

Aqueous Polyurethane Dispersions: A Comparative Study of Polymerization Processes

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ABSTRACT: Restrictions on volatile organic compounds have forced the producers of solvent-based polymers to develop safer products. Water dispersions of polyurethanes are successfully replacing solvent-borne products in the coating industry, but relatively little systematic work has been reported that compares polyurethanes obtained by different processes. In this study, polyurethanes were produced with three polymerization processes: in a solution, in a dispersion with the acetone process, and in a dispersion with the prepolymer mixing process. The same prepolymer was synthesized in all cases, and the reaction was concluded under the conditions required by the three different methods. In the first phase, nonextended polyurethanes were prepared with different functional group ratios (NCO/OH),

and an evaluation of the quality of the dispersions and solutions and of the morphology of the dry polymers was made by a comparison of the products from the three preparation routes. Second, the growth of the molecular weight in water was studied for the prepolymer mixing process. NCO-terminated prepolymers were dispersed in water and then extended by aliphatic diamines. The extender was added in different percentages that referred to the NCO equivalents of the prepolymer. This led to an evaluation of the effect of the dispersing medium on chain extension. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 716–723, 2003

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INTRODUCTION

In the past few decades, governments and international agencies have been placing more emphasis on the improvement of production processes and working conditions and on the reduction of the emission of toxic and polluting materials into the atmosphere. As any other industry, the polymer industry must conform to safety regulations that are becoming more and more pressing.

Polyurethanes are very interesting industrial products. They have a broad spectrum of commercial uses in many market areas because of their wide range of chemical and physical properties obtainable from different raw materials and synthetic processes. The various preparation methods have been developed essentially in two major reaction media, solvent-free and in solution, but the presence of a solvent is not acceptable with the aforementioned protection of the environment.

Aqueous polyurethane dispersions (binary systems in which polyurethane particles are dispersed in a continuous aqueous medium) have been on the market since the late sixties and have become commercially important since the early seventies. Their devel-

opment is essentially due to the good balance between their technological and environmental characteristics. The properties of these polyurethanes can be compared with those of their solvent-borne counterparts: significant results have been obtained in application areas such as textile and wood coating, leather finishing, and adhesives.

Waterborne polyurethanes represent a topical subject for the plastic industry, but so far little academic literature is available on the matter. For this reason, the development of new products is time-consuming and expensive.

Several processes have been developed for the synthesis of polyurethane dispersions.^{1–3} All of these have in common the first step, in which a medium molecular weight polymer (the prepolymer) is formed by the reaction of suitable diols or polyols (usually macrodiols such as polyethers or polyesters) with a molar excess of diisocyanates or polyisocyanates. In this reaction mixture, an internal emulsifier is added to allow the dispersion of the polymer in water; this emulsifier is usually a diol with an ionic group (carbossilate, sulfonate, or quaternary ammonium salt) or a nonionic group [poly(ethylene oxide)]. The internal emulsifier becomes part of the main chain of the polymer. The critical step in which the various synthetic pathways differ is the dispersion of the prepolymer in water and the molecular weight buildup. The most important processes are the acetone process, the pre-

