

Influence of the Chemical Structure of Soft Segment on the Properties of Polyurethane Acrylates

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Ultraviolet and heat-curable polyurethane acrylate prepolymers were synthesized from 4,4'-diphenyl methane diisocyanate, polyethylene adipate diol, polyhexamethylene carbonate diol, polycaprolactone diol and 1,6-hexamethylene diamine, acrylic acid. Effects of nature of the soft segments on the physical properties were investigated. It was found that the thermal stability increased from polycarbonate diol to polyester diol. Tensile modulus and strength decreased for polyurethane acrylate based poly (ethylene adipate) diol. DSC scans show that all of the model polymers exhibit thermal transitions including a glass transition below -35°C. These soft elastic segment structures, in addition to the physical and chemical cross-linked nature of hard segment, provide enough crosslink sites to have elastomeric behaviour.

Keywords: polyurethane acrylate, cross-linked, mechanical properties, thermal behaviour

Urethanes are mostly introduced into radiation curable formula as urethanes acrylates (or urethane vinyl ethers). There are aromatic and aliphatic urethane difunctional acrylates prepared by either one of two synthetic strategies:

- reaction of a diol with a diisocyanate to generate an oligomer of required molecular weight followed by end capping with a hydroxyl functional acrylate.

- reaction of a hydroxy functional acrylate with the appropriate diisocyanate to give an isocyanate functional acrylate followed by reaction with a suitable diol to give the resultant telechelic urethane acrylate oligomer.

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 [1-3], bending matter for magnetic media [4,5], mounts for printing ink [6], coating for optical fibres [7-9], carbon fibres [10], adhesives [11], gas and liquid separating membranes [12], etc.

Acrylated urethane comb-like 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 due to their cross-linked nature.

Polycaprolactone is commonly used as soft segment in polyurethanes, known to be biocompatible, slowly hydrolytically and enzymatically degradable and already used for several long term applications [13].

Aliphatic polyester and polycarbonate are two typical polymers with a good potential for use as biodegradable plastic, owing to their susceptibilities to lipolytic enzymes and microorganisms distributed widely in nature [14-17].

There is another polyurethane acrylate formation mechanism, that of producing polyurethane prepolymers with terminal isocyanate groups that further react with diamine to form one component type polyurethane urea prepolymers and they were end capped by acid acrylic

which forms curable urethane acrylate prepolymers [18,19].

In this paper it was obtained a series of polyurethane acrylates based on various soft segments, 4,4'-diphenyl methane diisocyanate, 1,6-hexamethylene diamine and acrylic acid hard segments. These synthesis reactions obtained polyurethane containing pendant acrylic groups. The soft segments were varied and their effects on the synthesis, structural and tensile properties and thermal response of these materials were investigated.

Experimental part

Materials

A series of polyurethanes acrylates (PUA), based on 4,4'-diphenylmethane diisocyanate (MDI) and 1,6-hexamethylene diamine (AH), acrylic acid (AA) as hard segment and a different chemical structure of polyol as soft segment were used in this study. Three kinds of polyols: poly (ethylene adipate) diol (PEA), poly (hexamethylene carbonate) diol (PHC), polycaprolactone diol (PCL) with a molecular weight of 2000 were used as the soft segment. The polyurethane acrylates were noted as polyol function in this way PUA-PEA, PUA-PHC, PUA-PCL

The samples were:

- poly (ethylene adipate) diol, poly (hexamethylene carbonate) diol, polycaprolactone diol with molecular weight of about 2000 were introduced in the flask and melted in an oil bath at 120-130 °C and dehydrated for 2 h at 2 mmHg.

