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Maribel Pineda, Françoise Méchin, Jean-Pierre Pascault. New polyurethane and polyurethane-acrylate materials prepared from aqueous dispersions. *Polymers In Dispersed Media (PDM)* 2004, Apr 2004, Lyon, France. hal-04285197

HAL Id: hal-04285197

<https://hal.science/hal-04285197>

Submitted on 14 Nov 2023

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NEW POLYURETHANE AND POLYURETHANE-ACRYLATE MATERIALS PREPARED FROM AQUEOUS DISPERSIONS

Maribel PINEDA, Françoise MECHIN, Jean-Pierre PASCAULT

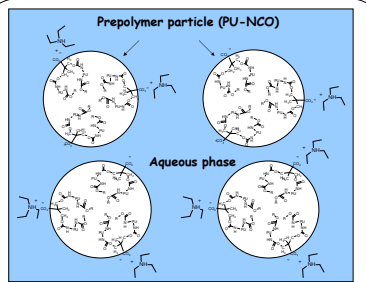
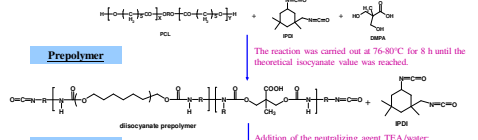
Laboratoire des Matériaux Macromoléculaires-IMP, UMR CNRS n°5627, INSA de Lyon, Villeurbanne, FRANCE

Object

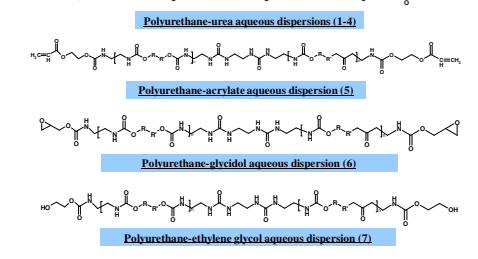
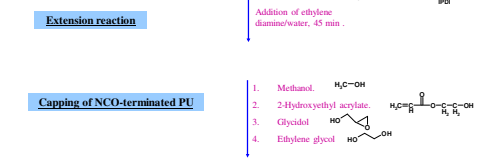
The synthesis of curable aqueous based polyurethane dispersions and the analysis of the mechanical properties of films thereof (case of a UV-curable polyurethane-acrylate dispersion, thermally-curable polyurethane-glycidyl dispersions and two-component curable polyurethane dispersions)

PU Ionomer Dispersion

Synthesis of PU-ionomer aqueous dispersion

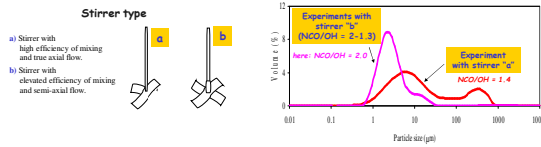


- Important parameters:**
- Addition rate of water solutions (TEA, EDA)
 - Stirring rate
 - Temperature during the dispersion formation

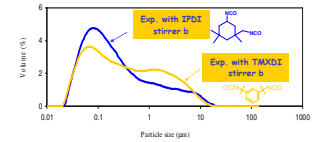


Process optimization

Effect of NCO/OH ratio prepolymer (viscosity at the time of phase inversion) and type of stirring device



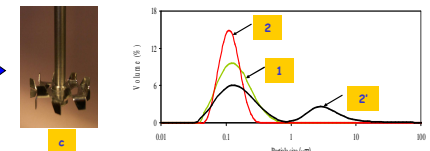
Effect of the diisocyanate nature, (stirrer "b")



Characteristics of prepolymer and final dispersions: experiments with IPDI and ratio NCO/OH=1.4, stirrer C

Experiment #	NCO/OH (theoretical 2.48)	M _n prepolymer (theoretical 6453) (g/mol)**	Temperature (prepolymer) (°C)	Temperature (TEA/H ₂ O) (°C)	Temperature (dispersion) (°C)	Mean diameter (µm)
1	2.57	5730	55	20	25	0.17
2	2.50	6030	55	21	27	0.12
3	2.58	6220	58	20	33	0.16
4	2.55	6580	58	20	34	0.20

