

# Synthesis and Characterization of Polyurethane Urea Acrylates: Effects of the Hard Segments Structure

Stefan Oprea

*Institute of Macromolecular Chemistry "Petru Poni," Aleea Grigore Ghica Voda, 700487 Iasi, Romania*

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**ABSTRACT:** A series of poly(ester-urethane-urea) acrylates were synthesized using poly(ethylene adipate) diol (PEA), 4,4'-diphenyl methane diisocyanate (MDI), different diamines and acrylic acid. On the basis of IR, stress-strain, thermogravimetric, and differential scanning calorimetry measurements of their cured materials, relations between their structure and physical properties were investigated systematically. The properties were compared with a polyurethane acrylate (PUA) elastomer in which the variable was the diamine modification. The mechanical analysis indicated that, when the short chain

of diamine was used, the strength and strain at break of the polymer was enhanced. The thermal stability and the glass transition of PUA increased with increased of diamine chain. The crosslinking process depresses crystallization of the soft segments and can be used to obtain protective films and finishing materials for the leather industry. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2509–2515, 2007

**Key words:** polyurethane-acrylate; diamines; structure-property relations; crosslinking; mechanical properties

## INTRODUCTION

Using polyurethane chemistry, adhesives, coatings, and encapsulants provide excellent performance properties such as toughness, flexibility, elongation, low  $T_g$ , low modulus, hydrolytic stability, etc. Because of these inherently good qualities, it made sense to use the urethane backbone and adapt it to a UV-curing "format." By putting into reaction isocyanate prepolymers with small, active OH-containing acrylated monomers (for example, hydroxyethyl acrylate, or methacrylate), it was shown that the active  $N=C=O$  group of the prepolymer was replaced by a terminal acrylate functionality.

Acrylated urethane comblike materials can potentially combine the high abrasion resistance, toughness, tear strength, and good low temperature properties of polyurethanes with the good optical properties and weatherability of the polyacrylates.

The low viscosity liquid oligomers possessed excellent processability, while the cured solid polymers had reasonable mechanical strength and good thermal stability because of their crosslinked nature.

Polymers containing acrylate or methacrylate pendant groups are candidates for radiation sensitive solid polymers since the acrylate groups may undergo crosslinking reactions under suitable conditions.<sup>1,2</sup>

The chain length, the molecular volume, and functionality can influence hard segment packing and crystallinity in the hard domains.<sup>3,4</sup> The phase separation in polyurethane urea was also dependent upon the number of methylene units within the diamine.<sup>5</sup>

The polyurethane urea with better phase separation exhibits better mechanical properties, such as higher elongation at breaking, greater toughness, and a slower rate of stress relaxation.<sup>6</sup>

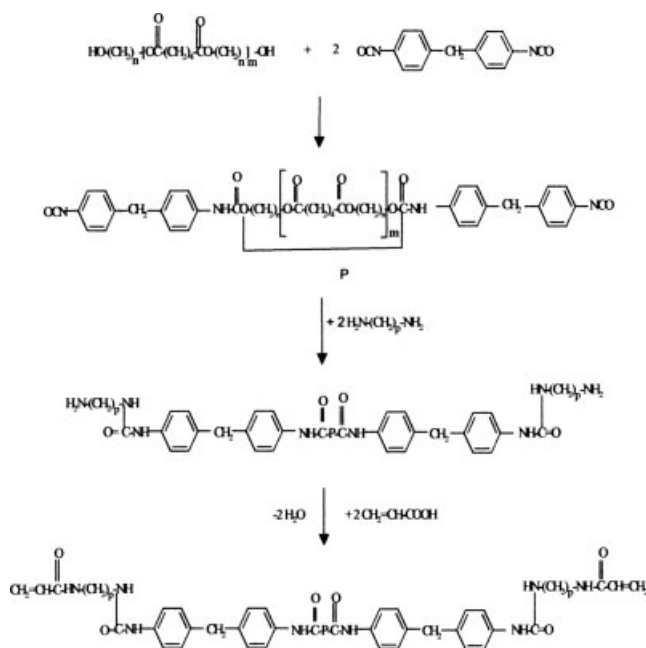
As a result of their high mechanical strength, flexibility, fatigue resistance, and biocompatible nature, polyurethanes have been proven to be potential candidates as materials for artificial organs.<sup>7,8</sup>