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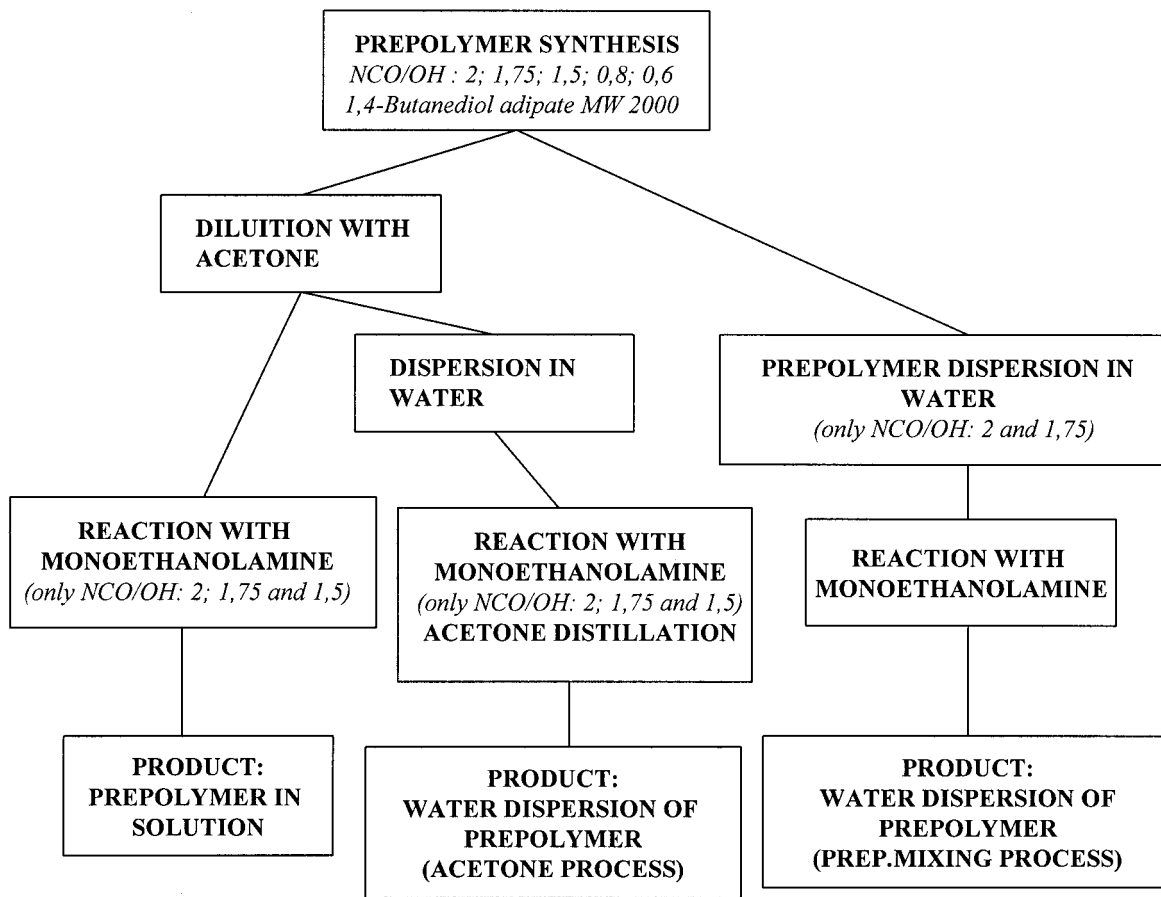


Figure 1 Synthetic approach to the prepolymers.

polymer mixing process, the melt dispersion process, and the ketimine process.

The aim of this work is to compare the synthesis of solvent-borne products with two different methods for the preparation of water-dispersed polyurethanes. The two chosen processes are the most common ones

used in industry: the acetone process and the prepolymer mixing process.

In the acetone process, a solvent (acetone) is added to the prepolymer, and the dispersion is formed by the addition of water to this solution. The extension is usually performed by the addition of a diamine to the

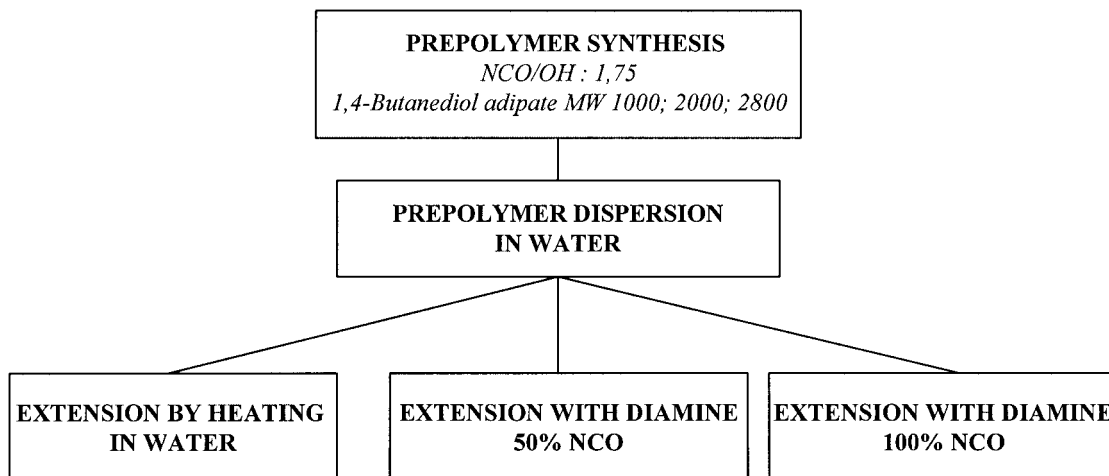


Figure 2 Synthetic approach to the polymers.

