm⁻¹) and strongly bonded and ordered urethane hard segments (1700-1680 cm⁻¹) were obtained by the deconvolution of C=O region (A) and analysis of the relative absorbances (B).

	(cm ⁻¹)	HTPB			BUTACENE		
		1737	1714	1689	1725	1699	1679
IPDI	A (%)	32,5	34,1	33,4	46,7	36,9	16,4
	B (%)	31,4	37,2	31,4	37,3	36,5	26,2
HMDI	(cm ⁻¹)	1727	1708	1693	1723	1699	1678
	A (%)	46,1	35,6	18,3	50,5	37,0	12,5
	B (%)	40,2	37,3	22,5	46,2	36,8	17,0
TDI	(cm ⁻¹)	1739	1717	1699	1737	1711	1687
	A (%)	49,1	31,8	19,1	48,3	32,0	19,7
	B (%)	45,4	33,5	21,1	44,3	33,5	22,2
MDI	(cm ⁻¹)	1737	1715	1697	1736	1712	1691
	A (%)	49,7	31,7	18,6	53,4	29,2	17,4
	B (%)	46,5	32,7	20,8	51,3	30,7	18,0

Deconvolution results indicate the presence of a substantial amount of the free carbonyl (around 50%, except for HTPB-IPDI with a value close to 30%), a reasonable amount of hydrogen bonded, disordered carbonyl (around of 35%, except for the samples based on aromatic diisocyanates, with a value close to 30%) and small amount of strongly hydrogen bonded carbonyl groups (around 20% for those PU samples containing aromatic rings as hard segments, and low values for the other ones). However, depending on these data, the more significant difference between both series is determined by the lower wavenumbers for the signals representative of well-ordered hydrogen bonded structure for the PUs based on Butacene (for PUs from HTPB ≥ 1690 cm⁻¹ vs from Butacene ≤ 1690 cm⁻¹).

SAXS

Ordering capability seems to be dependent on the lack or presence of Butacene in the macromolecular architecture. Furthermore, the mean interdomain spacing between hard domains ($d = 2\pi/q_{max}$) is also strongly dependent on the nature of diisocyanate, those aliphatic ones showing values higher than the spacing obtained for hard segments containing aromatic diisocyanates.

Conclusions

DMA and DSC analysis confirms the phase segregation in both systems. The relaxation time distribution associated with the SS mechanism is narrower than that ascribed to the HS relaxation, i.e., it involves a broader temperature range.

Quantitative information regarding the relative amounts of non-hydrogen bonded, loosely hydrogen bonded and strongly hydrogen bonded and ordered urethane HS were obtained by the deconvolution of C=O region and analysis of the relative absorbances. This quantification suggests different degrees of HS phase separation which depend on the macroglycol and chemical structure and the symmetry of the diisocyanate

Interdomain ordering between hard domains is observed in those macromolecular architectures containing HTPB as soft segments. The spacing values are dependent on the diisocyanate used.

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