

# Anionic Waterborne Polyurethane Dispersions Based on Hydroxyl-Terminated Polybutadiene and Poly(propylene glycol): Synthesis and Characterization

FERNANDA M. B. COUTINHO,<sup>1,2</sup> MARCIA C. DELPECH,<sup>1</sup> LAIRTON S. ALVES<sup>1</sup>

<sup>1</sup> Instituto de Macromoléculas Professora Eloisa Mano, IMA/UFRJ, C.P.: 68525, Rio de Janeiro, RJ, CEP: 21945-970, Brazil

<sup>2</sup> Departamento de Processos Industriais, IQ/UERJ, Rio de Janeiro, RJ, Brazil

Received 26 July 1999; accepted 30 June 2000

**ABSTRACT:** Nonpolluting systems based on anionic polyurethane aqueous dispersions were obtained. The prepolymer based on hydroxyl-terminated polybutadiene (HTPB), isophorone diisocyanate (IPDI), poly(propylene glycol) (PPG), and dimethylolpropionic acid (DMPA) were synthesized in bulk. After neutralization with triethylamine (TEA), the anionomer prepolymer was dispersed in water, followed by a chain-extension reaction with ethylenediamine (EDA). The prepolymers were characterized by Fourier transform infrared spectrometry (FTIR) and the average particle size of the aqueous dispersions was determined by laser light scattering (LLS). The mechanical behavior of polyurethane-cast films and the adhesive properties of the aqueous dispersions as coatings for wood were evaluated. It was observed that an increase in the HTPB content provoked an increase in the viscosity and in the particle size of the dispersions. The tensile strength and the modulus values of the films and the adhesiveness of the coatings in wood were also increased by increasing the HTPB content. On the other hand, the elongation of the polyurethane-cast films and the tackiness of the surface coatings decreased as the HTPB was increased. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 566–572, 2001

**Key words:** polyurethane; aqueous dispersions; anionomer; HTPB; IPDI; PPG

## INTRODUCTION

Environmental reasons are the cause for the increase of research, development, and production of waterborne systems, particularly those based on polyurethanes.<sup>1</sup> These materials find a special application as binders for paint and coatings formulations.<sup>2</sup>

Polyurethane coatings, in general, provide excellent chemical, solvent, and abrasion resistance, as well as toughness combined with good low-temperature flexibility. There are various ways of combining a wide variety of polyols and diisocyanates in order to produce tailored polyurethane products. These properties, in addition to the nonpolluting characteristics of waterborne systems, make polyurethane aqueous dispersions unique.<sup>3–6</sup>

The most common polyurethanes produced in industry and related in the literature are those using, as a polyol, a polyether or a polyester obtained in an organic or aqueous medium. Nowadays, many studies about waterborne polyure-

Correspondence to: F. M. B. Coutinho (fern@ima.ufrj.br).

Contract grant sponsors: Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq); CNPq/PADCT; PRONEX; Dow Química; Petroflex; Centro de Pesquisas da Eletrobrás (CEPEL).

*Journal of Applied Polymer Science*, Vol. 80, 566–572 (2001)  
© 2001 John Wiley & Sons, Inc.

thanes are being published but very few employing hydroxyl-terminated polybutadiene (HTPB) as a polyol.

HTPB is generally used in the preparation of adhesives, coatings, elastomers, and encapsulates and in many areas such as in the automobile, coatings and paints, building-trade, electronics, and medicine fields.<sup>7</sup> Another important field of polyurethane application is the spacecraft industry, in which HTPB-based polyurethanes are employed as binders in composite solid propellants<sup>4,8</sup> and in the manufacture of gas-separation membranes.<sup>9</sup>