-4,4'-diphenyl methane diisocyanate; Merck, was purified by vacuum distillation

-1,6-hexamethylene diamine, 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 (DMF), purified and dried by vacuum distillation on MDI,

Preparation of polyurethane acrylates

PUA was synthesized in three steps. In the first step, MDI and polyol were poured into a glass reactor under nitrogen gas. The reaction temperature was increased to 75°C and

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maintained for 2 h, so that 2 mol of MDI was reacted with 1 mol of polyol, resulting in a molecular structure carrying an isocyanate group at both ends. In the second step, over 2 mole diamine in 160 mL dimethylformamide solution, were added slowly, to the mechanically stirred prepolymer diisocyanate and the reaction mixture was stirred for another 2 h. In the third step, 2 mol of acrylic acid was poured into the reactor at room temperature. The result is a product which introduced a reactive vinyl group to the molecular ends as polymerizable groups. The reaction end point was determined by the disappearance of the NCO stretching peak (2270cm^{-1}) through IR spectroscopy. Changing the polyol 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 2 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.

Infrared Spectroscopy (FT-IR) was done using a VERTEX 7 Instruments equipped with a Golden Gate single reflection ATR accessory, spectrum range $600\text{--}4000\text{ cm}^{-1}$.

The thermal stability of polyurethanes was performed on a DERIVATOGRAF Q-1500 D apparatus (Hungary). The rate of the TGA scans was $10^\circ\text{C}/\text{min}$ in air atmosphere. The initial weight of the samples was about 50 mg and the temperature range $30\text{--}700^\circ\text{C}$.

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 100N cell and an extension rate of $10\text{ mm}/\text{min}$. Measurements were made at 25°C .

All the values given are average values of six measurements.

The differential scanning calorimetry (DSC) measurements involved a temperature range of -100 to 100°C and a Perkin Elmer 7 Series DSC, purging with N_2 and chilling with liquid N_2 . Runs were conducted on samples of about 10 mg at a heating rate of $10^\circ\text{C}/\text{min}$.

Results and Discussion

IR Spectroscopy

In all the polymer models the structural changes are fundamentally important for the IR study. 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 3284 cm^{-1} corresponds to hydrogen bonded $-\text{NH}$ groups. The absorption bands at 2920 and 2890 cm^{-1} in the spectra (fig.1), are associated with asymmetric and symmetric $-\text{CH}_2$ groups. The strong band at 1710 cm^{-1} is assigned to the $-\text{C}=\text{O}$ groups. The absorption of $(\text{C}=\text{O})$ (amide I) and (NH) and $(\text{CO}-\text{N})$ (amide II) appears at 1683 cm^{-1} and 1540 cm^{-1} , respectively. The band at 1232 cm^{-1} corresponds to $(\text{C}-\text{N})$ with (NH) (amide III) of $-\text{R}-\text{NH}-\text{COO}-$ groups.

To certify the curing of acrylates, the absorbance bands of acrylate at 1635 , 1410 , and 810 cm^{-1} are generally used. The characteristic $\text{C}=\text{C}$ absorption of urethane acrylate at 1635 cm^{-1} was used to determine the extent of polymerization in this study.

