

# FTIR, <sup>1</sup>H-NMR Spectra, and Thermal Characterization of Water-Based Polyurethane/Acrylic Hybrids

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**ABSTRACT:** Polyurethane (PU) polymer was synthesized following a prepolymer mixing process, by polyaddition of isophorone diisocyanate (IPDI), poly(propylene glycol) (PPG), 2-hydroxyethyl methacrylate (HEMA), and 2,2-bis(hydroxymethyl)propionic acid (DMPA). The PU anionomer having 2-ethoxymethacrylate terminal groups was dispersed in water by prior neutralization of carboxylic acid groups of DMPA with triethylamine (TEA), chain extended with hydrazine (H2N-NH2) in water and a dispersion polymerization with methyl methacrylate/*n*-butyl acrylate/acrylic acid mixture was performed. The above polymerization reactions lead to the formation of PU/acrylic hybrids having a chemical bond between PU and acrylic

moieties. Acrylic content was varied from 0 to 50 wt % and samples were purified to eliminate oligomers and impurities before characterization. The FTIR and <sup>1</sup>H-NMR spectra of these purified hybrid samples were obtained and bands and peaks assignments were discussed. Thermal properties (DSC and TGA) were also discussed. Breaking hydrogen bonds is the main reason for changes in properties with increasing acrylic content. Particle size data of dispersions is also presented and discussed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1207–1214, 2008

**Key words:** polyurethane/acrylic hybrids; FTIR; <sup>1</sup>H-NMR spectrum; thermal properties

## INTRODUCTION

Polyurethane (PU)-based coatings are one of the special systems with solvent and chemical resistance offering at the same time good weather stability. Films prepared from these systems have very good mechanical properties and by selecting the hard and soft composition the appropriate balance between hardness and flexibility can be achieved. The primary and secondary structures of the PU chains are responsible for these characteristic properties because the urethane groups can form hydrogen bonds forming therefore a stable physical network. It is well known that in the paint and coating market solvent-borne two components PU coatings have

been used for many years<sup>1</sup> but the requirements of products with reduced solvent content (low VOC's) have forced the development of new environmentally friendly products and technologies. Among other systems water-dispersible or water-soluble PU have been examined from both scientific and industrial points of view because of the excellent chemical and physical properties. A complete review of water-based PU including its structure and properties was published by Hirose et al.<sup>2</sup> Nowadays water-borne PU synthesis is a very common technology in the coating industry, but these products are in general more expensive than other products. In some applications there are cost restrictions and a combination with cheaper materials like acrylic dispersion is a common practice, combining the excellent mechanical and chemical properties of the PU resin with the low price of the acrylic component. For this reason, several articles were published discussing properties and applications of systems combining PU and acrylics. Recently Wang et al.<sup>3</sup> reported the properties of PU/acrylic latices made from miniemulsion polymerization and compared to blends. However no HEMA was used to bind both polymer chains and a microscopic mixture is formed. Brown et al.<sup>4</sup> also reported the mechanical and thermal properties of a system prepared using a commercial preformed PU and polymerizing acrylics

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obtaining therefore a microscopic mixture and compare to blends of both preformed polymers. An important point is that most of the characterization work on PU and hybrids materials has been made on normal samples, i.e., without purification, which include solvent, residual monomer, initiator, and their decomposition products.

In a previous article,<sup>5</sup> we reported the synthesis of PU/acrylic dispersions by a prepolymer process having a variable amount of acrylic component to prepare glossy topcoat paint formulations. Interesting changes in properties were found when varying acrylic content especially for a 30 wt % of acrylic, so to understand those changes a detailed study of those hybrids seemed to be a mandatory work. In this article, the FTIR, <sup>1</sup>H-NMR spectra, and thermal properties (DSC, TGA) of those PU/acrylic hybrid dispersions as well as the PU prepolymer and the equivalent pure acrylic latex are discussed after purification of dispersions. Particle size and density data of cleaned samples are also included.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BuA) were of technical grade donated by ADELFA S.A. and distilled before using. Methacrylic acid (MAA, Fluka), isophorone diisocyanate (IPDI, Aldrich), dimethylol propionic acid (DMPA, Aldrich), 2-hydroxy ethylmethacrylate (HEMA, Aldrich), *N*-methyl-2-pyrrolidone (NMP, Fluka), triethylamine (TEA), potassium persulfate (KPS, Ane-dra), hydrazine monohydrate (HZM, Aldrich), sodium dodecyl sulfate (SDS, Riedel-de Haën), and dibutyltin dilaurate (DBTDL, Aldrich) were of analytical grade. Polypropylene glycol 1000 (PPG1000, Voranol 2110) was kindly donated by RESIKEM and TEA by ADELFA S.A. MAA, IPDI, HEMA, KPS, HZM, SDS, and DBTDL were used as received. PPG was dried and degassed at 80°C at 1–2 mmHg before use. NMP and TEA were also dried before use. DMPA was dried at 100°C for 2 h in an oven. A typical base formulation is given in Table I and the synthesis of PU/acrylic hybrids is illustrated in Scheme 1.