TABLE I
Physical Properties of Prepolymer Solutions and Dispersions

Process	NCO/OH	Molecular weight	Dry content (%)	pH	Brookfield viscosity RVT 25°C R2/V20 (mPas)	Particle size (nm)	Storage stability (months)
Solvent	2.00	1665	51	—	150		>3 but <12
Solvent	1.75	2149	42	—	45		>12
Solvent	1.50	3175	43	—	68		>12
Solvent	0.80	7413	41	—	160		>12
Solvent	0.60	3628	42	—	56		>12
Acetone process	2.00	1665	31	—	20	82	>3 but <12
Acetone process	1.75	2149	32	8.0	20	47	>3 but <12
Acetone process	1.50	3175	33	7.9	34	40	>12
Acetone process	0.80	7413	29	7.8	22	38	>12
Acetone process	0.60	3628	31	7.8	12	94	>12
Prepolymer mixing process	2.00	1665	30	8.0	50	265 ^a	>3 but <12
Prepolymer mixing process	1.75	2149	30	8.8	30	127 ^a	>3 but <12

^a Bimodal distribution.

prepolymer solution or after the dispersion in water. The acetone is then removed by evaporation.

In the prepolymer mixing process, the hydrophilically modified prepolymer is directly mixed with water. If the mixture viscosity is too high, a small amount of a solvent such as *N*-methyl pyrrolidone can be added before the dispersion step. Chain extension is accomplished by the addition of diamines to the aqueous prepolymer dispersion.

The acetone process can be considered the link between the solvent synthesis and the prepolymer mixing process. In effect, the prepolymer is synthesized in solution and afterward dispersed in water. This method was the first developed for the preparation of water dispersions of polyurethanes. The prepolymer mixing process is extremely interesting for its conceptual simplicity: no solvent intermediation is needed, but the prepolymer is directly dispersed in water.

A model reaction was chosen with the lowest possible number of process variables. The same prepolymer was synthesized in all cases, and the reaction was brought to conclusion under the conditions required

by the three different methods. In the first phase, nonextended polyurethanes (prepolymers) were prepared with different functional group ratios (NCO/OH): an evaluation of the quality of the dispersions and solutions and of the morphology of the dry polymers was made by a comparison of the products from the three preparation routes. Second, the growth of the molecular weight in water was studied for the prepolymer mixing process. NCO-terminated prepolymers were dispersed in water and then extended by aliphatic diamines. The extender was added in different percentages referring to the NCO equivalents present in the prepolymer. This led to an evaluation of the effect of the dispersing medium on chain extension.

The monomers for these reactions were chosen for their extensive use in the industrial preparation of water-dispersed polyurethanes. Aliphatic diisocyanates are normally used because their kinetic reaction constants with water are lower than those with diamines, and this allows better control over the extension step in water.⁴ The chosen diisocyanate was isophorone diisocyanate.

TABLE II
Physical Properties of Polymer Dispersions

Polyester molecular weight	Extension (% NCO)	Dry content (%)	pH	Brookfield viscosity RVT 25°C R2/V20 (mPas)	Particle size (nm)	Storage stability (months)
1000	0	29	8.4	12	670 ^a	>12 little sedimentation
1000	50	30	8.5	16	404 ^a	>12 little sedimentation
1000	88	30	9.2	15	413 ^a	>12 little sedimentation
2000	0	30	7.5	14	98	>12 little sedimentation
2000	50	30	7.6	14	106	>12
2000	93	30	9.0	16	95 ^a	>12
2800	0	30	7.1	14	118	>12 little sedimentation
2800	50	29	7.7	15	227 ^a	>12 little sedimentation
2800	90	31	9.1	22	95 ^a	>12

^a Bimodal distribution.

