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Process Design of Fluorinated Polyurethane-Urea Anionomer Aqueous Dispersions

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Summary: A series of anionomeric polyurethane-ureas containing perfluoropolyether (PFPE) segments was obtained with a process consisting of a prepolymerisation step, followed by dispersion in water and chain extension. The anionomeric prepolymer can be dispersed in water according to the "prepolymer mixing method" (prepolymer added to water under stirring, or viceversa), then the diamine chain extender is added to form urea linkages. Some compositive parameters (amount of COOH groups in the polymer, diamine content) were optimised in order to obtain fine (diameter 60-90 nm), stable and narrow distribution polymer particles even with a limited amount of ionomer content (COOH = 0.20-0.25 eq/Kg). The fluid dynamics and process engineering of the dispersion step were finally discussed, defining optimal mixing conditions for obtaining controlled and highly reproducible results.

Keywords: anionomer; dispersion process; hydrophobicity; perfluoropolyether; polyurethane

Introduction

Aqueous emulsions of fluorine containing copolymers like fluoroalkyl-polyacrylates are widely used as protective coatings and surface treating agents in order to impart properties as water repellence, soil release and chemical resistance to a large number of substrates (glass, stones, textiles, paper, leather).[1]. More recently, a wide class of waterborne segmented polyurethanes containing bifunctionalised Perfluoropolyether (PFPE) macromers was studied and developed.[2,3] These products belong to the general family of ionomeric polyurethanes; both cationic as well as anionic systems were obtained. The PFPE oligomers combine many features typical of fluoropolymers like low refractive index and surface tension, high chemical inertness, lubricity, with the advantage of much better environmental impact than fluoroalkyl type chemicals[4]. On the other hand, the realisation of copolymers based on PFPE is not trivial since these oligomers

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show very peculiar (and sometimes troublesome) solubility and reactivity issues. Therefore, this article is focused to the design of the polymerisation / dispersion process of a selected class of waterborne polyurethane-ureas, with the aim to explore the effect of the main experimental parameters controlling the process.

Experimental Part

Materials. The perfluoropolyether dimethylol terminated oligomer (Fomblin® ZDOL, from Solvay-Solexis) used in this work has the following chemical structure:

$HOCH_2CF_2(OCF_2CF_2)_p(OCF_2)_qOCF_2CH_2OH$ $\quad (p/q = 2.1)$

and number average molecular weight = 1500. Other monomers (isophorone diisocyanate IPDI, dimethylolpropionic acid DMPA, ethylenediamine EDA) and chemicals (trietylamine TEA, dibutyl tin dilaurate DBTDL, N-methyl pyrrolidone NMP) were supplied from Aldrich.

Prepolymer synthesis. The perfluoropolyether ZDOL, IPDI and DMPA were charged in a reactor and kept under moderate stirring and N_2 atmosphere. The relative amounts were such that IPDI mols = 2(DMPA + ZDOL mols). Triethylamine (1:1 to COOH equivalents) diluted in dry NMP (10% w/w on the prepolymer) was added dropwise by cooling, then the reaction mixture was kept under stirring at 20°C for 90 min, until the prepolymer reached the theoretical residual isocyanate value (chemical titration).

Chain extension and dispersion in water. The following two experimental procedures belonging to the general "prepolymer mixing method" [5] were compared.

Process w-p: Water was added dropwise to the prepolymerisation reactor at +20°C keeping the agitation speed constant. After water dilution, aqueous EDA was added and the mixture was left to react at ambient temperature until no more NCO bands were present at the IR analysis (see below). The solid content of the final aqueous dispersion was 30±1% w/w, while the stoichiometric amount of EDA to be added was calculated as $NH_2/NCO_{(theoretical)}$ ranging from 0 (no chain extender) to 1, in a series of separate experiments.

Process p-w: Two glass reactors were put in series, connected by a glass funnel and thermostated separately. The former was used for the prepolymerisation step following exactly the same procedure as described before. The prepolymer was then poured in 5 minutes into the latter reactor containing water (solid 30% w/w), connected to a thermostatic bath in order to maintain the chosen temperature. Prepolymer dispersion was achieved by mechanical agitation of a disk flat blade turbine operating at speed of 50 s^{-1}. As in the previous case, the chosen amount of EDA ($NH_2/NCO = 0 \div 1$) was added after the prepolymer dispersion and stirring continued until no more NCO bands were detected at the IR analysis.