There is another polyurethane acrylate (PUA) formation mechanism, which produces polyurethane prepolymers with terminal isocyanate groups that further reacts with diamine to form one component type polyurethane urea prepolymers and they were end capped by acid acrylic, which forms curable urethane acrylate prepolymers.<sup>9,10</sup>

A large variety of properties depending on the frequency of the arrangement of acrylic structural units on the macromolecular chain was obtained, such as anticorrosive protective films and finishing materials for leather industry,<sup>11–13</sup> bending matter for magnetic media,<sup>14,15</sup> mounts for printing ink,<sup>16</sup> coating for optical fibers,<sup>17–19</sup> carbon fibers,<sup>20</sup> adhesives,<sup>21</sup> gas and liquid separating membranes,<sup>22</sup> etc.

Also, waterborne coating recently has been used to decrease air pollution and to improve aspects of occupational health and safety.<sup>23–27</sup>

Correspondence to: S. Oprea (stefop@icmpp.ro).



In this investigation, comblike acrylated polyester polyurethanes. These are based on polyester soft segments, 4,4'-diphenyl methane diisocyanate (MDI), diamino ethane, diamino butane, diamino hexane, and acrylic acid hard segments. These synthesis reactions obtained polyurethane-containing pendant acrylic groups. The hard segments were varied and their effects on the synthesis, structural, and tensile properties, and thermal response of these materials were investigated.

## EXPERIMENTAL

### Materials

Segmented PUAs of various hard segments were used in this study. The hard segments consist of MDI and different diamines and acrylic acid.

The samples were as follows:

- poly(ethylene adipate) diol (PEA) oligomer with molecular weight of about 2000;
- 4,4'-diphenyl methane diisocyanate (MDI), Merck, was purified by vacuum distillation;
- 1,2-diamino ethane (EA), 1,4-diamino butane (BA), 1,6-diamino hexane (HA), Merck, used without further purification;
- acrylic acid, Merck, was distilled at reduced pressure and the middle portions were stored at 0–4°C until use;
- dimethylformamide was purified and dried by vacuum distillation on MDI.

### Preparation of polyurethane urea acrylates

The polymers were synthesized in a multistep reaction as shown in Scheme 1,<sup>28</sup> where  $n = 2$  and  $p = 2, 4, 6$ ; P, saturated polyesters.

Segmented polyurethanes of soft-segment content and of various hard-segment structures were used in this study. The hard-segments consist of 4,4'-diphenyl methane diisocyanate and various diamines and acrylic acid.

The poly(ester-urethane) prepolymers were prepared in a melt using 20 g (0.01 mol) PEA and 5.5 g (0.022 mol) 4,4'-diphenyl methane diisocyanate. The diisocyanate prepolymers were synthesized in a 250-mL three-necked round-bottomed flask equipped with a mechanical stirrer incorporating a nitrogen inlet valve. Typically, 20 g (0.01 mol) of poly(ester) diol was introduced in the flask and melted in an oil bath at 120–130°C and dehydrated for 2 h at 2 mmHg. Then 5.5 g (0.022 mol) of 4,4'-diphenyl methane diisocyanate was added to the stirred poly(ester) diol and the temperature was held at 80°C for 1 h. In a 500-mL three-necked round-bottomed flask equipped with a mechanical stirrer incorporating a nitrogen inlet valve, 0.02 mol diamine was introduced in 160-mL dimethylformamide. To ensure the complete dissolution, it was added slowly, under mechanically stirred, to the prepolymer diisocyanate and the reaction mixture was stirred for another 2 h. Then 1.7 g (0.02 mol) acrylic acid was added and stirred for 30 min. The result is a product with double bonds at the ends of the macromolecular chain. The reaction was carried out in dimethylformamide at a dry substance concentration of 50%. Changing the diamine varied the chemical structure of the polyurethane acrylate material.