When the soft segments in polyurethane chains are formed by an oligobutadiene, instead of a polyether or a polyester, high segregation between the hard and soft domains occurs, due to the apolar character of the oligobutadiene chain.<sup>9</sup> As a consequence, some striking features, such as high resistance to acid or base hydrolysis, the ability of retaining elastomeric behavior at low temperatures,<sup>10</sup> low water permeability, and improved mechanical properties,<sup>11</sup> have been developed. Therefore, the presence of HTPB in polyurethane chains brings important characteristics to the final product. However, the high viscosity that this oligomer promotes in the reaction medium is a limitation factor in the water-dispersion process and usually solvents such as *N*-methylpyrrolidone (NMP)<sup>12</sup> have to be employed. This article relates a successful method for preparing waterborne polyurethanes based on HTPB in the complete absence of an organic solvent.

## EXPERIMENTAL

### Reagents

The following reagents were used without further purification in the waterborne polyurethane synthesis: dibutyltin dilaurate (DBTDL; Aldrich, Wisconsin, USA); dimethylolpropionic acid (DMPA; Aldrich); ethylenediamine (EDA), concentration: 98.8% PA-ACS (Reagen, Rio de Janeiro, Brazil); HTPB,  $\bar{M}_n$  (VPO) = 3500, hydroxyl number = 46.06 mg KOH/g (Petroflex, Rio de Janeiro, Brazil); isophorone diisocyanate (IPDI), concentration<sup>13</sup>: 98.6% (Hüls, Germany); poly(propylene glycol) (PPG): Voranol 2110,  $\bar{M}_v$  = 1220, hydroxyl number<sup>14</sup> = 55.42, and Voranol 2120,  $\bar{M}_v$  = 2490, hydroxyl number<sup>14</sup> = 106.24, dried under a vacuum<sup>4-6</sup> at 120°C (Dow Chemi-

cal, Sao Paulo, Brazil); and triethylamine (TEA; Union Carbide, USA).

### Synthesis

The synthesis of the prepolymers based on HTPB, PPG, DMPA, and IPDI, catalyzed by DBTDL, was carried out in the absence of a solvent at 100°C for 2 h under a N<sub>2</sub> atmosphere. After that period, the temperature was reduced to 50°C and aliquots were removed from the bulk for NCO content determination.<sup>1</sup> The prepolymer neutralization with TEA was proceeded at 50°C for 1 h. The temperature was reduced to 25°C and the dispersion of the bulk in water was carried out at high-speed stirring. Afterward, EDA was added to the dispersion that was kept at 35°C for 1 h to complete the chain-extension reaction between the amino groups of the chain extender and the NCO end groups of the prepolymer. Figure 1 shows the polyurethane aqueous dispersion synthesis scheme.