### Prepolymer synthesis

A 1000 mL six-neck separable flask with a mechanical stirrer, thermocouple, condenser, sampling tube, inlet system for dry N<sub>2</sub>, and pump feed inlet was used as a reactor. PPG1000, DMPA, NMP were charged into the dried flask. While stirring, the mixture was heated to 98°C and homogenized and bubbled dried oxygen for ~1/2 h, followed by low-

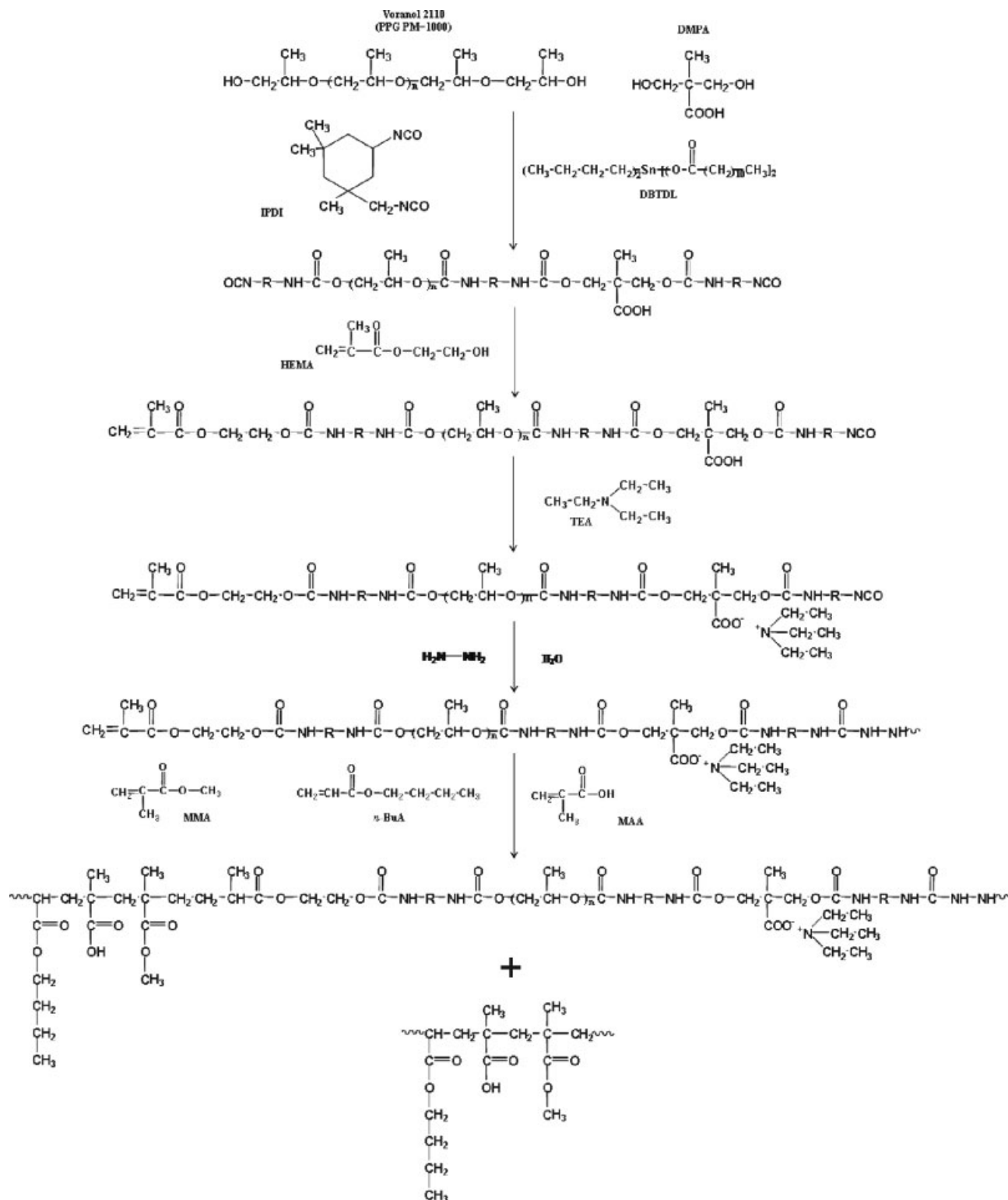
**TABLE I**  
Recipe for the Synthesis of Polyurethane/Acrylic Dispersions