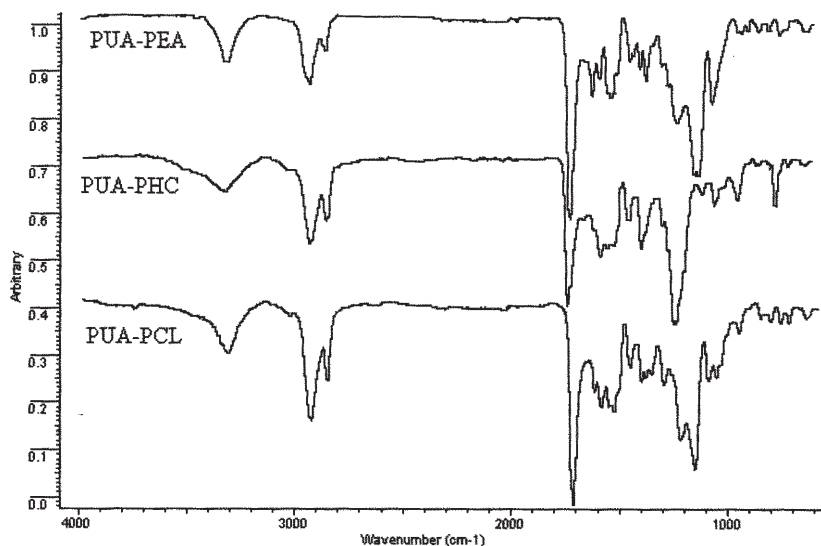


Fig. 1. IR spectra of polyurethane acrylates

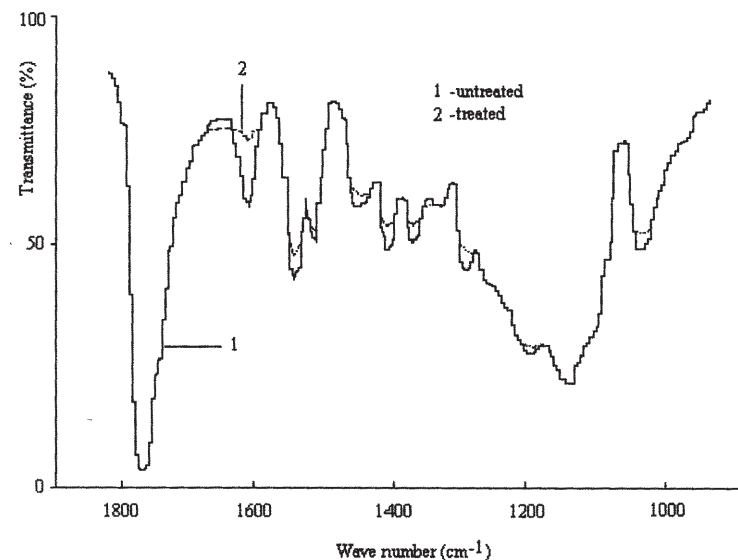


Fig. 2. IR spectrum of PUA-PEA untreated and thermal treated

After heat treatment at 120°C for 2 h both bands basically remained intact but the main observation was that the band at 1635 cm⁻¹, 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 cross-linked structure.

The idea of the double bond consumption is also sustained by the fact that, after thermal treatment, all samples become insoluble.

Thermogravimetric analysis

The thermal stability of the polymers was investigated by TGA. TG curves for formulations are presented in Figs.3,4. The decomposition of the polyurethane acrylates with PEA occurred at 330° C, at 360° C for PUA-PHC and finally at 370° C when PCL was used suggesting that degradation starts at the urethane bond. The maximum and final weight loss temperatures for PUA-PEA and PUA-PCL showed the same trend. This shows that the heat resistance of PUA is improved by the incorporation of polyester diol by increase of physical cross-linking. The weight loss with a maximum at 400 °C is associated with others segments of the remaining structure. We observed an initial weight loss of around 6% for PUA-PEA, 8% for PUA-PCL, 11% for PUA-PHC.

They all presented a similar weight loss profile with the first step appearing at around 10% weight loss, since the PU's have the same amount of urethane groups. Figure 3 illustrates irregular spacing (nonparallel) between isothermals, demonstrating the complexity of the process. Based on these results we suppose that the different kinetics degradation observed in our study is related to the different chemical structure of the polyol, which should influence the initial degradation step (below 10% conversion) becoming the degradation process more complex.

In the degradation process, PUA-PCL, began to decompose at a higher temperature but continued to lose mass at lower temperatures than PUA-PEA, because rigid segment content was lower.

The MDI based system can also have more complete microphase separation. The effect of restricting segmental motion in a three-dimensional network by chemical

