SYNTHESIS, DISPERSION AND PROPERTIES OF HYDROXY POLYBUTADIENE-BASED ANIONIC POLYURETHANE-UREA.

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ABSTRACT – Isocyanate-terminated low molar mass polybutadiene bearing carboxylate functions is synthesized and used to prepare aqueous polyurethane-urea dispersions. After evaporation of water, the properties of the resulting films were evaluated and exhibited good chemical, physical and mechanical behaviours.

INTRODUCTION

Hydroxy telechelic polybutadiene (HTPB) is used as polyol for synthesis of polyurethane (PU) networks [1-3]. Generally one shot process or prepolymer technique are used for the preparation of HTPB-based PU and aqueous dispersion route was not applied because HTPB-based PU are insoluble in water due to the hydrophobic character of segmented polybutadiene [4-6].
In this work, we have modified HTPB by introducing carboxylate functions and synthesized anionic polyurethane-urea dispersion. Thus, this study deals first with the synthesis of isocyanate-terminated HTPB aniomers then with the dispersion process and finally with the production of films and their properties (swelling in water, solubility in organic solvent, thermomechanical behaviour).

EXPERIMENTAL

Synthesis of polyurethane anionomers PU/α. : In the following, α is the number of carboxylic functions per chain of HTPB. First, 3.65 10^{-2} mol (50.0g) of HTPB was placed in a reactor equipped with mechanical stirrer (500 rpm), a switchable inlet for nitrogen and vacuum connector. HTPB was dried and degassed 1 h at 80°C by a graduated vacuum up to 10^{-1}-10^{-2} mm Hg. Then, the reactor is raised to the required temperature under nitrogen. The apparatus is fitted with a condenser and a mercury device to monitor nitrogen flow. For PU/α, α x 3.65 10^{-2} mol of DMPA (e.g. 8.94 10^{-2} mol (12.0 g) for PU/2.45) was placed in a flask in dry 2-butanone (30 wt % of the overall reactants) at room temperature. α x 3.65 10^{-2} mol of triethylamine (e.g. 8.94 10^{-2} mol (9.03g) for PU/2.45) was

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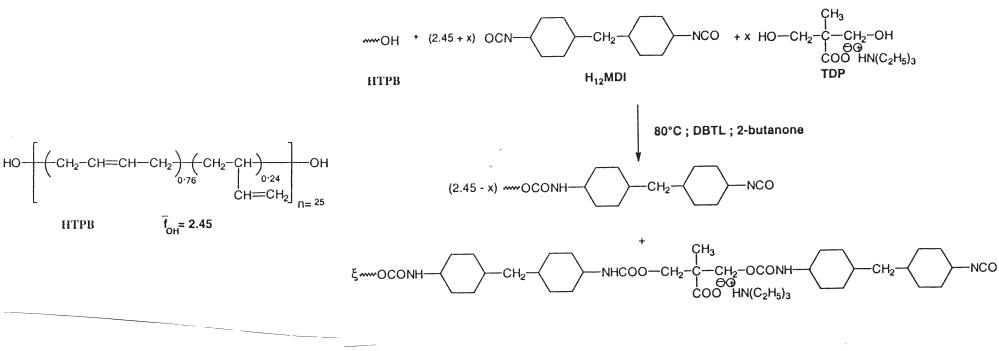
added into the inhomogeneous mixture. After stirring for 15 min, salt of DMPA was dissolved. This solution was placed into a reactor with degassed HTPB and dry 2-butanon (70 wt % of overall reactants). After stirring 15 min under nitrogen atmosphere to 60, 70 or 80°C, $(2.45 + \alpha)$ x $3.65\ 10^{-2}$ mol of H_{12}MDI (e.g. $17.9\ 10^{-2}$ mol (46.9g) for PU/2.45) was introduced carefully as rapidly as possible and DBTL catalyst is added ($1.13\ 10^{-3}$ mol l^{-1}). After stirring for 7 h, a yellow viscous liquid is obtained.

Dispersion : Water was added to prepolymer (12.5 g/min) under stirring (magnetic stirrer ; 500 rpm).

Preparation of films : Films are obtained after water evaporation, at room temperature, in a PTFE mould, from 30% dry matter aqueous dispersions.

SYNTHESIS

Isocyanate-terminated HTPB bearing carboxylate functions were prepared according to the following scheme by using H_{12}MDI and different amounts of triethylamine dimethylol propionate (TDP) in order to study the influence of ionic contents :



Characteristics of PU/α, where α is the number of carboxylic function per chain of HTPB, are reported in Table 1.