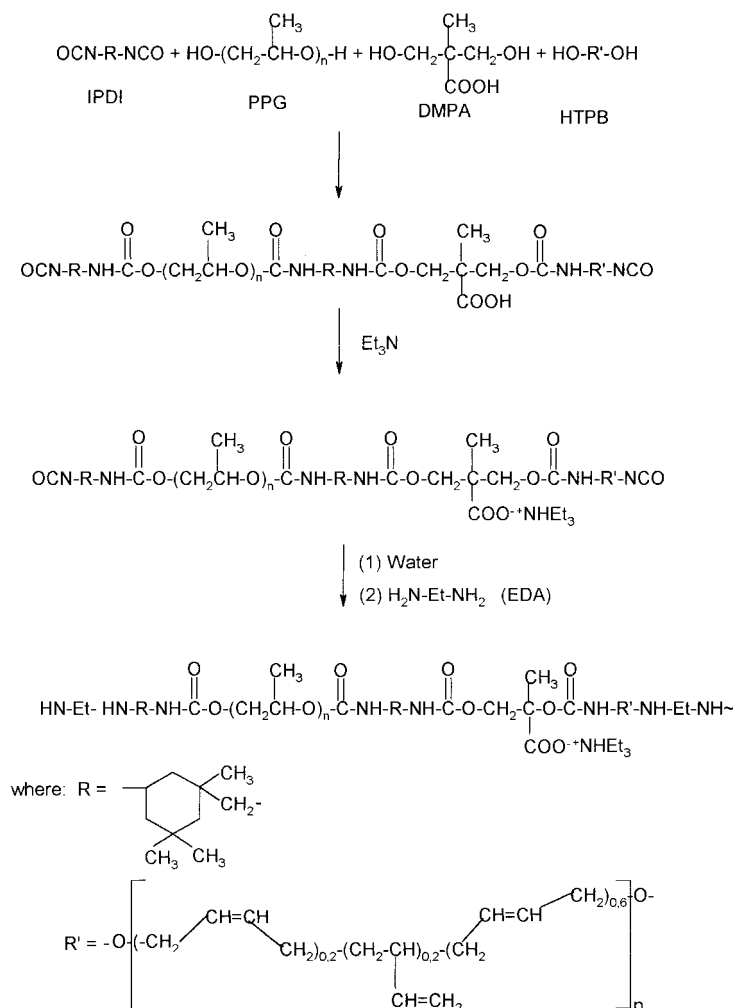
Polyurethane aqueous dispersions with a solid content of 35 ± 2.5% (w/w) were obtained by varying the HTPB content from 10 to 50% (w/w) and the DMPA content from 1 and 5% (w/w), both related to the prepolymer total mass and the molecular weight of PPG. The prepolymers were synthesized in two different NCO/OH ratios: 1.5 and 3.0.

### Characterization

Prepolymer FTIR spectra were performed using a Perkin-Elmer 1720 spectrometer calibrated with a polystyrene standard. The resolution employed was 2 cm<sup>-1</sup>. The prepolymer, after the reaction of NCO end groups with methanol, was put directly on the KBr cell.

Average particle sizes were determined using a Malvern Sizer Microplus MAF 5001 laser scattering analyzer (wavelength = 633nm). The aqueous dispersions, diluted in distilled deionized water, were filtered and submitted to ultrasound, in the equipment, before analysis. Films were obtained by casting the dispersions on Teflon level surfaces and allowing them to dry at room temperature for 7 days or at 60°C for 12 h.<sup>4,6</sup>

TGA measurements were performed in an analyzer Model HI-RES TGA 2950, T.A. Instruments, calibrated with an aluminum standard, under a nitrogen flow, at a heating rate of 10°C/min and temperature range from 25 to 600°C. The tensile tests performed were an adaptation of the ASTM-D



**Figure 1** Polyurethane aqueous dispersion synthesis.

412-83, D 638-84, and D 882-83 methods.<sup>6</sup> The test specimens ( $5 \times 70 \text{ mm}^2$ ) were cut from polyurethane films. A test machine INSTRON 4204, equipped with a 1-kN load cell and pneumatic grips, was used at a crosshead speed of 50 cm/min.

The adhesive properties of the dispersions as coatings for wood were evaluated according to a standard test.<sup>15,16</sup> An apparatus known as a pull-off adhesion tester was used. This apparatus permits the application of a concentric load to a single surface, so that coatings can be tested even though only one side is accessible. Measurements are limited by the strength of adhesion bonds between the loading fixture and the specimen surface or the cohesive strength of the substrate (wood plates). In this work, a pull-off adhesion tester, an Elcometer 106 number 2 (1–7 MPa scale), was used.