Molecular characterization. ^{19}F-NMR spectroscopy was carried out with a Varian 300 MHz instrument and used in order to check the conversion of ZDOL in the prepolymerisation step. FT-IR spectroscopy was used in order to check the end of the polymerisation process, by monitoring the disappearance of NCO band at 2260 cm^{-1} with a Perkin Elmer FT spectrometer. Molecular weights of the final polymers were estimated by intrinsic viscosity measurements in a solvent mixture made of trifluorotoluene / trifluoroethanol 8/2.

Particle size measurements. Average particle dimensions and polydispersity of the final polyurethane dispersion were measured by dynamic laser light scattering with a Brookhaven goniometer and correlator, equipped with argon-ion laser operating at 514.5 nm.

Rheological measurements. Viscosity measurements and flow curves were obtained at +20°C with a Rheometric Scientifics rotational rheometer.

Contact angle measurements. Static contact angles against bidistilled water and the highest purity n-hexadecane droplets were measured at +23°C over bar coated surfaces (film thickness 5-10 μm), using a Kruss telescopic goniometer according to the sessile drop method.

Results and discussion

Prepolymerisation. The polymerisation was carried out in two steps, which can be named in a general way a) prepolymer synthesis and b) chain extension. DMPA is the hydrophilic monomer which acts as "internal emulsifier" of the polymer system, allowing its water dispersibility without the need of surfactants. It is recognised [5] that the greater the DMPA content, the higher the hydrophilic character of the polymer, which means aqueous dispersions with better stability and smaller particle size, but potentially lower water repellence of the final product. The main problem met in prepolymer synthesis was the quite poor physical compatibility between PFPE and the hydrogenated monomers (especially DMPA). It was however observed the the triethylammonium salt of DMPA is much more soluble in the reaction medium even at moderate temperatures.

The extent of overall reaction was controlled by chemical titration of NCO groups. Figures 1 and 2 shows the comparison among the NCO-time and TEA-time trends of prepolymerisation carried out in very different experimental conditions. The results are expressed by plotting the ratio between the actual (titrated) amount of the chemical group present at time t, and its theoretical amount at the end of reaction. The prepolymerisation carried out in very mild conditions (absence of tin catalyst and room temperature) allows a quite fast prepolymer formation with a minor loss of NCO functionality (for side reactions, hydrolysis), and minimized TEA evaporation.

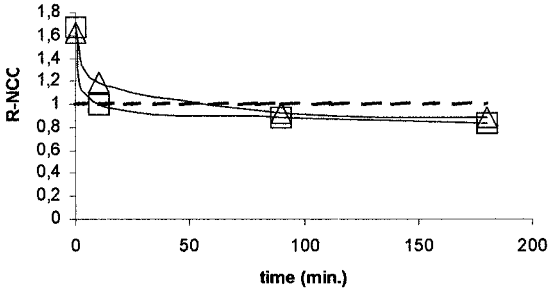

Figure 1: comparison of NCO-time trends of prepolymerisations carried out at T = +80°C, catalyst 0.1 g/eqNCO (squares), and T = +20°C, no catalyst (triangles). R is defined as the ratio between actual (titrated) and theoretical (100% reacted) NCO group

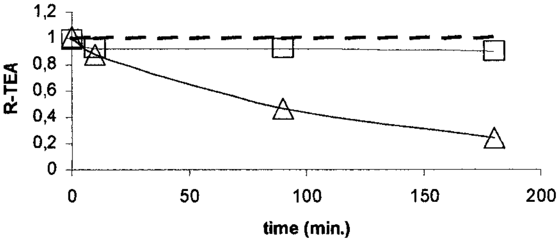

Figure 2: comparison of TEA-time trends of prepolymerisations carried out at T = +80°C, catalyst 0.1 g/eqNCO (triangles), and T = +20°C, no catalyst (squares). R is defined as the ratio between actual (titrated) and theoretical (100% of charged) TEA groups

Those results seem somewhat surprising, since functional perfluoropolyethers like ZDOL generally show quite poor reactivity towards isocyanates in uncatalysed reactions, likely due to electronic effect of the neighbouring perfluorinated chain. A possible explanation is that the triethylammonium carboxylate of DMPA may act as a true catalyst; in effect this behaviour is not observed if DMPA alone (without TEA) is employed in the synthesis.