One can notice that when initial ratio $[NCO]_o/[OH]_o$ decreases chain extension decreases too according to free H_{12}MDI percent. In fact, we demonstrate that H_{12}MDI, which reacts twice faster on TDP than on HTPB, limits strongly HTPB extension as TDP concentration increases (0.5 to 2.45). Moreover, as α decreases, viscosity in 2-butanone (50% w/w) decreases, although molar

mass, determinated by SEC in dilute solution, increases. The phenomenon is attributed to aggregation of hard segments of PU and/or ionic interactions at high solid contents.

Table 1 : Experimental conditions, average molecular weights and characteristics of PU/α.

polymer	$[NCO]_o/[OH]_o$	Mn^{theo}	$Mn^{(1)}$	$Mw^{(1)}$	I	% free $H_{12}MDI^{(2)}$	Viscosity$^{(3)}$ (cp)
HTPB	0	1370	1950	4500	2.3	-	-
PU/0.5	1.71	2260	3900	9100	2.3	18	50
PU/1.0	1.55	2510	3400	6800	2.0	14	130
PU/2.0	1.38	3000	3800	4800	1.7	9.5	300
PU/2.45	1.33	3230	2700	4400	1.6	7.5	350

1) calculed by SEC, in dichloromethane, at the end of the reaction.
2) at the end of the reaction.
3) in 2-butanone, 50% w/w.

DISPERSION

A kinetic study of the disappearance of isocyanate functions as PU anionomer solutions are dispersed in water shows that about 50% are consumed after 24 h without amine whereas practically instantaneous vanishing of NCO groups is observed as 1,2-diaminoethane is added just after dispersion. Conductivity and viscosity dependences of PU aniomer solutions during addition of water are shown in Figures 1 and 2. The dispersion process can be divided into three steps [7,8] :

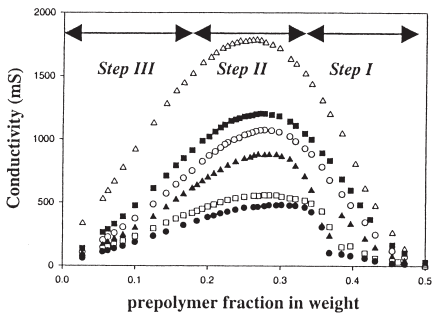


Figure 1 : Conductivity variations of PU/α during addition of water at 20°C. Δ : PU/2.45 ; ■ : PU/1.225 ; O : PU/1.0 ; ▲ : PU/0.8 ; ❑ : PU/0.5 ; ● : PU/0.4.

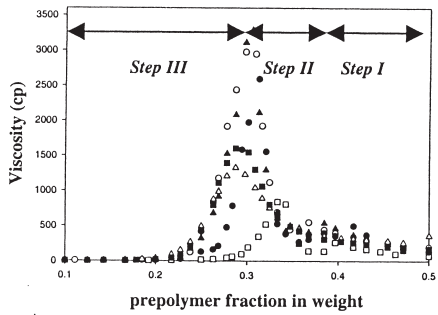


Figure 2 : Viscosity variations of PU/α during addition of water at 20°C. Δ : PU/2.45 ; ■ : PU/1.225 ; O : PU/1.0 ; ▲ : PU/0.8 ; ❑ : PU/0.5 ; ● : PU/0.4.

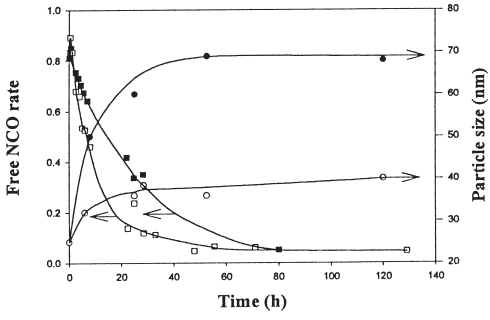


Figure 3 : Particle size (●,O)and free NCO (■, ❑)during chain extension versus time for PU/1.0 in water (23/77 w/w : O, ❑) and in 2-butanone/water (23/23/54 w/w : ●,■).

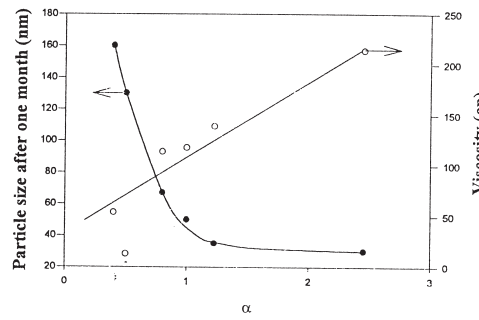


Figure 4 : Particle size and dispersion viscosity (25°C) versus α.