Films from the synthesized polymers have been obtained on glass plate by thermal treatment at 120°C for 4 h. During the removal of the solvent, the double bonds polymerize, a film of polyurethane acrylate with urea, and an amide structure being formed. Cured film samples were used for tensile testing and thermal study.

### Measurements

The infrared spectra were run on a Specord M80 Carl Zeiss Jena Spectrometer using KBr pellet technique. Films for study were vacuum dried to remove residual solvent.

Stress–strain measurements were performed on dumbbell-shaped samples cut from thin films at room temperature on a TIRAtest 2161 apparatus, Germany, equipped with a 100 N cell and an extension rate of 10 mm/min. Measurements were made at 25°C. All the values given are means of six measurements.

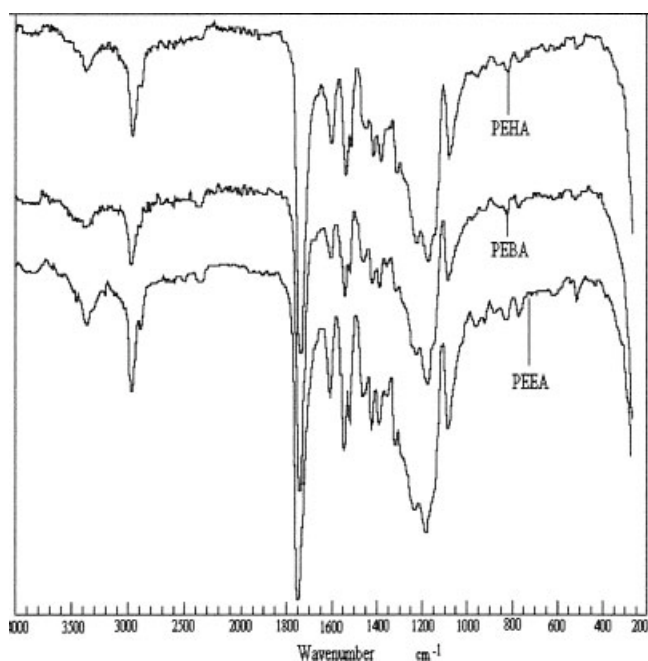


Figure 1 IR spectra of PEEA, PEBA, and PEHA.

Thermogravimetric analyses were performed on a DERIVATOGRAPH Q-1500D apparatus (Hungary) in a temperature range from 0 to 600°C. The heating rate was 12°C/min in atmospheric air and sample size was 50 mg.

The differential scanning calorimetry (DSC) measurements involved a temperature range of -100 to 250°C and a PerkinElmer 7 Series DSC, purging with N<sub>2</sub>, and chilling with liquid N<sub>2</sub>. Runs were conducted on samples of about 10 mg at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

To study the structure-property relationships of cured films, a selected number of short chain diamines and acrylic acid were used to obtain polymers with varying structure of the hard segment. The diamines were EA, BA, and HA. The corresponding poly(urethane-acrylate)s were PEEA(PUA with EA), PEBA(PUA with BA), and PEHA(PUA with HA). Among the flexible polyols, PEA of molecular weight 2000 was used.

In all the polymer models, the structural changes are fundamentally important for the IR study. Hard segment structure can be characterized by the carbonyl group of the urea linkage and NH group located entirely in the hard segment.

Participation in hydrogen bonding decreases the frequency of the NH vibration and increases its intensity, making this absorption useful in the study of

hydrogen-bond effects. The absorption at 3384 cm<sup>-1</sup> corresponds to hydrogen bonded -NH groups. The absorption bands at 2980 and 2900 cm<sup>-1</sup> in the spectra (Fig. 1) are associated with asymmetric and symmetric -CH<sub>2</sub> groups. The strong band at 1730 cm<sup>-1</sup> is assigned to the -C=O groups. The absorption of (C=O) (amide I) and (NH) and (CO-N) (amide II) appears at 1633 and 1566 cm<sup>-1</sup>, respectively. The band at 1262 cm<sup>-1</sup> corresponds to (C-N) with (NH) (amide III) of -R-NH-COO- groups.