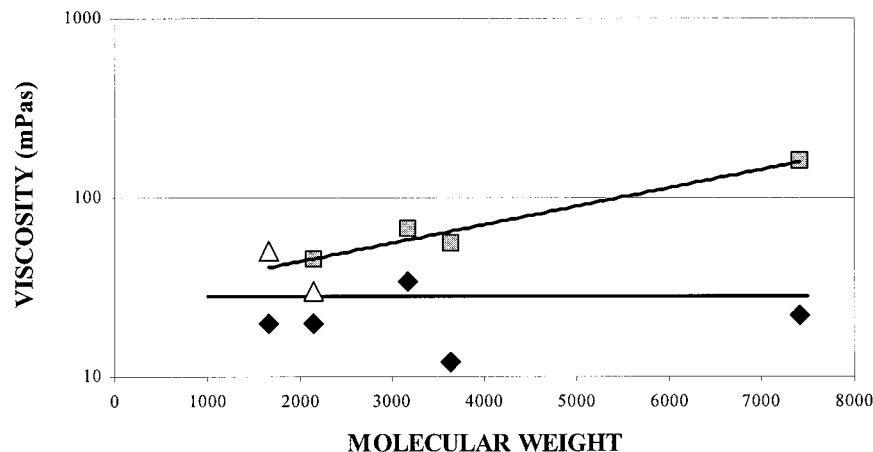


Figure 3 Dependence of the viscosity on the molecular weight: (■) solutions, (◆) acetone process, and (△) prepolymer mixing process.

A polyester was used as a macrodiol. 1,4-Butanediol adipate is a common raw material for water-dispersed polyurethanes, and it is a crystalline substance: this characteristic could be exploited while the morphology of the end products was evaluated. Three different molecular weights of this reactant were used (1000, 2000, and 2800 g/mol).

The dispersing agent of choice was 1,2-dimethyl propionic acid neutralized with triethylamine; in each case, it was added as 3.3% of the total dry substance of the polymers so that each product had the same ionic content. Acetone was used in the homonymous process and as a solvent for the solution synthesis.

An extended scheme of the synthetic approach for the prepolymers is shown in Figure 1. From 1,4-butanediol adipate (molecular weight = 2000), five different prepolymers were prepared with different NCO/OH ratios. These were dissolved in acetone and there terminated (as necessary) with a monoamine (monoethanol amine). The products obtained were solutions of urethane prepolymers (the solution process). Some portions of the acetone solutions were instead dispersed in water and terminated as necessary with the monoamine, and then the acetone was removed by distillation; this yielded water dispersions of prepolymers (the acetone process). The dry prepolymers with the lowest viscosity (NCO/OH = 2 and 1.75) were also directly dispersed in water and there terminated with the monoamine. The obtained products were water dispersions of prepolymers (the prepolymer mixing process).

The scheme of the extended polymer synthetic approach is shown in Figure 2. Three prepolymers were prepared with the same NCO/OH ratio of 1.75 but with different molecular weights of the macrodiol. Each prepolymer was then dispersed in water and extended with three percentages of an aliphatic diamine (1,2-propylene diamine). The disappearance of

the NCO peak in the IR spectrum was considered the end of the reaction for all the extension percentages.

RESULTS AND DISCUSSION

The initial level of the evaluation of the obtained products is the comparison of the physical properties of the solutions and dispersions, which are summarized in Tables I and II. As expected, the viscosity of the solutions was dependent on the molecular weight of the dissolved prepolymer. According to the theory of polymer solutions, the regression curve of the logarithm of the viscosities versus the molecular weight is a straight line with a slope value of approximately 1, which corresponds to the region of low molecular weights below the so-called critical molecular weight.^{5,6}

On the contrary, the prepolymer dispersions, obtained from the same reagents and with the same polymerization ratios that the two synthetic approaches used, showed practically the same viscosity at all molecular weights. This different behavior can be clearly seen in Figure 3. The dispersion of the extended polymers had low viscosity values, and this confirmed that high molecular weights could be prepared without the rheology of the end product being affected.