Component	Weight (g)	Mole
Prepolymer reaction		
Isophorone diisocyanate	130.00	0.58
2-hydroxy ethylmethacrylate	15.22	0.18
Polypropylene glycol 1000	177.22	0.18
Dimethylol propionic acid	17.81	0.13
Dibutyl tin dilaurate	0.51	–
<i>N</i> -methyl-2-pyrrolidone	35.62	–
Neutralization reaction		
Triethylamine	13.45	0.13
Dispersion and chain extension reaction		
Neutralized prepolymer	390.0	
Water	593.0	
Hydrazine monohydrate	5.41	
Batch emulsion polymerization		
Dispersion	700.0	
Acrylic monomers mixture (MMA/ <i>n</i> -BuA/MAA)	Variable	
Water	Variable	
Potassium persulfate	1.5 wt % on monomer base	

ering the temperature to 90°C and addition of a mixture of IPDI and DBTDL catalyst. The mixture was allowed to continue at this temperature for ~ 2 h. The prepolymer solution was cooled to 45°C and HEMA was added slowly and allowed to react for ~ 90 min and the temperature was raised to 60°C and kept constant for 90 min. until the isocyanate (NCO) content reached the desired value. This low temperature and addition of HEMA strategy was performed to have mono-acrylated diisocyanates and a small amount of diacrylated diisocyanate.<sup>6,7</sup> The free isocyanate content was determined using the conventional *n*-dibutylamine back-titration method.<sup>8</sup> The same technique was also applied to raw materials. Upon obtaining the theoretical NCO value (ca. 4.7%) the mixture was cooled to 55°C and TEA was fed in slowly over 50 min. After neutralization the temperature was lowered to room temperature.

### Dispersion and chain extension

An aqueous dispersion of PU was obtained by adding the PU prepolymer to water at 30°C. The dispersion was performed at about 300 rpm in an ordinary glass reactor for about 15 min. After dispersion the appropriate amount of HZM was added to perform the chain extension reaction at 30°C for 45 min. The resulting PU dispersion with solid content of about 40 wt % was divided into several parts for subsequent reaction.



**Scheme 1** The synthesis of PU/acrylic hybrid dispersions.

### Emulsion polymerization

The emulsion polymerizations of PU-acrylic mixtures were performed in batch mode using a glass reactor (1000 mL) with a water jacket for temperature con-

trol. To about 700 g of PU dispersion, prepared as described in point 2.3, different amounts of an acrylic mixture of MMA/*n*-BuA (80/20 wt %) and then MAA (1 wt % on acrylic base) were added. The mixture was degassed with nitrogen and then dis-

persion polymerized at 80°C using KPS (0.15% on monomer base) as initiator. The resulting product was a stable dispersion with a solid content of ~ 30 wt %. Because of the surfactant-free polymerization technique used in the present study the maximum amount of acrylic incorporated was 50 wt %. Attempt to include higher concentration leads to coagulation.

The pure acrylic dispersion was prepared by emulsion polymerization of MMA/*n*-BuA/MAA mixture in the same relation as in the PU-acrylic hybrids using in this case 3% of SDS as emulsifier on monomer base.

### Polymer dispersion cleaning

Dispersions were cleaned before analyzing using dialysis membranes Spectra/Por (Biotech made from polyvinylidene difluoride (PVDF) 15 mm diameter and molecular weight cut-off (MWCO) 1000,000 Da, to eliminate residual monomers, initiator, and water soluble compounds, mainly NMP as it interferes in the FTIR and NMR spectra.

### Particle size of dispersions

Particle size was determined by light scattering (LS) with a Malvern 4700 instrument. This technique gives an intensity weighted average particle size,  $d_{\text{intavg}} = \frac{\sum (n_i I_i d_i)}{\sum (n_i I_i)}$ , where  $I_i$  is the intensity of light scattered from  $n_i$  particles of diameter  $d_i$  being close to the *z*-average particle size

$$d_z = \frac{\sum (n_i d_i^7)}{\sum (n_i d_i^6)}$$

### Polymer characterization

#### Density

Density was determined using a Micromeritics Accu-Pyc 1330 He-pycnometer. Samples were dried overnight at 60°C and several measurements were taken until constant reading.

#### FTIR spectroscopy

The FTIR spectra of PU prepolymer and PU-acrylate hybrids were measured in the transmission mode using a FTIR Spectrum One spectrometer. PU and PU/Ac films were prepared by spontaneous evaporation at room temperature of a diluted solution placed on a CaF<sub>2</sub> window. The number of scan per experiment was 64.

#### <sup>1</sup>H-NMR spectra

The <sup>1</sup>H-NMR spectra were recorded using a 300 MHz Bruker AC-P spectrometer, in CDCl<sub>3</sub> or deuterated DMSO at room temperature and 128 scans.