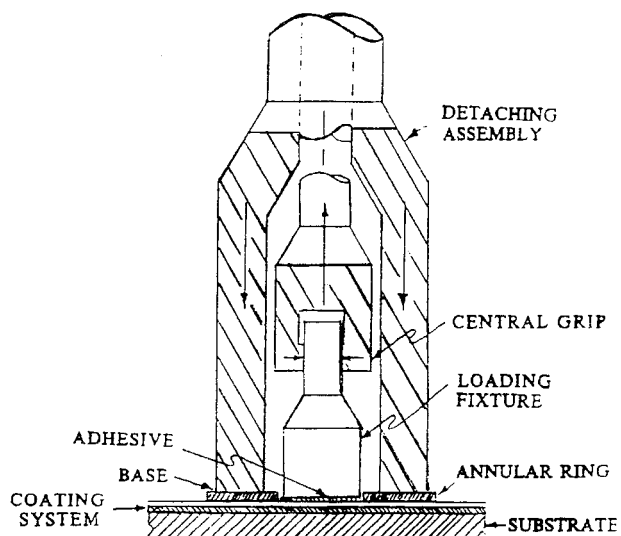
Due to the destructive nature of the test, the type of wood chosen had to be very hard (ipê, from

a native Brazilian tree). The wood test specimens (substrate) measuring  $20 \times 20 \times 1 \text{ cm}^3$  were first rubbed with sandpaper before the application of water dispersions with a painter's brush. Then, the dispersion was applied on the substrate and let to dry at room temperature for 7 days. Then, four aluminum fixtures were fixed on the surface of each coated wood plate (substrate) with a bi-component adhesive. The systems were maintained at room temperature for another 7 days, to complete the evaporation of the volatiles from the adhesive. Figure 2 shows a schematic representation of the adhesion tester.

## RESULTS AND DISCUSSION

### Prepolymer Characterization by FTIR

The prepolymers were characterized by infrared spectroscopy. Figure 3 shows the FTIR spectra of



**Figure 2** Schematic representation of a pull-off adhesion tester.

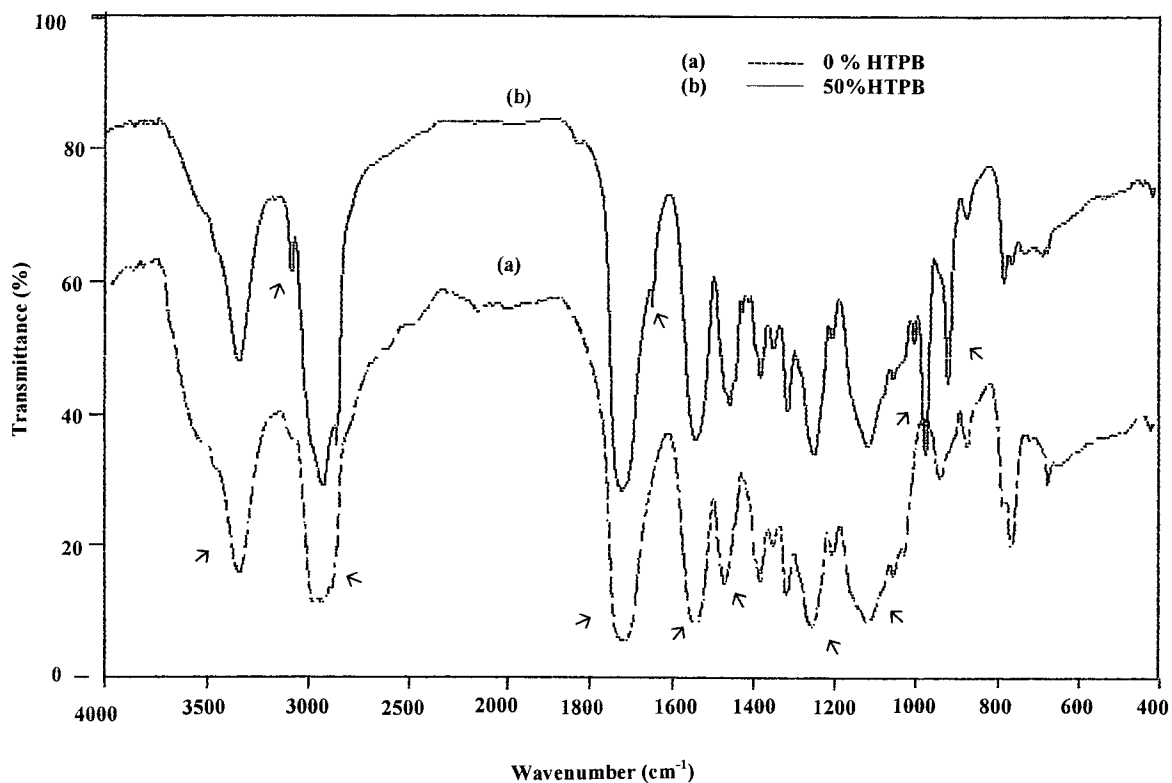
prepolymers (a) without HTPB and (b) with 50% (w/w). The main characteristic group absorptions in the spectra are summarized in Table I.