The particle size analysis allowed a comparison between the two different ways of dispersing the prepolymers in water. Almost all the products (both the polymers and prepolymers) could be considered good dispersions, as the particle sizes were quite small and the incidental sedimentation was always negligible. In any case, the acetone process led to better products (smaller particle sizes and monomodal distribution) than the prepolymer mixing process. This was probably due to the gradual passage of the prepolymer in water, which is typical of the acetone process; the

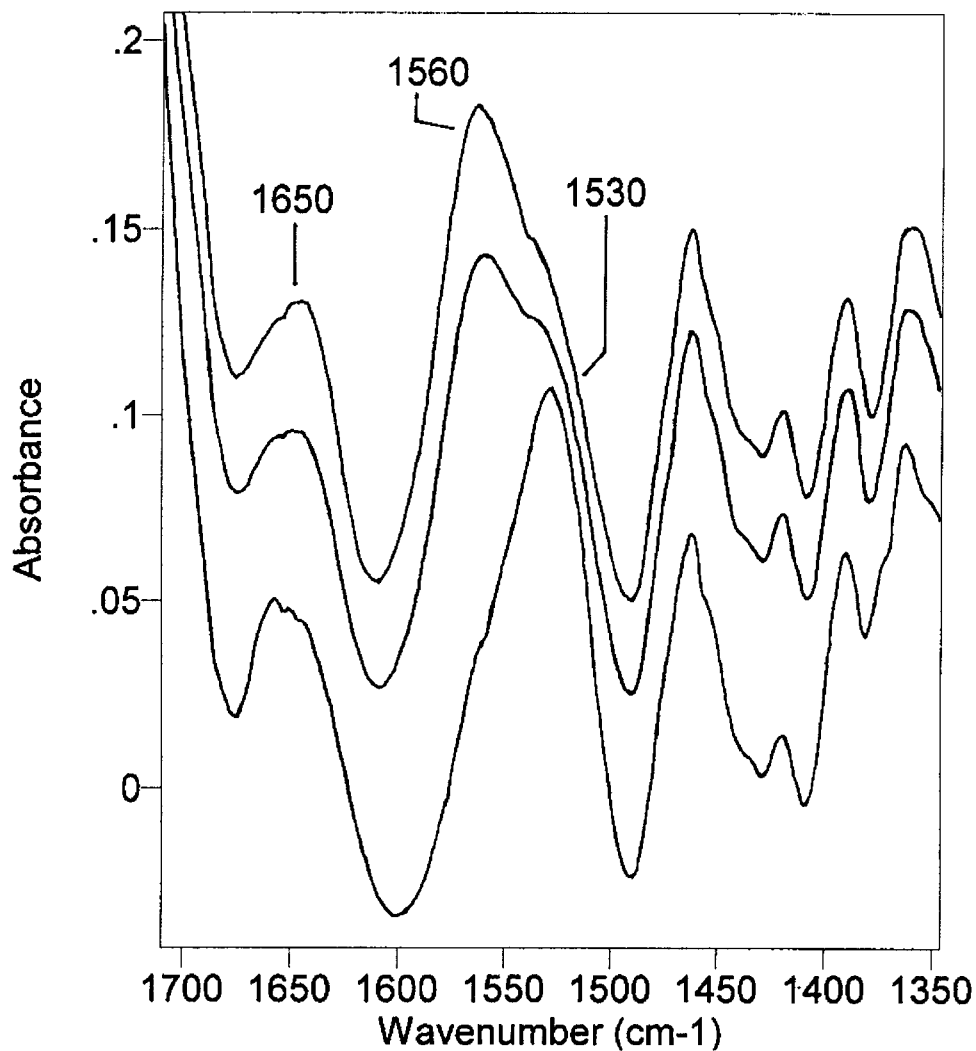


Figure 4 IR spectra ($1300\text{--}1700\text{ cm}^{-1}$).

presence of the solvent, in fact, allowed a better separation between the particles in formation than that obtainable by the direct dispersion of the polymer into water. Bimodal distributions with higher dimension particles could be found in dispersions obtained with the prepoly-

mer mixing process, particularly when the molecular weight of the dry prepolymer before dispersion was low. For both dispersion systems, the best results were reached with higher prepolymer molecular weights, which resulted in products with smaller particle sizes.