*NCO/OH PCL:DMPA = 1.4; FINAL SOLID CONTENT= 35%
 **From size exclusion chromatography according to polystyrene standards
 ***Prepolymer #2 was divided in 2 parts; dispersion #2 was obtained with a standard turbine instead of the high efficiency impeller c and shows 2 populations

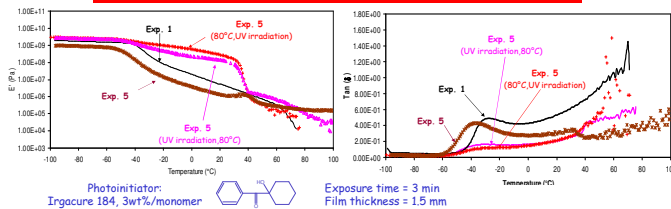


precise control of temperature and addition rates at every stage
 ⇒ well-defined, reproducible molar masses and size distributions for both prepolymer and final PU dispersions, stability > 9 months

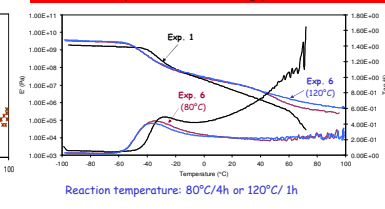
The thermal and mechanical properties

drying conditions: 12 days at room temperature & atmospheric pressure, then 24 h at 60°C, under a vacuum → film thickness ≈ 1mm

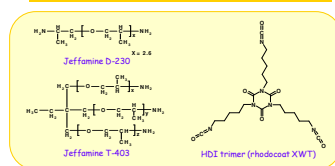
Effect of the photopolymerization reaction on the PU-acrylate (5) network



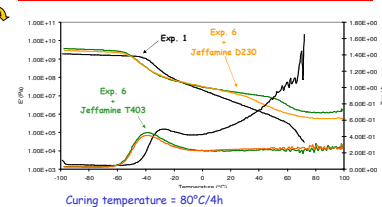
Effect of temperature on the PU-glycidol (6) network



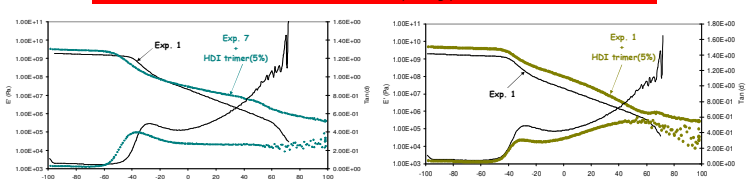
External crosslinkers for the PU dispersions



Effect of crosslinkers on the PU-glycidol (6) network



Effect of HDI trimer crosslinker on the PU-Ethylene glycol (7) and PU-urea (1) network



• PUA networks still incompletely crosslinked
 → too high initial molar mass for PUA macromolecules?
 → too low amount of photoinitiator?
 • Using additional crosslinkers, entirely crosslinked materials are obtained
 → the functionality of the macromolecular precursors is close to 2
 → strong improvement of the thermal and mechanical behavior

Conclusions and future work

- A reproducible process was designed for the preparation of stable aqueous dispersions of isocyanate-terminated polyurethane macromolecules with versatile post-curing modes
 - Important parameters for prepolymer synthesis:
 - Reproducibility in the reaction time, molar mass and mass distribution (viscosity)
 - Effect of several ratios:
 - NCO:OH
 - PCL:DMPA
 - % of DMPA neutralization
 - Parameters for the formation of PU aqueous dispersion:
 - Control of the size distribution and stability
 - Rayneri Turbotest mixer/dispersing turbine
 - Initial velocity 1800 rpm
 - Final velocity 1500 rpm
 - Addition rate of TEA solution
 - Temperature during T°C= 30-35°C dispersion formation T°C= X°C
- Starting from the same aqueous dispersions of isocyanate-terminated PU and using various chemistries (one- or two-component, thermal or UV initiation), thin or thick films with very good mechanical properties and thermal resistance can be obtained. One-component systems could still be further improved (better UV-crosslinking, use of self-assembling end units...)