Chain extension and dispersion in water. In waterborne polyurethane technology[5], chain extension of the prepolymer is generally carried out by adding diamines in aqueous or organic phase and therefore the final polymer should be more correctly classified as a polyurethane-urea. The two methods from the "prepolymer mixing process" were compared. They have marked different rheological behaviour, since in the former case the dispersion is reached through a phase inversion mechanism which involves a viscosity increase, reaching a maximum. Figure 3 shows the comparison between the viscosity evolution trend of the same fluorinated polyurethane obtained by the two processes.

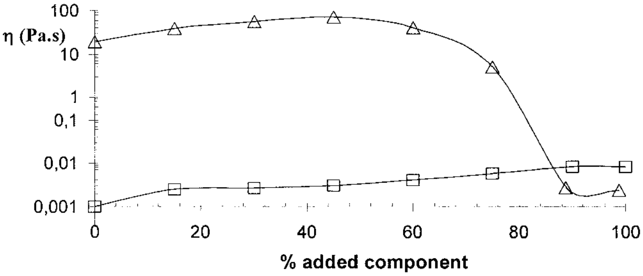

Figure 3: rheological profiles of p-w (squares) and w-p (triangles) dispersion processes

A further rheological study is reported in Figure 4 (flow curves of aqueous dispersion obtained at various amounts of prepolymer dispersed in water). All the aqueous dispersion possess a shear thinning behaviour at low shear, whereas at shear rates of practical interest for mixing and application, viscosity is as low as 5-10 mPa.s at 20°C at 30% solid. The addition of EDA chain extender increases slightly viscosity but doesn't change the phenomenology of the flow curve.

Other important parameters to be considered for a complete control of the process are the ionomer content (COOH groups in the polymer), the stoichiometric ratio NH_2/NCO used, the temperature of chain extension, the geometry of mixing and intensity of agitation.

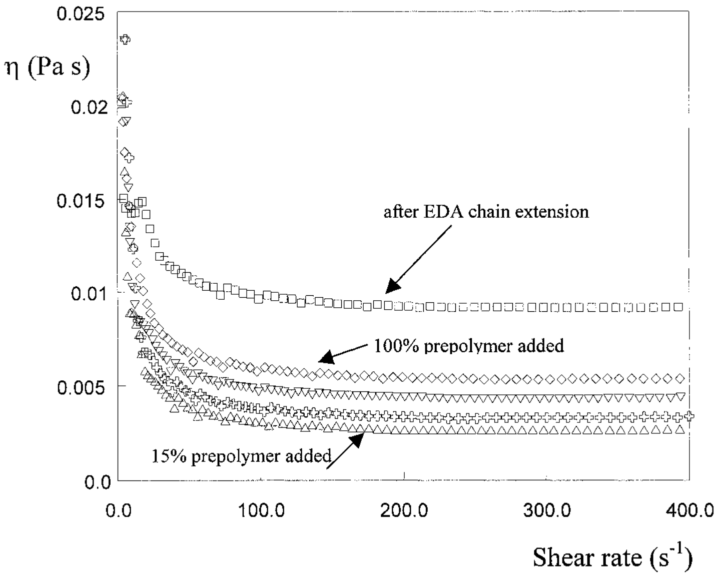

Figure 4: flow curves of polyurethane-urea aqueous dispersions at various solid content

The results of a first series of experiments are reported in table 1. It can be seen that the particle diameter decreases by raising the COOH content as expected (runs 1-4 and 6). Moreover, dispersions obtained by polymers with acidity less than 0.20 meq/Kg (corresponding to DMPA = 2.7% by weight) show poor stability and settle in few days at ambient temperature. A direct comparison between the p-w and w-p methods (runs 4 vs. 5) shows that the former process allows the obtainment of a finer dispersion, keeping fixed the composition parameters like [COOH]. All dispersions obtained with stoichiometric ratio $NH_2/NCO = 1$ have quite high pH (9-11), while lower values closer to neutrality (pH 7-8) are obtained in runs 7 and 8, carried out with large defect or absence of diamine chain extender. This fact would suggest that stoichiometric equivalence of diamine is too high, likely because part of isocyanate end groups can be hydrolysed during the extension process in water.