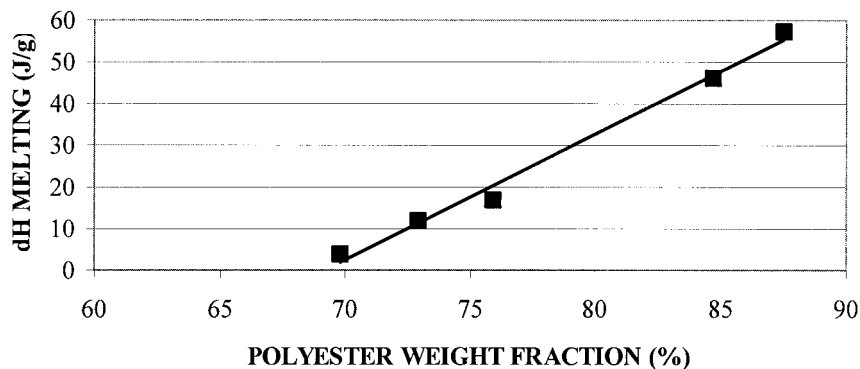


Figure 5 Dependence of the melting dH on the polyester weight fraction for the prepolymers in an acetone solution.

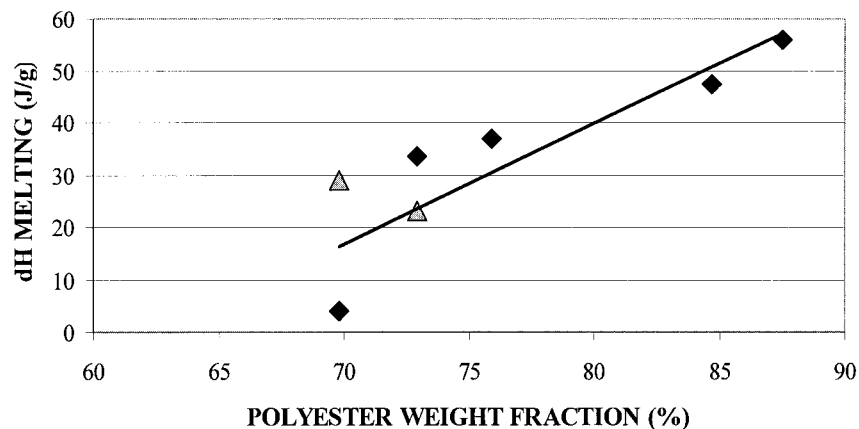


Figure 6 Dependence of the melting dH on the polyester weight fraction for the prepolymer dispersions: (◆) acetone process and (▲) prepolymer mixing process.

The end-product molecular weight influenced the storage stability of the dispersions. As can be seen in Tables I and II, higher molecular weights resulted in better storage durability. In fact, the extended polymers dispersions were all stable for more than 12 months, and the minor sedimentation that they had came from the efficiency of the dispersing stage. Non-extended prepolymers with molecular weights lower than 2200 g/mol were unstable in both solution and dispersion.

A further level of analysis is the evaluation of the different properties of the dry prepolymers and polymers. The first characterization was made with IR spectroscopy. This analysis was used during the synthesis to check the end of the polymerization reaction, verifying the disappearance of the ν NCO at 2265 cm^{-1} and the appearance of the ν N—H at $3000\text{--}3400\text{ cm}^{-1}$.

IR spectra also contained all the information relating to the primary structure of the final polymer, particu-

larly the peaks at 1650 (amide I, ν C=O), $1530\text{--}1560$ (amide II, δ N—H and ν C—N), 1240 (amide III, ν C—N and δ N—H), and $1160\text{--}1175\text{ cm}^{-1}$ (antisymmetric ν C—O—C). The amide I peak indicated the formation of urea groups by the reaction of NCO with amine, and its intensity correlated directly to the relative quantities of these groups in the polymer. The shape of the amide II peak was not always monomodal; this could indicate the presence of two different kinds of N—H groups. One hypothesis could be the simultaneous presence of ureic and urethanic N—H, but this does not explain the difference between the spectra of the prepolymers obtained from exactly the same raw material quantities, as shown in Figure 4. In fact, the prepolymers in solution had a predominant 1530-cm^{-1} peak, whereas the prepolymers in water dispersions had a more intense 1560-cm^{-1} peak. This could denote the presence of different types of N—H groups, such as the allophanic groups.