#### Thermal properties

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7. This instrument operates from room temperature but using an intracooler accessory the lower operating temperature was extended to -30°C. However the useful range starts at about -20°C, so scans were performed from this lower value to +100°C, at a heating rate of 20°C min<sup>-1</sup>. Samples were first heated at 100°C at 40°C min<sup>-1</sup> and cool down at 50°C min<sup>-1</sup> before scanning to erase thermal history.

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA-7 in air from 30 to 800°C at a heating rate of 20°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Dispersions properties

Table I shows the composition and particle size of systems prepared in this work. It can be seen that the particle size of all systems is similar falling between 210 and 250 nm and as expected the hybrids have bigger particle sizes than the pure PU or acrylic dispersions, because of the polymerization method. According to Hirose et al.<sup>2,9</sup> this particular method where both components have carboxylic functionality, gives core-shell particle structure and the PU component occupies the shell region of the particle. The final size should be attributed to a balance between the relative amount of PU dispersion acting as colloidal stabilizer and the acrylic monomer. In this work a medium value of about 230 ± 20 nm is found.

### Polymer characterization

#### Density

The incorporation of 10 wt % of acrylic component increases the polymer density as compared to the pure PU (Table II). However, higher incorporation of acrylic decreases the density reaching a minimum value for 30 wt %. Additional acrylic component increases the density of hybrids. The presence of the acrylic component modifies the PU chain interactions and for 30 wt % the interaction should be maximum, leading therefore to a less compact structure. The particular behavior of the hybrid system at this composition is observed in other properties (see later).

**TABLE II**  
Summary of Composition (wt %), Particle Diameter and Density Data for the Polyurethane/Acrylic Hybrids Systems Studied in this Work

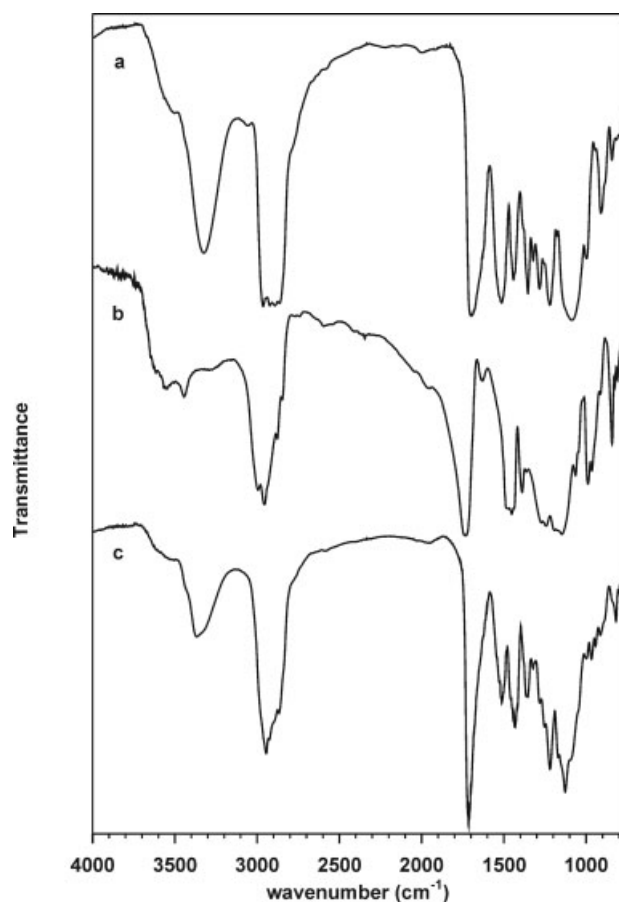
Dispersion type	Acrylic content (wt %)	Particle diameter <sup>a</sup> (nm)	Density (g cm <sup>-3</sup> ) <sup>b</sup>
PU dispersion	–	131	1.100
PU/Ac 90/10	10	250	1.165
PU/Ac 80/20	20	213	1.130
PU/Ac 70/30	30	256	1.128
PU/Ac 60/40	40	220	1.141
PU/Ac 50/50	50	232	1.163
Acrylic dispersion	–	127	1.187

<sup>a</sup> Determined from DLS studies.