The sharp peak shape and the frequencies for both -NH and -C=O absorptions suggested that most of the urethane groups in the polyurethane are H-bonded.

To certify the curing of acrylates, the absorbance bands of acrylate at 1635, 1410, and 810 cm<sup>-1</sup> are generally used. The characteristic C=C absorption of urethane acrylate at 1635 cm<sup>-1</sup> was used to determine the extent of polymerization in this study.

After heat treatment at 120°C for 4 h, both bands basically remained intact but the main observation was that the band at 1635 cm<sup>-1</sup>, specific to the double bond from the acrylic group, disappeared (Fig. 2). The disappearance of the double bonds pointed out that the polymer passed to a crosslinked structure.

The idea of the double-bond consumption is also sustained by the fact that, after thermal treatment, all samples become insoluble. The reactions evidencing the phenomena presented earlier may be expressed in the following equations (Scheme 2).<sup>28</sup>

The capability of the ester -C=O, in addition to urethane -C=O to bond with the urethane -NH would interfere with a regular packing.

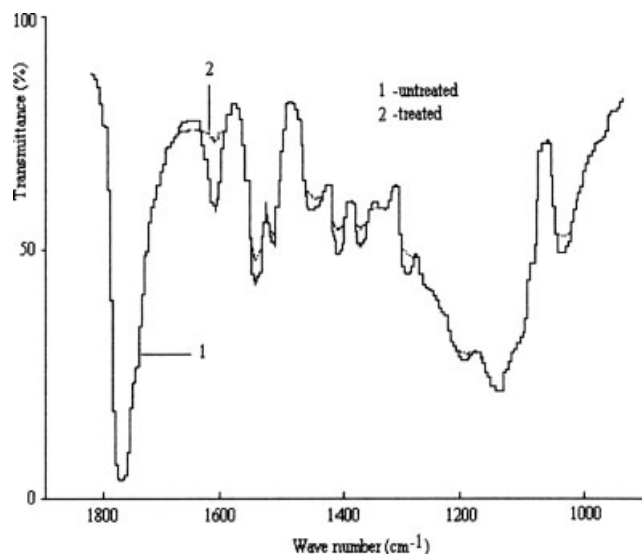
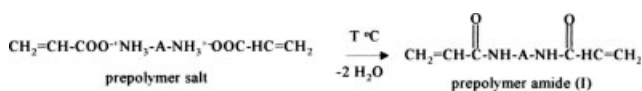


Figure 2 IR spectrum of PEEA untreated and thermal treated.