The main difference between the two spectra [Fig. 3(a,b)] is the presence of an absorption at  $3074\text{ cm}^{-1}$ , a weak absorption at  $1640\text{ cm}^{-1}$ , and two strong absorptions at  $967$  and  $912\text{ cm}^{-1}$ , due to the presence of HTPB double bonds inserted into the polyurethane chains. Those bands are indicated by arrows in spectrum (a) and the characteristic absorptions of the other groups are also indicated by arrows in spectrum (b). Differences were not observed in the HTPB-based prepolymer spectra as far as the HTPB content, PPG molecular weight, and NCO/OH ratio were concerned.

### Aqueous Dispersion Characterization

The apparent viscosity of the aqueous dispersions varied from 30 to 220 cP, when higher molecular weight PPG was employed, and from 20 to 420, in those where the lower molecular weight PPG was used. In a general way, the dispersion viscosity increased as the HTPB content was increased. The pH of the aqueous dispersions varied in the range from 8 to 10.

It was observed that the dispersions synthesized with a DMPA content equal to 1%, with or



**Figure 3** Infrared spectra of polyurethane prepolymers synthesized with PPG ( $\bar{M}_v = 2490$ ), 5% DMPA (w/w), and NCO/OH = 1.5: (a) without HTPB; (b) with 50% HTPB (w/w).

**Table I** Characteristic FTIR Absorptions Present in the Spectrum of the Polyurethane Prepolymer Synthesized with 50% (w/w) Content of HTPB

| Wavenumbers<br>(cm <sup>-1</sup> ) | Bonds  | Vibrational Modes <sup>8,17-22</sup>                |
|------------------------------------|--|---|
| 3335                               | N—H urethane in hydrogen bond                | Stretching vibration                                |
| 3074                               | C—H vinyl group                              | Stretching vibration                                |
| 2917 and 2846                      | C—H methyl and methylene groups (PPG)        | Asymmetrical stretching and symmetrical stretching  |
| 1713                               | C=O urethane free and forming hydrogen bonds | Stretching vibration                                |
| 1640                               | C=C vinyl group                              | Stretching vibration                                |
| 1532                               | C—N—H urethane                               | Stretching vibration (CN)<br>Bending vibration (NH) |
| 1450                               | C—H methyl and methylene groups (PPG)        | Asymmetrical bending vibration                      |
| 1374                               | C—H methyl group (PPG)                       | Symmetrical bending vibration                       |
| 1242                               | C—O—C  | Asymmetrical stretching                             |
| 1110                               | C—O urethane and ether groups                | Stretching vibration                                |
| 967 and 912                        | C—H vinyl group                              | Out-of-plane bending vibrations                     |

without HTPB addition, were not stable, presenting sedimentation 24 h after their synthesis. That content of neutralized ionic sites (carboxylate groups) was not sufficient to stabilize the aqueous dispersion. On the other hand, the dispersions containing 5% (w/w) of DMPA in relation to total prepolymer mass were stable even 1 month after their synthesis.