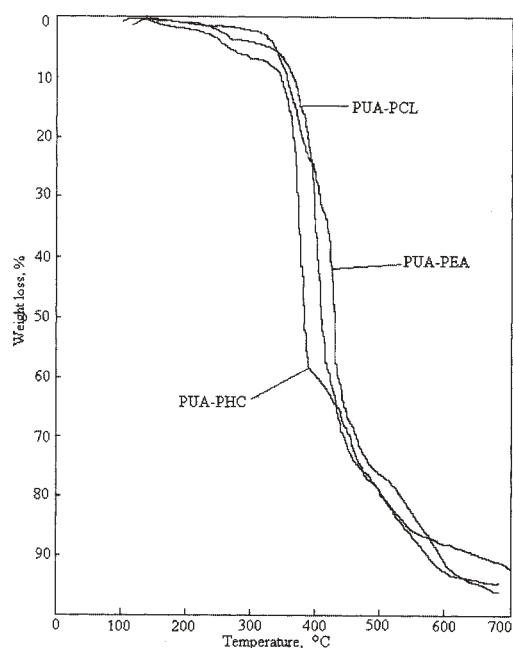


Fig. 3. TG curves of polyurethane acrylates synthesized with different types of polyols

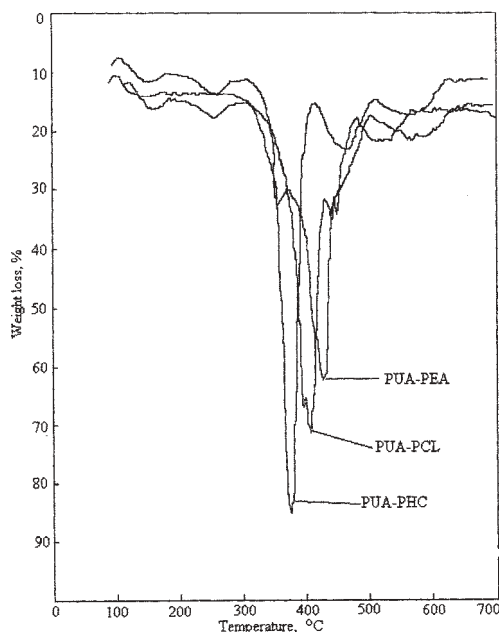


Fig. 4. DGT curves of polyurethane acrylates synthesized with different types of polyols

crosslink sites is similar to that of microdomain physical cross-links, except that the former is irreversible. The crystalline polyester domain acts as an additional physical crosslink site below its melting temperature[20].

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

Generally, increase in glass transition temperature, T_g, is attributed to a certain degree of phase mixing of hard and soft segments. It was found that with changing the nature of polyol the degree of phase separation increases which would also decrease the influence of hard segment on the soft segment T_g. It is known that (physical) cross-links can have a major influence on the soft segment T_g. This suggests that in this case the physical cross-links have a larger influence on the soft segment T_g.

DSC scans show that all of the model polymers exhibit thermal transitions including a glass transition below -35°C and endothermic transitions at higher temperatures (fig.5). The lower temperature of the endothermic transition (Endo1) has previously been identified with the disruption of the soft segment/hard segment bonds [20,21] or the disruption of the short-range order within the hard segment microdomains [22].

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.

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

The increase in T_g could be attributed to the decrease in polarity and additional flexibility due to the increasing number of methylene groups in the polyol chain.

Mechanical properties

The stress-strain curves of the different polyurethane acrylates are shown in figure 6. Characteristic values derived from these curves are presented in Table 1.

Clearly three different regimes are visible. First, the behaviour at low deformations can be explained as the pure elastic deformation belonging to regular elastomers[24].