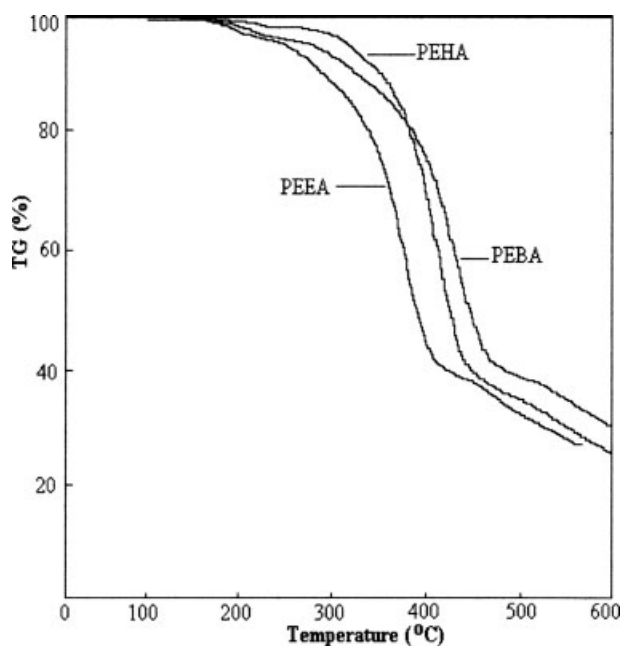


Scheme 2

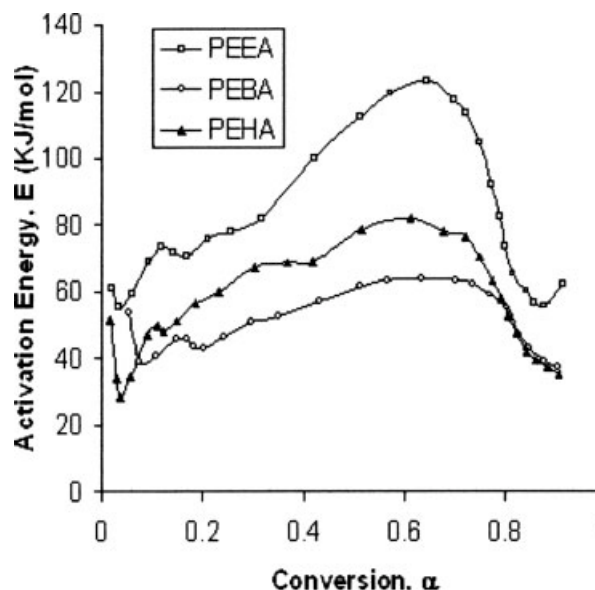
### Thermogravimetric analysis

The thermal stability of the polymers was investigated by TGA. TG curves for formulations are presented in Figure 3. It was proposed that the thermal degradation of polyurethane is primarily a depolycondensation process, which starts at about 250°C and presents a bimodal profile.<sup>29</sup> The initial decomposition of the polyurethane urea acrylates with EA occurred at 250°C, at 260°C for PEBA, and finally at 280°C when HA was used. The maximum and final weight loss temperatures for PEEA and PEBA showed the same trend. This shows that the heat resistance of PEBA is improved by the incorporation of 1,4-diaminobutane. In the degradation process, PEHA began to decompose at a higher temperature but continued to lose mass at lower temperatures than PEBA, because rigid segment content was lower. It can be observed that the former promotes more symmetry to the rigid segments and stronger interactions between the chains by hydrogen bonding even in smaller quantities.

Analysis of the thermograms (Fig. 4) by Reich and Levi methods<sup>30</sup> and Coats and Redfern methods<sup>31</sup>



**Figure 3** TG curves of polyurethane-urea acrylates synthesized with different types of diamines.



**Figure 4** Activation energy versus conversion.

leads to the curves showing the activation energy modification as a function of conversion for the polyurethanes acrylates.

The activation energy of polymer decomposition was derived from the TG curves by applying an analytical method proposed by Coats and Redfern.<sup>31</sup> The integral equation used has the form (Scheme 3): where  $g(\alpha)$  is the kinetic model function;  $\alpha$ , the decomposed fraction at any temperature,  $T$ ;  $\phi$ , the heating rate;  $A$ , a numerical constant; and  $E$  stands for activation energy.

The slope of the plot of left hand side against  $1/T$  is a straight line, from which the energy of activation  $E$  was calculated.

Constant values for the activation energy were obtained for  $\alpha > 0.1$ . For  $\alpha < 0.1$  appears an important decrease of activation energy with conversion degree. The conclusion that could be drawn is that in the initial moments, the reaction occurs autocatalytically. This is possible due to the weak bonds or oxygen attack. It is well known that the presence of oxygen traces in polymer decomposition has a catalytically or initiating role in thermal or thermoxidative decomposition.