Some values of the aqueous dispersion average particle size are shown in Table II. The particle external layer is formed by the hydrophilic portions present along the polyurethane chains as carboxylate groups; urethane groups, provenient from prepolymer chain; and urea groups, formed in a chain-extension reaction. The results presented in Table II show that HTPB insertion led to a remarkable increase in the particle size. This is probably due to the nonlinear and irregular

structure, caused by the presence of the repeating units of different configurations (1,4-*trans*, 1,4-*cis*, and 1,2-vinyl), hindering the chain compaction during the dispersion.<sup>4,18</sup> The hydrophobic character of the HTPB segment is another important factor that hinders the dispersion in water, resulting in the formation of large particles. The same behavior was observed in relation to the length of the PPG segment. Larger particles were formed when higher molecular weight PPG (increase of the hydrophobic character) was employed in the prepolymer synthesis. Despite these observations, the great majority of aqueous dispersions prepared in this work were stable.

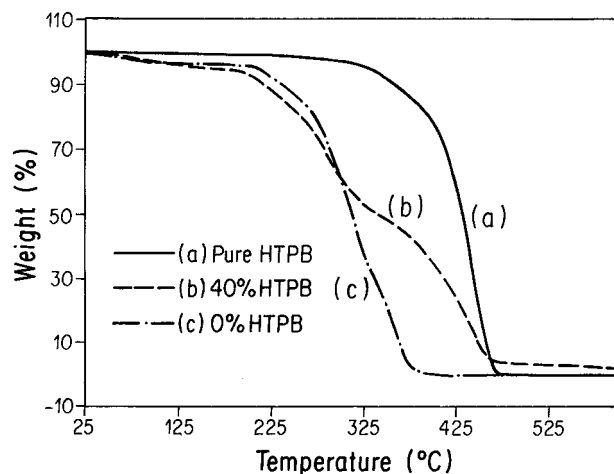
As far as the NCO/OH ratio is concerned, the lower ratio (1.5), in which the hydrophilic urethane and urea groups' contents were smaller, led to the formation of larger particles. The highest

**Table II** Average Particle Size of Aqueous-dispersion Polyurethanes

| % PBLH <sup>a</sup> | PPG ( $\bar{M}_V$ ) = 2490 |              | PPG ( $\bar{M}_V$ ) = 1220 |              |
|---------------------|----------------------------|--------------|----------------------------|--------------|
|                     | NCO/OH = 1.5               | NCO/OH = 3.0 | NCO/OH = 1.5               | NCO/OH = 3.0 |
| 0                   | 0.65                       | 0.22         | 0.47                       | 0.70         |
| 5                   | 3.80                       | 0.55         | —                          | —            |
| 10                  | 3.52                       | 0.55         | 0.70                       | 0.85         |
| 30                  | 4.02                       | 2.35         | —                          | —            |
| 50                  | 82.46                      | 12.57        | 9.80                       | —            |

% DMPA = 5% (w/w) in relation to the total mass of the prepolymer; (—) not determined.

<sup>a</sup> Percent (w/w) in relation to the total mass of the prepolymer.



**Figure 4** Thermogravimetric curves obtained for (a) pure HTPB; cast films from polyurethane aqueous dispersions synthesized with PPG ( $\bar{M}_v = 2490$ ), 5% DMPA (w/w), and NCO/OH = 3.0 and (b) with 40% HTPB (w/w) and (c) without HTPB.

NCO/OH ratio (3.0) favored smaller particle formation. Although higher amounts of urethane and urea groups could increase chain stiffness and, consequently, hinder particle formation, that was not observed, and in this case, the higher hydrophilic character of the urethane and urea groups was a stronger factor in the particle formation than was the chain stiffness.