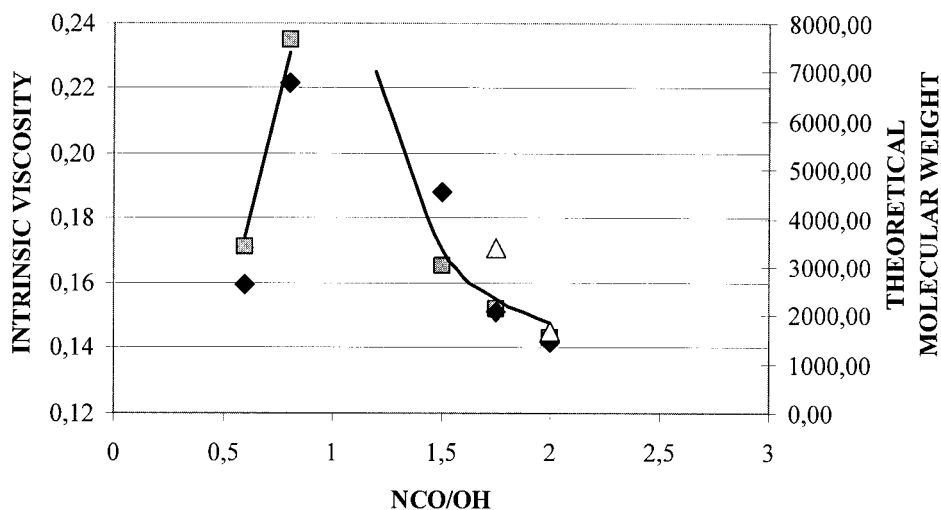


Figure 7 $[\eta]$ versus the NCO/OH ratio for the prepolymers: (■) solution, (◆) acetone process, (△) prepolymer mixing process, and (—) theoretical molecular weight.

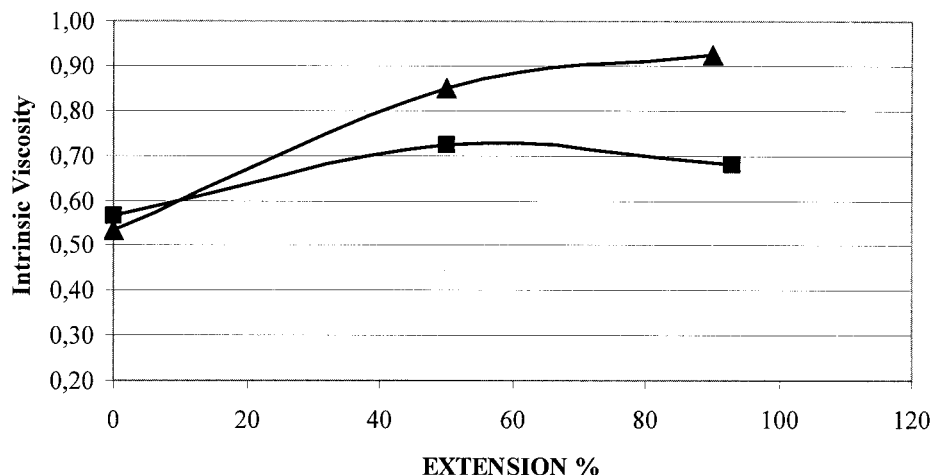


Figure 8 $[\eta]$ versus the extender percentage for the prepolymers: (■) butanediol adipate (molecular weight = 2000) and (▲) butanediol adipate (molecular weight = 2800).

