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EVIDENCE OF CHEMICAL CLUSTERS PRESENCE IN END-LINKED MULTIMODAL POLYURETHANE NETWORKS THROUGH THERMOMECHANICAL ANALYSIS

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INTRODUCTION

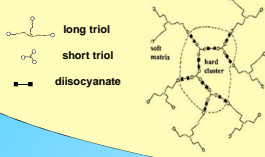
Aim : Illustrate the presence of chemical clusters in polyurethane (PU) networks, since due to poor electronic and too weak hardness contrast, SAXS, TEM and AFM studies are impossible.

● From a chemical point of view

What are chemical clusters ?

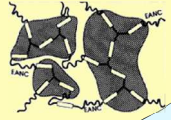
⇒ Reaction induced (nano)inhomogeneities

● From a mechanical point of view



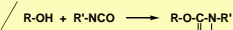
Clusters can be described as assemblies of covalently bonded units of short chains reacted with a crosslinker, distributed in a matrix constituted of longer chains.

One has to consider clusters like large point-like crosslinks, linked with elastically active network chains (EANCs). The functionality of such clusters is higher than f , the functionality of the crosslinker. The bulk part of the clusters is composed of networks chains that are elastically inactive.

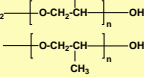


MATERIAL

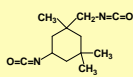
POLYURETHANE NETWORK



Poly(propylene glycol) triol (PPO)



Isophorone diisocyanate (IPDI)

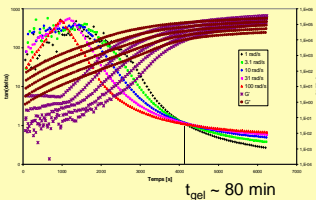


PPO Supplier	\bar{M}_n [g.mol ⁻¹]	\bar{M}_w [g.mol ⁻¹]	\bar{P}_n	\bar{P}_w	T_g [°C]	ΔC_p [J.g ⁻¹ .K ⁻¹]
Dow	450	2,97 - 3,18	2,1	-64,9	0,64	
Dow	700	2,81 - 3,12	3,5	-69,9	0,66	
Polimer Europa	1500	2,94	6,1	-71,7	0,75	
Aldrich	2900	2,86	15,6	-72,8	0,66	
Aldrich	4100	2,89	23,0	-73,2	0,61	
Dow	4700	2,68 - 3,10	26,5	-73,6	0,63	

Characteristics of the PPO used

NETWORK SYNTHESIS

- The synthesis was carried out at room T, with a stoichiometric ratio $r = \frac{[NCO]}{[OH]}$ of 1.05
- The synthesis has been prepared in one stage, by mixing the components during 5 min under vacuum.
- For comparison between mixing time and gel point, the **isofrequency method** has been used. It consists in following the loss factor during the whole network synthesis at 5 different frequencies; the time at which the loss factor is the same for all frequencies is the gel point.



SAMPLE DESCRIPTION

Two sets of end-linked triol-based PU have been synthesized:

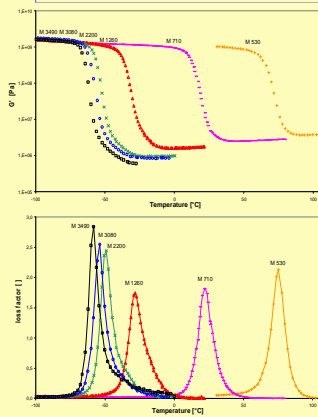
- monomodal PU, prepared with one PPO and
- multimodal PU, containing a mixture of short and long PPO, which are expected to form the chemical inhomogeneities.

The sample code indicates the kind of **distribution of PPO molar masses** (mono-, bi- or tri-modal : M, B and T respectively), followed by the **average molar mass between two crosslinks** (M_c).

Sample name	\bar{M}_c PPO triol [g.mol ⁻¹]						Urethane bonds [mol.kg ⁻¹]
	450	700	1500	2800	4100	4700	
M 530	100	-	-	-	-	-	3,79
M 710	-	100	-	-	-	-	2,83
M 1260	-	-	100	-	-	-	1,80
M 2200	-	-	-	100	-	-	0,91
M 3080	-	-	-	-	100	-	0,65
M 3490	-	-	-	-	-	100	0,57
B 2200	40	-	-	-	-	80	0,91
T 730	87	6	-	-	-	7	2,75
T 800	87	-	4	-	-	9	2,51
T 850	87	-	2	-	-	11	2,35

Network composition (molar % of each PPO triol) and corresponding number of urethane bonds N_u

Monomodal networks

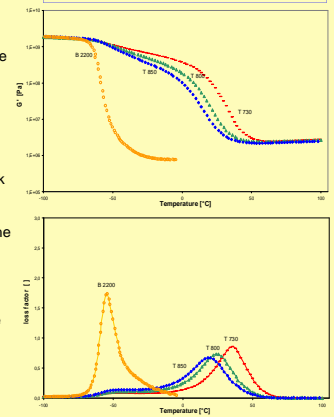


DYNAMIC MECHANICAL ANALYSIS

✓ This set of PU covers a large range of T_g from -58 to 76 °C.