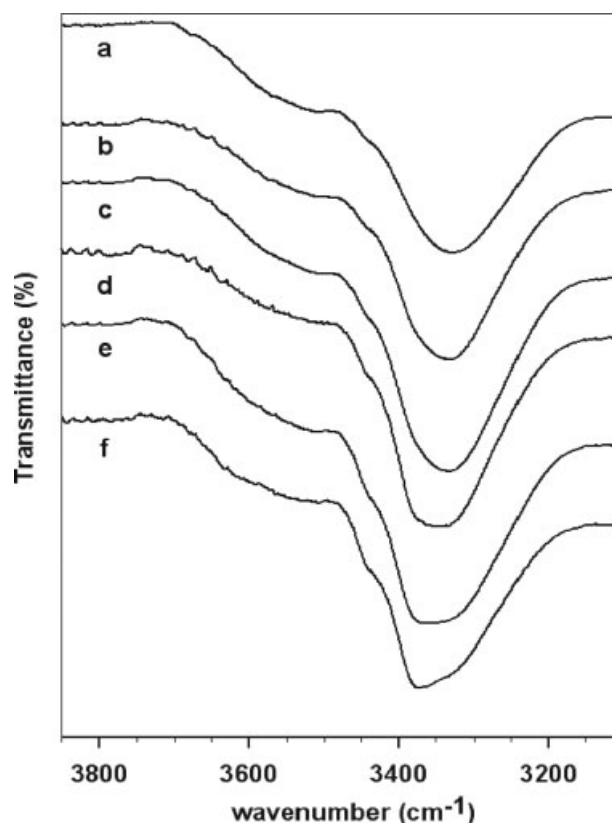
<sup>b</sup> Measured by helium pycnometry.

### FTIR analysis

PU properties depend on the segmented structure, on the extent of the phase mixing, as well as on hydrogen bonds between *N*–H and carbonyl or ether oxygen atoms. The urethane and PPG interactions may be interrupted by putting a polymer,



**Figure 1** (a) FTIR survey spectra of pure PU, (b) pure acrylic polymer, (c) and hybrid system with 50 wt % of acrylic component.

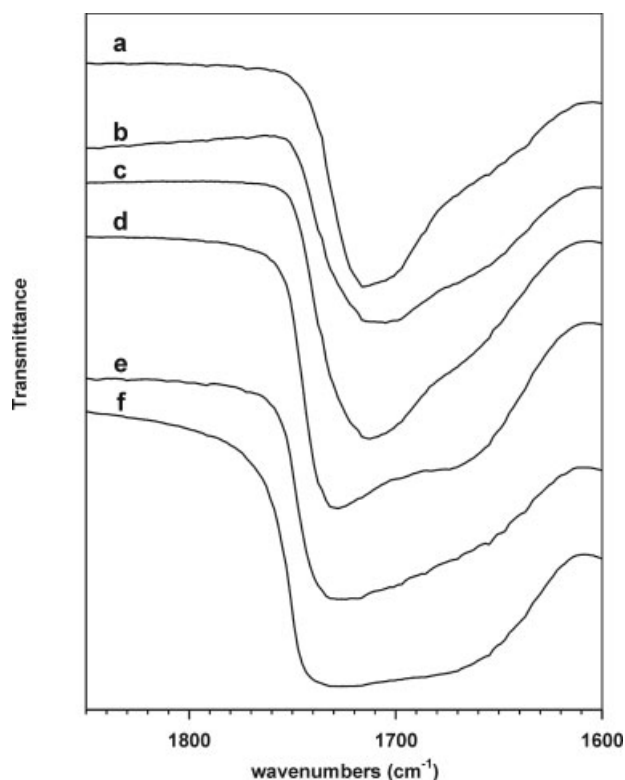


**Figure 2** (a) FTIR spectra in the *N*–H stretching region of pure PU, (b) 10 wt % of acrylic, (c) 20 wt % of acrylic, (d) 30 wt % of acrylic, (e) 40 wt % of acrylic, and (f) 50 wt % of acrylic.

which may sterically hinder the interactions. FTIR spectroscopy is a powerful tool for studying any changes in the H-bond interactions. In the next section, observed changes in the infrared spectra are discussed taking into account this property.

Figure 1 shows the FTIR survey spectra of base PU, acrylic polymer and of the hybrid composite containing 50 wt % of acrylic component. The FTIR spectrum of pure PU shows typical bands corresponding to the hard segments: *N*–H (1532, 3330 cm<sup>-1</sup>), C=O (1714 cm<sup>-1</sup>), C–O–C (1242 cm<sup>-1</sup>) groups and to soft segments C–H (1374, 1460, 2870 to 2970 cm<sup>-1</sup>) groups. The spectrum of the hybrid compound shows additional bands mainly in the 3500–3350 cm<sup>-1</sup> and in the 1200–600 cm<sup>-1</sup> regions. Some features are observed also in the C=O stretching region.