The 10% decrease in the activation energy may be due to several phenomena, such as<sup>28</sup>

1. dehydration of the  $-\text{COO}^-\text{NH}_3^+$  structure, occurring with water removal and energy consumption,

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[ \frac{AR}{\phi E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT}$$

**Scheme 3**

2. double bond polymerization, provoked by the thermal effect, accompanied by energy elimination,
3. transurethanation reactions running with low molecular product elimination and energy consumption (40 kcal/mol).<sup>32</sup>

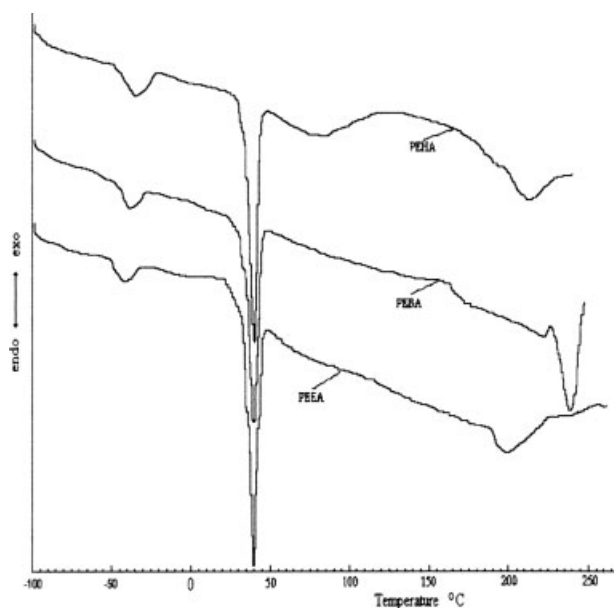
Processes 1 and 2 being prevalent, the overall phenomenon is accompanied by a decrease in the activation energy.

With conversion values of over 25%, the activation energy increases, probably due to the primary chemical bond splitting, occurring with energy consumption. This trend is usually attributed to a decrease in the free volume and mobility due to the bonding of soft segments with rigid urethane blocks and to an increase in phase mixing at lower polyester molecular units.

The MDI-based system can also have more complete microphase separation. The physical crosslinks are important for providing dimensional stability and for stopping cold flow in the uncured materials. The effect of restricting segmental motion in a three-dimensional network by chemical crosslink sites is similar to that of microdomain physical crosslinks, except that the former is irreversible. The crystalline polyester domain acts as an additional physical crosslink site below its melting temperature.

The urea structure has higher hydrogen-bonding capability, higher rigidity, and tends to promote more complete phase separation when compared with the urethane linkage.

The hard or rigid segments, which are in a glass or semicrystalline state, provide dimensional stability



**Figure 5** DSC curves of the synthesized polyurethane acrylates.

**TABLE I**  
Temperatures Peak for Polyurethane Urea Acrylates

Sample	$T_g$ (°C)	Endo 1 peak (°C)	Endo 2 peak (°C)
PEEA	-40	30	200
PEBA	-38	31.5	240
PEHA	-35	34	215

by acting as thermally reversible and multifunctional crosslinks and also as reinforcing fillers.

They are formed of urethane groups originating from diisocyanates and also contain urea groups and crosslinkable double-bonded ends.

In these cases, the differences appear in the first step but in the next step the activation energy is higher. This is explained by the increase of the energy necessary for breaking the bonds between the macromolecular chains formed by polymerization of double-bonded ends.

#### DSC analysis

DSC scans show that all of the model polymers exhibit three prominent thermal transitions including a glass transition below  $-35^\circ\text{C}$  and two endothermic transitions at higher temperatures. The lower temperature of the endothermic transition (Endo1) has previously been identified with the disruption of the soft segment/hard segment bonds<sup>33,34</sup> or the disruption of the short-range order within the hard segment microdomains<sup>35</sup> (Fig. 5).

The higher temperature of the endothermic transition (Endo2) is related to the breakup of interurethane hydrogen bonds.<sup>33,34</sup> This series of transitions is representative for the two phases that are present in the polymer and reflect the relative amounts of hard and soft segments present. Table I lists the peak endothermic temperatures.