Molecular weights of polymers were estimated by intrinsic viscosity measurements. Higher molecular weights can be achieved by using a stoichiometric defect of EDA chain extender (runs 7 and 8). This is in agreement with the previous observation, since it is known that in step growth polymerisations maximum molecular weights are achieved when no reagent excess is used.

Table 1: some characteristics of PFPE containing polyurethane urea anionomers (process p-w if not otherwise specified, ambient temperature)

run	NH_2/NCO molar	[COOH] eq/Kg	$[\eta]_{30^{\circ}C}$ mL/g	solid (% w/w)	pH	Particle diameter (nm)	Polydispersity index
1	1.0	0.20	14.0	28	9.5	147	0.11
2	1.0	0.25	8.0	30	10.5	80	0.06
3	1.0	0.30	11.8	30	11.1	65	0.15
4	1.0	0.40	9.0	34	10.0	75	0.13
5	1.0 (process w-p)	0.40	10.0	30	10.4	103	0.16
6	1.0	0.50	8.5	28	10.3	47	0.19
7	0.5	0.30	21.5	30	8.2	64	0.15
8	0	0.30	23.0	30	8.4	67	0.11

Another set of polymerisations was performed according to the p-w process. In particular, the effect of EDA stoichiometry was explored in order to find out the optimised amount of diamine chain extender in terms of higher molecular weights (intrinsic viscosity) and lower pH. In order to avoid as much as possible uncontrolled hydrolysis of isocyanate end groups, the polymerisations were carried out at T < +20°C. Results are shown in table 2: it appears that the optimum stoichiometry, estimated by a balance of higher $[\eta]$ e pH tending to neutrality, is comprised between 0.95 and 0.98. Polymerisation temperatures lower than +15°C seem to cause a certain increase of particle size especially at lower acid content. Definitely, designing the polymer and the process with stoichiometric ratio NH_2/NCO = 0.95, COOH concentration as low as 0.22 eq/Kg, and temperature always kept under +20°C (during both prepolymerisation and chain extension in water) allows the achievement of stable and high fluorine content polyurethane aqueous dispersion.

The DMPA content needed with PFPE based anionomer dispersions (2.7÷3.0%) is quite similar to values reported in many paper for non-fluorinated polyurethane dispersions, but in our case smaller polymer particles were measured by light scattering. In fact, typical DMPA values as high as 2.5% - 5.0%, frequently about 3.5%, are reported for anionomer dispersions based on aliphatic diisocyanates and macroglycols like polytetramethyleneglycole [6], polypropyleneglycole [7], polycarbonates [8] and polyesters [9]. In all these cases, aqueous polyurethane dispersions with particle diameter in the range 100 – 400 nm were obtained. Much finer polymer dispersions (diameter 36 – 62 nm) were measured by Hourston *et al.* [10] with a series of chemically different polyurethane anionomers based on aliphatic diisocyanates. In that case, however, a DMPA content as high as 4.9% in the polymer is indicated.

Table 2: selected polymerisations following the p-w process

NH_2/NCO molar	[COOH] eq/Kg	T (°C)	$[\eta]_{30°C}$ mL/g	Solid (% w/w)	pH	Particle diameter (nm)	Polydispersity index
0.90	0.22	5	11.2	29	7.2	238	0.26
0.90	0.22	15	11.2	28	7.0	105	0.17
0.90	0.25	5	16.1	30	7.5	75	0.13
0.90	0.25	15	9.2	29	7.2	74	0.19
0.90	0.28	5	15.2	29	7.7	53	0.12
0.90	0.28	15	15.2	29	7.5	56	0.10
0.95	0.22	5	15.6	29	7.0	91	0.13
0.95	0.25	15	11.8	28	7.3	68	0.07
0.95	0.28	5	15.2	29	7.3	58	0.08
0.98	0.20	15	10.2	29	9.4	95	0.16
0.98	0.22	15	15.2	30	9.3	85	0.12
0.98	0.25	15	15.2	29	9.8	76	0.12
0.98	0.28	15	14.5	29	8.0	65	0.08

Dispersion engineering. From the pioneering work of Dieterich [5], the number of scientific papers appearing in the open literature about ionomeric polyurethanes has been progressively increasing. Most of them contain accurate description of polymerisation process especially from the chemical mechanisms side, but less attention was given to chemical engineering issues like equipment (vessel and impellers), mixing and fluid dynamics.