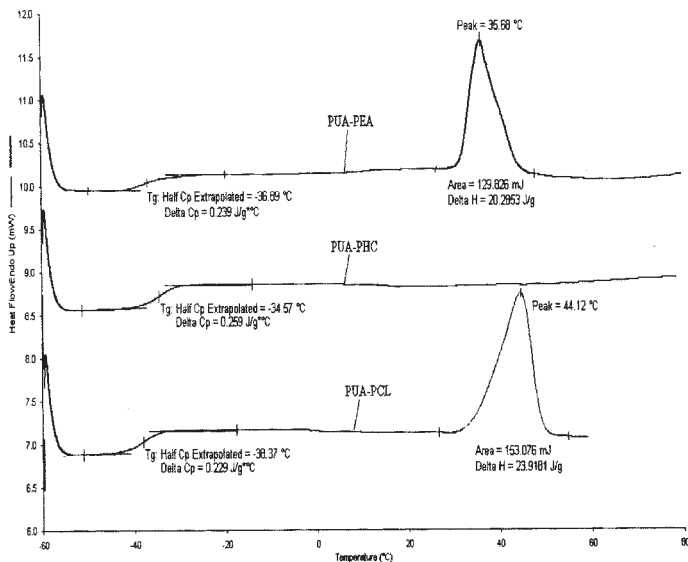


Fig. 5 DSC traces for polyurethane acrylates obtained

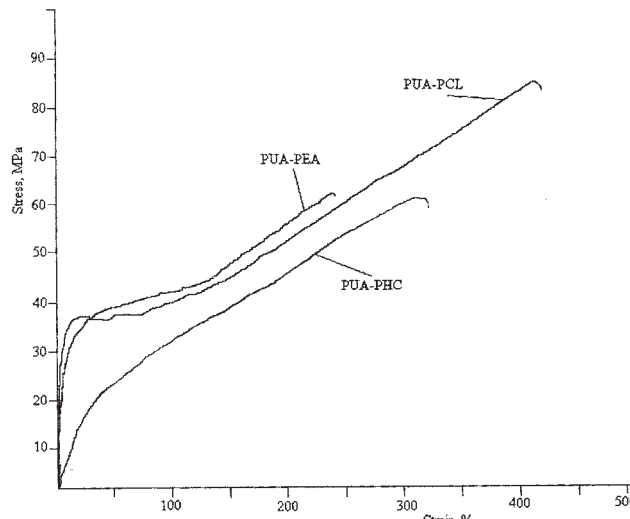


Fig. 6. Tensile stress-strain curves for polyurethane acrylates

Table 1
TENSILE PROPERTIES POLYURETHANE ACRYLATES OBTAINED

Sample code	E ₁ MPa	L1 %	FR MPa	AR %	FM MPa	AM %	E MPa
PUA-PEA	35	28	35,9	44	36	44	98
PUA-PHC	30	75	64	307	64,4	306,5	46,6
PUA-PCL	48	18,3	94,2	492	94,6	492	158,7

E₁ – effective modulus to first transformation of phase; L1- elongation to first transformation of phase; FR- tensile stress at break; AR- elongation at break; FM- tensile stress at maximum; AM – elongation at maximum; E- modulus

Secondly, the area has a plastic flow. This is much the same for PUA-PCL from polymers studied, indicating a great possibility of shear induced crystal fragmentation.

Thirdly, at strains above 200% an upswing in some of the curves can be observed, which can be attributed to strain induced crystallization of soft segment chains.

Table 1 shows the dependence of the permanent deformation stress and strain on the soft segment nature. An increase in hard segment content leads to an increase in yield stress, while an increase in hard segment content also leads to a decrease in strain at the yield point. The accompanying stress depends on crystallinity and lamellar thickness[25].

Uniform hard segments are used and consequently only the soft segment crystallinity, and lamellar thickness influence the permanent deformation stress. If no crystalline polyester is present the stress is only dependent on the percentage crystalline hard segment since the thickness of the hard segment crystalline lamellae is constant[26]. For the strain at break and in a lesser extent also for the stress at break, an increase is found for the lower hard segment content polyurethanes. Most likely this is due to the difference in soft segment structure of these polymers and not due to the difference in hard segment content.

The polyurethane with higher number of methylene units in the soft chain is expected to have lower modulus in rubbery plateau region.

Higher tensile modulus means higher stiffness of the material, and this higher tensile modulus is due to the crystallinity of PCL.

Conclusions

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

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

The mechanical properties of these poly (urethane urea) acrylates were strongly influenced by the chains of polyols and the tensile strength and the elongation achieved maximums when the polycaprolactone diol was used. Polyurethanes with polycaprolactone diol segments show an additional crystalline polycaprolactone diol phase.

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

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