Figure 2 shows the spectra of NH and OH stretching region of PU and hybrids systems with increasing content of acrylics. A shift to higher wavenumbers in the NH stretching bands is observed. The presence of acrylic component changes the hydrogen bonding interactions. Low acrylic content (10 and 20 wt %) does not seem to be enough to modify this interaction, but acrylic content of 30 wt % and



**Figure 3** (a) FTIR spectra in the carbonyl stretching region of pure PU, (b) 10 wt % of acrylic, (c) 20 wt % of acrylic, (d) 30 wt % of acrylic, (e) 40 wt % of acrylic, and (f) 50 wt % of acrylic.

higher shifts the maximum NH absorption to higher frequency. Figure 2(a) shows that the spectrum of pure PU exhibits a strong absorption at  $3325\text{ cm}^{-1}$  arising from the hydrogen bonding between  $N-H$  and carbonyl groups, whereas the free  $N-H$  stretching vibration appears as a shoulder at about  $3445\text{ cm}^{-1}$ . The shoulder at about  $3515\text{ cm}^{-1}$  is assigned to the OH stretching of the DMPA component. A close examination indicates the presence of another component at  $\sim 3250\text{ cm}^{-1}$  corresponding to the  $NH-O-$  hydrogen bonding involving the oxygen atom of the polyether of the PU.<sup>10</sup>

The broad shoulder in the range  $3700-3500\text{ cm}^{-1}$  and centered at about  $3600\text{ cm}^{-1}$  increases in intensity with higher acrylic content, due to the increasing amount of carboxylic groups. Also, when increasing the acrylic content a shoulder at  $3440\text{ cm}^{-1}$  is observed and assigned to the OH groups from the acrylic component. In the  $C=O$  stretching region (see Fig. 3) a progressive change in the absorption pattern is observed when the acrylic content increases up to 20 wt %. The band at about  $1710\text{ cm}^{-1}$  is attributed to H-bonded  $C=O$  in the PU and the band at  $\sim 1728\text{ cm}^{-1}$  to carbonyl  $C=O$  stretching vibrations of the acrylic MMA, *n*-BA, and MAA ester groups. Interesting enough are the sharp changes from 20 to 30 wt %. An increasing intensity because

of the increasing amount of carboxylic groups is also observed in the  $1680-1650\text{ cm}^{-1}$  region, this is attributed to associate and crystalline  $C=O$  group of acrylic component.<sup>11</sup>

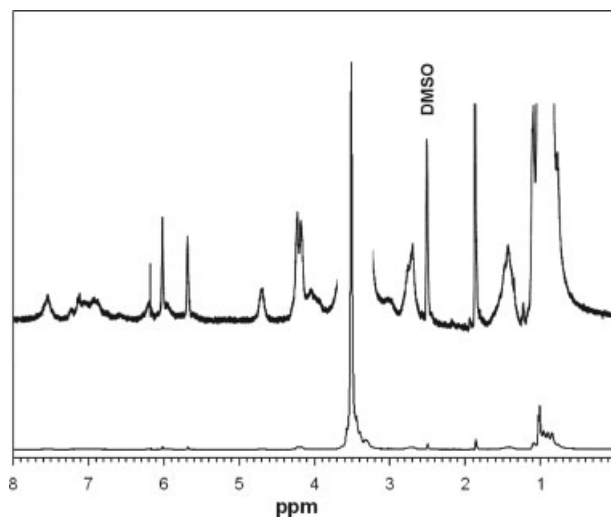
#### NMR analysis

*NMR spectra of PU.* The  $^1\text{H-NMR}$  spectrum of pure PU is shown in Figure 4. The H signal from the urethane group is not always observed but in this case a weak and broad band at  $\sim 6.9\text{ ppm}$  is observed and therefore assigned to this peak. Additional peaks are observed around  $7.5\text{ ppm}$  which are also assigned to the urethane groups.<sup>12</sup>

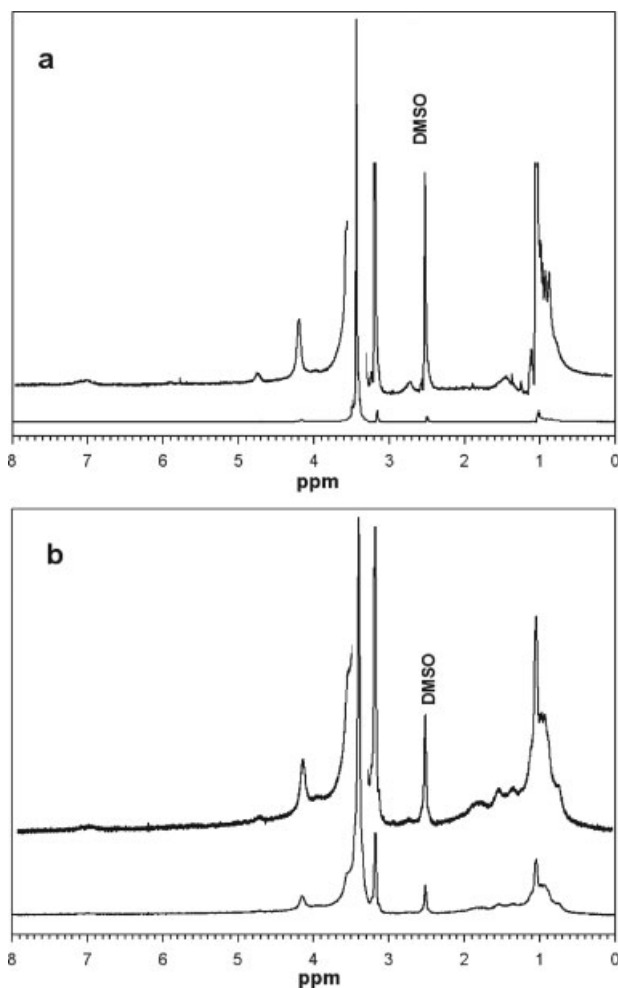
Using group contribution to chemical shift the signal at  $4.7\text{ ppm}$  is assigned to the methine proton ( $-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-$ ) of PPG close to the urethane group. In the same way it was found that the methine hydrogen of PPG far from the urethane group has a chemical shift at about  $3.3\text{ ppm}$ , and the methylene hydrogen at about  $3.6\text{ ppm}$ . The strong multiplet signal at about  $3.50\text{ ppm}$  is assigned to these protons.