#### Film-formation Characteristics

Films with a thickness in a range varying from 0.3 to 0.8 mm were obtained. The insertion of HTPB into the polyurethane chain led to the formation of yellowish films, due to thermooxidative processes.<sup>4</sup> The dispersions synthesized with a NCO/OH ratio = 1.5, with a lower content of urethane and urea groups, formed transparent and flexible films. In the absence of HTPB, a tacky surface was formed, but by increasing the HTPB content, the tackiness gradually disappeared. Waterborne polyurethane synthesized with a NCO/OH ratio = 3.0 formed rigid films without tack. The increase of HTPB incorporation into the polyurethane chain resulted in a gradual increase of the chain stiffness, and at 30% (w/w) content, the film became brittle and wrinkled.

#### Thermogravimetric Analysis (TGA)

TGA curves are presented in Figure 4, which shows the curve profile of pure HTPB and polyurethane samples synthesized with and without

HTPB, PPG ( $\bar{M}_v = 2490$ ); NCO/OH = 3.0 and 5% DMPA (w/w). The pure oligobutadiene and the polyurethane sample synthesized without it showed only one step of degradation, but a two-step degradation profile appeared<sup>9</sup> when HTPB was inserted into the polyurethane chain. Polyurethane curves showed the start of degradation at the same temperature: 211°C. However, in observing the curve profile, it can be noted that HTPB improved the thermal stability, considering the whole degradation process. The first-step degradation, between 211 and 355°C, corresponds to urea and urethane bond breaking and the second step, in the range from 355 to 475°C, is related to HTPB decomposition.<sup>9</sup>

#### Mechanical Evaluation

Table III shows the values of some mechanical properties obtained for aqueous-dispersion polyurethane-cast films. The increasing HTPB content provoked an increase in the elastic modulus and tensile strength values and a decrease in elongation at break. The results show that the insertion of HTPB in the chains improved the resistance of polyurethane chains by diminishing the elasticity of the material. The resistance was also increased by a higher content of urethane

**Table III** Tensile Properties of Polyurethane Cast Films

| Reaction NCO/<br>OH/% PBLH | Mechanical Properties |           |                |
|----------------------------|-----------------------|-----------|----------------|
|                            | $\epsilon$ (%)        | $E$ (MPa) | $\sigma$ (MPa) |
| PPG ( $\bar{M}_v = 2490$ ) |                       |           |                |
| 1.5/0                      | 1461.0                | 0.74      | 0.40           |
| 1.5/15                     | 978.6                 | 1.39      | 7.42           |
| 1.5/50                     | 509.1                 | 10.25     | 10.07          |
| 3.0/0                      | 493.0                 | 67.69     | 22.60          |
| 3.0/10                     | 471.1                 | 141.80    | 23.49          |
| PPG ( $\bar{M}_v = 1220$ ) |                       |           |                |
| 1.5/0                      | 955.3                 | 1.95      | 3.05           |
| 1.5/10                     | 290.7                 | 5.87      | 17.08          |
| 1.5/50                     | 451.9                 | 18.30     | 14.81          |
| 3.0/0                      | 349.5                 | 427.70    | 30.97          |
| 3.0/10                     | 247.6                 | 411.15    | 30.27          |

DMPA 5% (w/w) in relation to the total mass of the prepolymer; % PBLH in relation to the total mass of the prepolymer;  $\epsilon$ , elongation at break;  $E$ , elastic modulus;  $\sigma$ , tensile strength.

**Table IV Tensile-strength Values Obtained from Adhesion Tests of Polyurethane Aqueous Dispersions**

| NCO/OH//% PBLH | Tensile Strength (MPa) |
|----------------|------------------------|
| 1.5//5         | 4.5                    |
| 1.5//10        | 4.5                    |
| 1.5//15        | 5.0                    |
| 1.5//20        | 5.0                    |
| 1.5//30        | 5.0                    |
| 1.5//50        | 5.5                    |
| 3.0//20        | 4.8                    |
| 3.0//30        | 5.8                    |
| 3.0//40        | 6.0                    |

and urea linkages, due to the increase in the formation of hydrogen bonds. As expected, an increase in the PPG molecular weight (increase in the length of the soft segment) provoked an increase in the elongation-at-break values and, consequently, in the elasticity of the films, diminishing the values of the tensile strength and modulus.