The dispersion process can be analysed as an heterophase multicomponent system, where particles of dispersed phase form during polymerisation. A number of factors concur to the determination of particle size since the droplet is formed from the balance of mechanical agitation (shear stress breaking the dispersed phase), viscosity, density and interfacial tension.[11] In the present work particular care was given to the selection of mixing equipment. Agitation was carried out with a disk 6-blade turbine (Rushton turbine). The other parameters considered were the the vessel diameter T, impeller diameter D, their ratio D/T, the speed of agitation N. The dispersion process will be more efficient and uniform when turbulent flow is achieved. The flow regime can be estimated by using dimensionless Reynolds number $Re=ND^2\rho/\eta$, being ρ = density and η = viscosity of the system under agitation. In particular, it is generally assumed that turbulent flow is obtained for $Re \geq 10^4-10^5$ for turbine impellers. As far as power consumed is concerned, it is given by $P=N_p.N^3D^5\rho/g$ (g = gravity constant) being the dimensionless power number N_P function of Re and of impeller type. In the turbulent regime, N_P assumes nearly constant values and empirical N_p vs. Re plots are available in the technical literature [12] for the various impellers. In particular for the flat blade turbine, N_p can be estimated as low as 5.0 at high Re numbers. The geometrical ratio D/T influences the homogeneity of mixing and definitely the polydispersity of particles formed. In order to have a sufficiently small mixing time (at least of the order of 10^{-1} s), a D/T ratio high enough should therefore be adopted. The following geometrical parameters were therefore used for the experiments: $N = 50\ s^{-1}$, $V = 1{*}10^{-3}\ m^3$, $T = 0.140$ m, $D = 0.07$ m. The density ρ of the system (1090 Kg/m^3) was calculated as a first approximation by assuming additivity of specific volumes of components, while viscosity value was averaged (0.055 Pa.s). From the above set of parameters, the corresponding set of values were calculated for the dispersion experiments carried out: $Re \approx 48000$, $N_P = 5.0$ and therefore $P = 116$ W. Stirring rate and power values are quite compatible with a conventional lab equipment. It would indicate that the dispersion process was carried out in conditions very close to the turbulent flow regime. It is worth noticing that polymer dispersions of reduced size (60-90 nm) and polidispersity (well below 0.2) were obtained in these conditions with excellent reproducibility. On the other hand, operating at lower N or reducing D involved a significant loss of reproducibility of results, and more polydisperse particles were formed. As anticipated, the problem was particularly severe by adopting the w-p process: actually the very wide fluctuations of viscosity during addition of the prepolymer make impossible to carry out the polymerisation with controlled Re and, moreover, the power of the lab equipment is not enough to allow a correct mixing during the phase inversion step.

Properties of the materials. The effect of COOH content on water adsorption and contact angle was finally evaluated. The main results are summarized in table 3. The surface water as well as oil (hydrocarbon) repellence of the fluorinated anionomers is high enough and apparently not influenced by the content of DMPA in the polymer. The results are not surprising since it is known that segmented copolymers containing PFPE segments, like in general all fluorine containing copolymers, are characterized by a not homogeneous composition profile with strong enrichment of fluorinated structures close to the polymer-air interface [13].

Table 3: static contact angle vs. H_2O and n-hexadecane, and water adsorption data

[COOH], eq/Kg	0.20	0.25	0.35
θ (vs. water, degrees)	104±3	106±3	104±3
θ (vs. n-hexadecane, degrees)	59±2	59±2	60±1
Δ weight in H_2O (after 800 hours)	+14%	+5%	+25%

On the other hand, the presence of COOH groups has an effect on bulk hydrophobicity. This furtherly underlines the importance of designing a process capable of producing fine polymer dispersions with high reproducibility without using an excessive level of internal emulsifier.

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