Protons from the HEMA moiety are assigned to the peak at  $4.22\text{ ppm}$  due to one of the methylene hydrogen of ethyl group. The other methylene group is expected at about  $3.5\text{ ppm}$  overlapping with the signal of protons from PPG, the signal at  $1.90$  of methyl group on the double bond and the geminal H of the double bond at  $5.70$  and  $6.02\text{ ppm}$  (all these peaks disappear in the NMR spectrum of hybrids). Methylene group peaks of DMPA are expected at about  $4.2$  and  $3.5\text{ ppm}$ . The peak very close to  $4.17\text{ ppm}$  and several other peaks at about  $3.30-3.45\text{ ppm}$  are observed and assigned to these protons.

*NMR spectrum of acrylic component.* The  $^1\text{H-NMR}$  spectrum (not shown here) of acrylic polymer

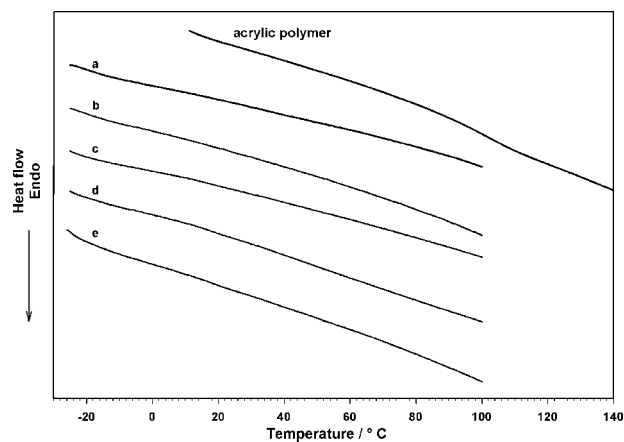


**Figure 4**  $^1\text{H-NMR}$  spectrum of pure PU.



**Figure 5**  $^1\text{H-NMR}$  spectra of PU/acrylic hybrid system containing (a) 10 wt % of acrylic and (b) 50 wt % of acrylic.

consisting of MMA, *n*-BuA, and MAA (48.25/48.75/3.00 wt %) is similar to the reported for MMA/*n*-BuA (70/30 wt %).<sup>13</sup> The main peaks are those for  $-\text{O}-\text{CH}_3$  of MMA at 3.59–3.64 ppm and for  $-\text{O}-\text{CH}_2-\text{CH}_2-$  (butyl group) of *n*-BuA at 4 ppm. *NMR spectrum of hybrids systems.* Figure 5 shows the  $^1\text{H-NMR}$  spectra of PU/Acrylic hybrid (90/10) and (50/50). Note the simplicity of spectra despite the complex composition of systems. Peaks from acrylic components are observed. For the 10 wt % acrylic content the signal from the *n*-butyl group is observed at 4.15 ppm. This peak increases in intensity and shifts slightly to lower chemical shift (about 4.1 ppm) when increasing acrylic content. This indicates that during polymerization the presence of the other component modifies the interactions. The peak attributed to the methyl group of MMA is expected about 3.5–3.6 ppm overlapping with the signal of protons from PPG. According to Gottlieb et al.<sup>14</sup> the signal observed at 3.15 ppm is a residual HOD peak from the DMSO NMR solvent.