#### Adhesive Properties of Coatings in Wood

Table IV shows the tensile strength values obtained for the coatings applied on wood. The coatings were formed from aqueous dispersions synthesized with PPG ( $\bar{M}_v = 2490$ ) and 5% DMPA (w/w).

The adhesion between coating and substrate is considered satisfactory when the disruption of the system occurs due to cohesive failure of the substrate,<sup>15,16</sup> which occurred in all tests performed in this work. In spite of the low sensibility of the test, which has only a comparative value, a tendency to an increase in the tensile strength by increasing the HTPB content in the polyurethane chain can be observed, showing an improvement in the adhesiveness. The presence of HTPB seems to favor the adhesion of the coating on a wood surface.

#### CONCLUSIONS

We developed a method of synthesis of HTPB-based polyurethanes in the complete absence of a solvent. The dispersions were stable for over 1 month. The increase in HTPB content increased the apparent viscosity of the dispersions, the average particle size, the thermal stability, the me-

chanical resistance of cast films, and the adhesiveness of the coatings on wood surface.

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), CNPq/PADCT, PRONEX, Dow Química, Petroflex, and Centro de Pesquisas da Eletrobrás (CEPEL).

#### REFERENCES

- Hoffman, J. *Chem Mark Rep* 1997, 252, 18, FR12, p. 510.
- Mennicken, G.; Wiczorrek, W. *Polyurethane Handbook*; Hanser: Munich, 1985.
- Tirpak, R. E.; Markusch, P. H. *J Coat Technol* 1986, 58, 738, 49.
- Coutinho, F. M. B.; Delpech, M. C.; Alves, L. S., submitted for publication in *Polim Cien Tecnol* 2000, 10(1), 40.
- Coutinho, F. M. B.; Delpech, M. C.; Moura, P. M. Q.; Mello, S. D. S. *Polym Bull* 1996, 37, 1.
- Coutinho, F. M. B.; Delpech, M. C. *Polym Test* 1996, 15, 103.
- Scharpman, F.; Couvercelle, J. P.; Bunel, C. *Polymer* 1998, 39, 965.
- Haska, S. B.; Bayramli, E.; Pekel, F.; Özkar, S. *J Appl Polym Sci* 1997, 64, 2347.
- Huang, S.-L.; Lai, J.-Y. *J Appl Polym Sci* 1995, 58, 1913.
- Zawadzki, S. F.; Akcelrud, L. *Polym Int* 1997, 42, 422.
- Chen, T. K.; Hwung, C. J.; Hou, C. C. *Polym Eng Sci* 1992, 32, 115.
- Frisch, K. C.; Xiao, H. X.; Suthar, B. EP 0 807 647 A1, 1997.
- ASTM D 1638-74, 1979.
- Book of American Society for Testing and Materials Standards, ASTM D 4274-88, 1992.
- British Standard Method of Test for Paints—BSI, ISO 4624-1978, 1979.
- Book of American Society for Testing and Materials Standards, ASTM D 4541-93, 1994.
- Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5<sup>th</sup> ed.; Wiley: Singapore, 1991.
- Alves, L. S. Master Thesis, Universidade Federal do Rio de Janeiro, Brazil, 1999.
- Delpech, M. C. Doctorate Thesis, Universidade Federal do Rio de Janeiro, Brazil, 1996.
- Kandil, S. H.; El-Kholy, A.; El-Shirbiny, M.; El-Sheikh, Z. *Polym Degrad Stab* 1988, 22, 349.
- Colthup, N. B.; Daly, L. H.; Wiberly, S. E. *Introduction to Infrared and Raman Spectroscopy*, 2<sup>nd</sup> ed.; Academic: New York, 1975.
- Nakayama, K.; Ino, T.; Matsubara, I. *J Macromol Sci Chem A* 1969, 3, 1005.