Step I : Viscosity and conductivity increase slowly with water addition (except for high ionic content in the case of conductivity). The solution can be considered as an organic medium with aggregation of unsolvated salt segments stabilized by coulombic forces.

Step II : When more water is added, the solution becomes turbid. This result indicates that water solvates ionic segments and progressively contracts hydrophobic segments to leads to ionic microspheres.

Step III : Viscosity drops sharply and conductivity decreases linearly. The phase inversion is complete and most of the carboxylate groups of polymer chains are located on particle surface. Then, this dispersion consists in a continuous aqueous phase with dispersed particles swelled by 2-butanone

Hydro-organic medium increases interparticles crosslinking. Therefore, it is suitable to evaporate 2-butanone before chain extension to produce fine crosslinked particles of anionic polyurethane-urea (Fig. 3).

The increase of TDP content leads to a double effect (Fig. 4) [9-11] :

- decrease of particle size by an increase of hydrophily,
- increase of effective particle diameter due to the formation of an electrical double layer and increase of viscosity which is proportional to the effective volume fraction of the dispersed phase.

FILM PROPERTIES

Swelling in water is poor for crosslinked films and large when a monoamine (diethylamine) is used. Similarly, the percentage of extractable material (soluble uncrosslinked HTPB or TDP-based small molecules) is low only after aa efficient crosslinking (Table 2).

Table 2 : Behaviour of films prepared with different crosslinking agents.

amine type	% extractable mass in THF at 25°C	% extractable mass in THF at reflux	% swelling in water at 25°C
without amine (in water)	6	15	1.5
1,2-diaminoethane	2	8	2
diethylamine	100	100	11

Dynamic mechanical properties of films are given in Figures 5 and 6.

In Figure 5, two changes are observed for storage modulus versus temperature curves of the different PU/1.0. The first decrease is assiociated to the glass transition temperature of the soft segment of HTPB and the second change to the melting of hard segments. The crosslinking by 1,2-diaminoethane or water largely increases the rubbery plateau value.

In Figure 6, above the glass transition temperature zone (Tα) of soft segment of HTPB, storage modulus E' at the rubbery plateau increases with TDP content. Therefore, the effects of TDP (and consequently of initial amount of $H_{12}MDI$) are to increase the number of urethane linkage (hydrogen bonds) and the ionic interactions by carboxylate functions (coulombic forces) [11].

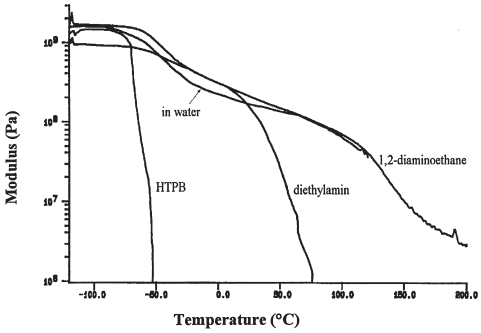


Figure 5 : Storage modulus E' of PU/1.0 films and HTPB with different chain extenders.

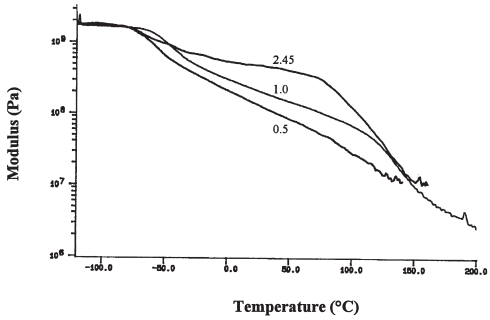


Figure 6 : Effect of TDP content on PU/α films crosslinked with 1,2-diaminoethane.

These results show clearly firstly that there is a very good coalescence of crosslinked particles during film formation and secondly that rather strong physical bonds are formed.

CONCLUSION

The development of these aqueous PU applications has been motivated by environmental considerations to reduce solvent emissions in the atmosphere and to eliminate free isocyanate during application [12]. We have shown that it was possible to synthesize isocyanate-terminated HTPB aniomers without dramatic chain extension, and to produce stable urethane-urea dispersions. The resulting films have a strong resistance and good mechanical properties.

ACKNOWLEDGEMENTS

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