- ✓ Whereas the glassy state is rather independent of network composition, the rubbery state presents a large distribution of equilibrium moduli (ratio of 5.6 between all networks).
- ✓ In multimodal networks, T_g is much more vaguely defined. This is to be correlated with the distribution of PPO triols with different molar masses inside the networks. Indeed, trimodal PUs contain long PPO triols, which will relax at low T, whereas medium and shorter network chains relax at higher T.
- ✓ The height of the loss factor peaks is smaller for multimodal PUs, indicating a less homogeneous network with a broader distribution of relaxing times.
- ✓ B 2200 presents a single domain structure at the thermomechanical scale, but the asymmetric shape of the tan δ peak indicates many short chains relaxing at higher temperatures. **Chemical clusters** are thus expected to manifest themselves at higher temperatures ranging from -50 to 0 °C.
- ✓ T networks exhibit a structure with two domains: one soft, at low T, containing long chains, and another containing shorter PPO chains and hard chemical clusters. Since these loss peaks are broad, **clusters** are **not chemically pure** and contain also long chains.
- ✓ T 730 has the highest main T_g , since it contains the highest molar fraction of short chains.

Multimodal networks



RUBBER ELASTICITY

Among all theories, the most often used have been developed on the basis of network chains having a Gaussian distribution of end-to-end distance. Moreover, these models assume that this distance transform affinely with macroscopic fluctuations.

- In the **phantom model**, the crosslinks can fluctuate freely around their mean position:

$$G_{ph} = (v_c - \mu_c)RT = (1 - \frac{2}{f_c}) \frac{\rho}{M_c} RT$$

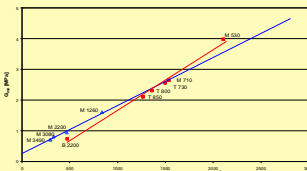
- For an **affine network**, free crosslink fluctuations are totally suppressed:

$$G_{af} = v_c RT = \frac{\rho}{M_c} RT$$

- **Langley and Graessley** have developed a phenomenological model, which takes into account entanglements contribution:

$$G_{LG} = (v_c - h\mu_c)RT + G_e T_c = (1 - \frac{2h}{f_c}) \frac{\rho}{M_c} RT + G_e T_c$$

According to these three theories, G_{exp} should be proportional to the number of EANCs:



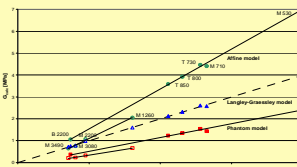
Two slopes can be drawn: one containing M 3490, M 3080, M 2200 and M 1260 and the second grouping all multimodal networks plus M 710 and M 530.

This can be explained by calculating the actual number of EANCs:

$$(v_c)_{equivalent} = (v_c)_{chem} + (v_c)_{ent} - (v_c)_{inact}$$

⇒ M 710 and M 530 have a different structure from that of the monomodal networks

RUBBER ELASTICITY INVESTIGATIONS



Comparison between G_{exp} and G_{calc} for 3 theories

M 710 and M 530 lie within the curves containing hard domains. Unlike chemical clusters, which are permanently covalently bonded, these hard domains could be temporarily crosslinked with spatial neighbours through a high density of urethane bonds (which is resp. 500 and 665 % higher than for M 3490).

A **threshold of N_u for hard domains formation** in monomodal networks seems to lie between 1.6 and 2.8 mol.kg⁻¹.

Networks without clusters	Networks containing clusters
$r^2 = 0.9957$	$r^2 = 0.9985$
$(1 - \frac{2h}{f_c}) = 0.63$	$(1 - \frac{2h}{f_c}) = 0.55$
$\bar{f}_c = 2.89$ implies $h = 0.53$	$0.5 < h < 1$ implies $\bar{f}_{cmax} = 4.42$
$G_e T_c = 0.31$ MPa	$G_e T_c = 0.16$ MPa

Fit parameters for Langley-Graessley model

✓ A global network average functionality of 4.4 is found. Clusters have thus a functionality higher than 4.4.

✓ The probability of entanglements is reduced in networks containing clusters or hard domains, since the matrix volume is reduced.

CONCLUSION

- The first contains monomodal networks, having a urethane bond density lower than 1.6 mol.kg⁻¹, they have a normal behaviour according to the rubber elasticity theory.
- The second group contains multimodal networks having chemical clusters with a functionality higher than 4.4
- The third group, containing M 530 and M 710, behave like PU with clusters, and led us to think about hard domains, similar to clusters, temporarily linked through urethane bonds. The threshold for hard domain formation lies between 1.6 and 2.8 mol of urethane bonds per kg.