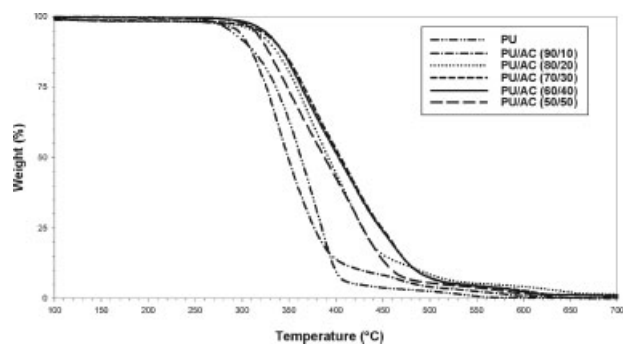
**Figure 6** DSC curves for pure acrylic and hybrids systems, (a) 10 wt % of acrylic, (b) 20 wt % of acrylic, (c) 30 wt % of acrylic, (d) 40 wt % of acrylic, and (e) 50 wt.% of acrylic.

#### Thermal analysis

*Differential scanning calorimetry.* DSC curves for the pure acrylic and the five hybrids samples are shown in Figure 6. Acrylic glass transition is observed at about 84°C as expected for the composition. In the contrast for the hybrid systems the DSC traces are almost featureless and no clear  $T_g$  is observed for all acrylic content.

The soft-segment glass transition corresponding to polypropylene glycol (PPG) of  $M_n = 1000$  is approximately  $-30^\circ\text{C}$ , out of our measurement range.<sup>15</sup> According to Hourston et al.<sup>16</sup> the  $T_g$  of the hard segment is expected at about 80°C, however the detection using DSC is not always possible.<sup>17</sup> One reason for this lack of signal is the low sensitivity of DSC analysis for detecting second order transitions; more sensitivity methods like dynamic mechanical thermal analysis are required.<sup>16</sup>

Brown et al.<sup>4</sup> and Kukanja et al.<sup>18</sup> have also reported the lack of a clear transition in PU/acrylic systems. In our case the lack of a clear  $T_g$  in the studied range of temperature suggests a good



**Figure 7** TGA decomposition curves of pure PU and hybrids systems.

**TABLE III**  
**Thermal Stability Indexes (IDT,  $T_5$ , and  $T_{50}$ ) for the Polyurethane/Acrylic Systems**

Polymer type	IDT (°C) <sup>a</sup>	$T_5$ (°C)	$T_{50}$ (°C)
PU	198	288	363
PU/Ac 90/10	207	296	349
PU/Ac 80/20	235	312	393
PU/Ac 70/30	235	319	406
PU/Ac 60/40	215	324	403
PU/Ac 50/50	215	314	388
Acrylic	177	292	389

<sup>a</sup> Initial decomposition temperature.

compatibility between both types of polymers and therefore no phase separation. Work using small angle X-ray scattering (SAXS) indicates that increasing acrylic content up to 50 wt % the typical scattering peak of PU disappeared and a more homogeneous system is obtained.<sup>15</sup>

**Thermogravimetric analysis.** The decomposition curves of pure acrylic, PU, and hybrids are shown in Figure 7. The thermal stability can be analyzed by using different values from those curves. A convenient way of expressing thermal stability is using the IDT and the thermal indexes  $T_5$  and  $T_{50}$ , i.e., the initial decomposition temperature, and the temperatures corresponding to a 5% and to 50% of weight loss. Thus, with the initial decomposition temperature and the thermal indexes as the criterion of thermal stability, it can be inferred that the thermal stability of hybrids increases with the acrylic content up to 30 wt % and then decreases (see Table III). Interesting enough is that the thermal indexes for this particular composition are higher than the pure acrylic polymer, indicating a synergetic effect. This behavior can be attributed to the presence of stronger interactions in the pure PU, between the PU and the acrylic chains through H-bonds.<sup>19</sup> Additionally and according to Liu et al.<sup>20</sup> the presence of a relatively easy thermal degradation segment in the PU matrix produces char residuals and a resistant effect toward the polymers. In our case the acrylic decomposes more rapidly than the PU matrix (IDT = 177°C). This increased stability indicates that hybrids can be used as a better fire-retardant coating than pure PU.

## CONCLUSIONS

Different PU/acrylic hybrids with variable amount of acrylic component have been prepared and carefully characterized. The results of the different studies performed on these systems indicate that a good compatibility between both components is achieved

by using the hybrid synthetic route. The hybrid with a composition of about 30–40 wt % of acrylics, shows interesting properties like lower density and better thermal stability and it will be the subject of further studies. PU coatings are known for the capacity of forming films with high gloss and the hybrids systems prepared in this work have been used for glossy topcoat paint formulation.<sup>5</sup> It was found that it is possible to incorporate as much as 30 wt % without losing initial gloss properties leading to economical products.

Despite the intrinsic incompatibility of both types of polymers no evidence of phase separation was found in the range of concentration used in this study. To determine the maximum amount of acrylic component in a PU matrix without phase segregation, new PU/acrylic systems have been prepared using an acrylic polymer with lower  $T_g$  to allow a full range of composition of film-forming hybrids to be prepared. Several studies including SAXS are in progress and the results will be the subject of future articles.

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