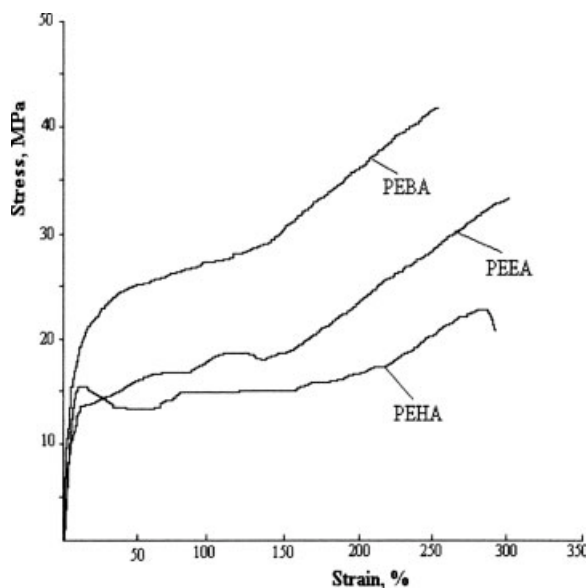
PEEA, PEBA, and PEHA have an increase of the hard segment. This is reflected in the DSC data of the higher temperature of the endothermic transition (Endo 2).

This change suggests that there may be increased interaction between the hard and soft segments as the hard segment content is increased.

The soft segments  $T_g$  increases as the hard segment content increases.

The increase in  $T_g$  could be attributed to the decrease in polarity and additional flexibility because of the increasing number of methylene sequence in the amine chain.

Because of the limited mobility of the long hard segments, only the short ones can align to form ordered structures. The endotherms appearing between 200 and  $250^\circ\text{C}$  are the so-called long range order structures.<sup>36</sup>



**Figure 6** Tensile stress–strain curves for polyurethane urea acrylates.

### Stress–strain measurements

Figure 6 shows the relationships between tensile strength and elongation and the molecular structure of diamine.

The stress–strain response of the materials was typical for a thermoplastic elastomer. An initial strong stress–strain response was followed by strain softening at about 20% strain.

A plateau region where there was little increase in stress with strain, preceded strain hardening. In PEEA and PEBA, strain hardening began at about 150% strain after the plateau region. Strain hardening began around 220% strain in PEHA, with a relatively long plateau region before strain hardening.

Considering the effect of diamine modification on stress–strain behavior of polyurethane acrylates, the higher modulus of polyurethane acrylates with BA in the hard segment was due to higher structured hard segment.

The modulus of the 1,4-butane diamine chain extended samples shows slightly higher values compared with the other two. This is probably due to the difference in the hard segment structure depending on the number of methylene groups. The even diamine adopts the lowest energy fully extended conformation, which allows hydrogen to bond in both directions, perpendicularly to the main axis. The polyurethane with higher number of methylene units in the chain extender is expected to have lower modulus in rubbery plateau region.<sup>37</sup>

In the case of 1,4-butane diamine, the hard segments will form well ordered association because of the effective hydrogen bonding, resulting in micro-

crystalline hard segment domains dispersed in the soft segment matrix.

The high molecular symmetry and chain segment mobility of 1,4-butane diamine make it partially crystalline at room temperature. Because the crystalline regions play a similar role to crosslinks in improving mechanical properties, the tensile properties of crystallizable BA-based material are superior.

It seems that the symmetrical structure of HA gives the highest flexible chain of PEHA with lower tensile properties.

The hard segment formed in the reaction of NCO end groups with EA is more polar than the one formed in the reaction with HA and, as a consequence, a higher cohesion was developed in the polymer chains.

The poorer tensile properties exhibited by PEHA are probably due to a very rigid interconnecting hard microdomain structure where, possibly, the hard domains have formed a more brittle matrix.

### CONCLUSIONS

A series of poly(urethane urea) acrylates were synthesized successfully with different diamines in hard domain.

The structure of poly(urethane urea) acrylates was affected by the presence of the different diamine chain, as evidenced by their mechanical properties and glass transition.

The mechanical properties of these poly(urethane urea) acrylates were strongly influenced by the chain of diamines and the tensile strength and the elongation achieved maximums when the 1,4-diamino butane was used.

The strength of hydrogen bonding in polymers possessing urea groups per hard segment generated an optimal balance between excellent mechanical properties and good processability and solubility.

The thermal properties were higher in case when the 1,6-diamino hexane was used.

The cured films show excellent properties and provide the foundation for many potential applications.