Thermal analysis was used to characterize the crystallinity of the end products. All the prepolymers showed an endothermic peak in the heat run. This melting temperature was similar for all the products, and it was in the same interval of the melting temperature of the polyester used for the synthesis. The enthalpy of these peaks was correlated with the relative quantity of the macrodiol present in the product: the higher the polyester content was, the higher the melting enthalpy was (Figs. 5 and 6). It was possible to affirm that the crystalline domains of the end product were constituted by the soft segment of the polyurethane and that the amorphous section of the material contained the rest of the segments.

A difference could be found between the water-dispersed and solution prepolymers: the latter had lower melting enthalpy values, which indicated a worse separation between the crystalline and amorphous areas. This could be ascribed to the different film formation mechanisms. In the solvent-borne products, each polymer chain was separated from the others by the solvent, and this evaporated gradually, preventing till the last any direct contact between the chains; on the contrary, in the water-dispersed particles, the polymer chains were already in direct contact, developing the best interactions. Higher crystallinity was, therefore, obtained with the prepolymer mixing process in which the solvent was completely absent. In any case, in the solid dry state, the organization of the crystalline domains was quite rapid, and the endothermic peak was detectable also in heating runs that followed previous melting and cooling.

It was more difficult to detect the melting points of the extended polymers. In fact, this was only possible in a first heating run starting from ambient temperature, but it became impossible when the polymer was already melted and cooled down because the kinetics of the crystallization needed longer times than those

usable in the analysis. This was probably due to the lower mobility of the high molecular weight chains. No melting occurred when the butanediol adipate used in the synthesis had a molecular weight of 1000: the shorter length of the polyester segment made it difficult for the polymer to establish the interactions that led to crystallinity.

The determination of the intrinsic viscosity ($[\eta]$) was used to gain information on the molecular weight of the prepared polymers. A method was specifically developed because none was recorded in the scientific literature for this kind of anionically modified polyurethane. The polymers were dissolved in dimethylformamide, and $[\eta]$ was determined with a Desreux Bishoff capillary viscometer. The results of this analysis of the prepolymers are given in Figure 7, along with the theoretical molecular weights of the products. A good correlation was found between the theoretical molecular weights and the measured $[\eta]$ values.

The water-dispersed prepolymers had higher $[\eta]$ values at high NCO/OH ratios. The increase in the viscosity was probably due to the beginning of the water-mediated extension reaction that took place at the same time as the dispersion for the prepolymers containing free NCO. This effect was more evident for the polymers obtained with the prepolymer mixing process, in which the NCO groups were more readily in contact with water.

The $[\eta]$ values of the extended polymers are represented in Figure 8. Heating the NCO prepolymers in water yielded polymers with higher $[\eta]$ values than those found for terminated prepolymers (Fig. 7). This means that in the presence of water, it was possible to obtain a real extension of the prepolymer. This increase in the molecular weight was more accentuated in the presence of a true chain extender, the diamine.

The $[\eta]$ values of 50 and 100% extended polymers did not differ by a significant value. High molecular weights can be obtained without the addition of the entire amount of a diamine that can react with all the NCO groups present in a prepolymer. Therefore, the determination of the exact NCO value of a prepolymer dispersion in water is not necessary, and this avoids a complicating and time-consuming operation in industrial practice.

CONCLUSIONS

This work allowed the comparison of three different synthetic processes for the production of polyurethane polymers. The dispersion step was critical for the achievement of the final properties of the products:

- The particle sizes depended on the synthetic pathway (better dispersions were obtained with the acetone process than with the prepolymer mixing process).
- The $[\eta]$ values of the polymers prepared with the acetone process were comparable to those of the solution polymers, whereas the products prepared with the prepolymer mixing process experienced the effects of water interaction more.
- Higher crystalline properties were achievable with the prepolymer mixing process.

The water dispersions all had the same viscosity, which did not depend on the molecular weight of the polymer; on the contrary, the solution viscosities increased with increasing molecular weights. The possibility of extension via heating in water without the calibration of the exact amount of the diamine provided an excellent solution to industrial applications. Furthermore, the two dispersing processes could be controlled to obtain products with the desired characteristics, and the prepolymer mixing process had the advantage of eliminating the use of the solvent. This work allowed the setting up of a methodology for the comparison of different synthetic processes and the gaining of information about the properties of dispersions and polymers that could be useful to their chosen applications.

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