### References

- Shama, S. A.; Tortorello, A. J. *J Appl Polym Sci* 1991, 43, 699.
- Kim, B. K.; Paik, H. *J Polym Sci Part A: Polym Chem* 1999, 37, 2703.
- Petrovic, Z. S.; Javni, I.; Divjakovic, V. *J Polym Sci Part B: Polym Phys* 1998, 36, 221.
- Liaw, D. *J Appl Polym Sci* 1997, 66, 1251.
- Wang, C. B.; Cooper, S. L. *Macromolecules* 1983, 16, 775.
- Sung, C. S.; Smith, T. W.; Sung, N. H. *Macromolecules* 1980, 13, 117.
- Schauwecker, H. H.; Gerlach, T.; Planck, H.; Bucherel, E. S. *Artif Organs* 1989, 13, 216.

8. Pennings, A. T.; Knol, K. E.; Hoppen, H. J. *Colloid Polym Sci* 1990, 2, 268.
9. Lai, Y.; Baccei, L. J. *J Appl Polym Sci* 2039 1991, 42.
10. Oprea, S.; Vlad, S.; Ciobanu, C.; Macoveanu, M. *Eur Polym J* 1999, 35, 1269.
11. Scholnick, F.; Buechler, P. R.; Diefendorf, E. J. *JALCA* 1988, 83, 83.
12. Scholnick, F. *Leather Manuf* 1988, 1, 9.
13. Murray, K. P.; Hoffman, W. E. U.S. Pat. 4,818,780 (1989).
14. Murray, K. P.; Ansel, R. E. U.S. Pat. 4,822,241 (1989).
15. Kazunori, S.; Minoru, Y. *Jpn Pat.* 63,264,621 (1989).
16. Toru, O.; Keiichi, B. *Jpn Pat.* 63,312,309 (1989).
17. Moschovis, E. P.; Stanton, J. J.; Coady, C.J. U.S. Pat. 4,794,133 (1989).
18. Yoshiaki, K.; Yasuo, O. *Eur Pat.* 301,733 (1989).
19. Tomotaka, O.; Hiroshi, N. *Jpn Pat.* 63,265,931 (1989).
20. Makoto, S. *Jpn Pat.* 64,000,185 (1989).
21. Gould, F. E.; Johnston, C. W. U.S. Pat. 4,439,585 (1984).
22. Gould, F. E.; Johnston, C. W. U.S. Pat. 4,780,512 (1988).
23. Chen, S. A.; Hsu, J. S. *Polymer* 1993, 34, 2769.
24. Kim, J. Y.; Suh, K. D. *Macromol Chem Phys* 1996, 197, 2429.
25. Kim, J. Y.; Suh, K. D. *Colloid Polym* 1996, 274, 1025.
26. Kim, J. Y.; Suh, K. D. *Polym Bull* 1996, 36, 737.
27. Song, M. E.; Kim, J. Y.; Suh, K. D. *J Appl Polym Sci* 1996, 62, 1775.
28. Oprea, S.; Stanciu, A.; Vlad, S. *Polymer* 2001, 42, 7257.
29. Coutinho, F. M. B.; Delpech, M. C. *Polym Degrad Stab* 2000, 70, 49.
30. Reich, L.; Levi, W. D. *Makromol Chem* 1963, 66, 102.
31. Coats, A. W.; Redfern, J. P. *Nature* 1964, 201, 68.
32. Speckhard, A. T.; Cooper, L. S. *Rubber Chem Technol* 1986, 59, 405.
33. Seymour, R.; Cooper, S. *Macromolecules* 1973, 6, 48.
34. Seymour, R.; Cooper, S. *Polym Lett* 1971, 9, 689.
35. Leung, L. M.; Koberstein, J. T. *Macromolecules* 1986, 19, 706.
36. Seymour, W. R.; Cooper, L. S. *J Polym Sci B* 1971, 9, 689.
37. Camberlin, Y.; Pascault, J. P. *J Polym Sci Polym Chem Ed* 1993, 20, 415.