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Poly(urethane-methacrylate)s. Synthesis and characterization

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Abstract

A series of poly(ester-urethane-urea)s containing pendant methacrylate functionality has been prepared, characterized and formulated into polyurethane methacrylate elastomers using a prepolymer process. Poly(ester-urethane-methacrylate)s were polymerized in a two-step process: synthesis of an isocyanate terminated prepolymers prepared from an excess molar concentration of 4,4′-methylene diphenyl diisocyanate with poly(ester)diols [Mn ~ 2000] and reaction the product with hexamethylenediamine and neutralization with methacrylic acid.

In general, these materials exhibit physical properties similar to those of linear segmented polyurethanes rather than conventional thermal or radiation-cured oligomer based on polyurethane methacrylates.

The cured materials were characterized by IR, stress–strain, thermogravimetric and thermally stimulated depolarization current experiments. Properties were compared to a polyurethane elastomer control in which the variable was the polyester diols' modification. The polyester diols modification produces polymers with decreased modulus, tensile strength, elongation. The crosslinking process depresses crystallization of the soft segments and improves tensile properties and can obtain protective films and finish materials for leather industry.

Introducing diamine and methacrylic structural units extends the hard urethane segments.

Keywords: Polyesters; Polyurethane-methacrylate; Glass transition temperature

1. Introduction

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.

In this urethane acrylate system, the polyurethane backbone may contain polyether or polyester soft segment, diisocyanate/short chain diol hard segment, and acrylate pendant groups, which are highly responsive to radiation.

The low viscosity liquid oligomers possessed excellent processability, while the cured solid polymers had reasonable mechanical strength and good thermal stability due to 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 [1,2].

The microphase-separated morphology of the polyurethane provides initial mechanical strength, while further crosslinking can enhance mechanical properties especially at higher temperatures.

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 [3,4].

To introduce a polyurethane formation mechanism other than general diisocyanate polyaddition, polyurethane prepolymers with terminal isocyanate groups were by diamine to form one component-type polyurethane-urea prepolymers and this were end capped by acid acrylic to form curable urethane acrylate prepolymers [5,6].

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 finish materials for leather industry [7–13], bending matter for magnetic media [14,15], mounts for printing ink [16] coating for optical fibres [17–19], carbon fibres [20], adhesives [21], gas and liquid separating membranes [22], materials for medical usage [23], etc.

Recently, polyurethane–acrylates elastomers with biomedical and enzyme immobilization properties [24,25]

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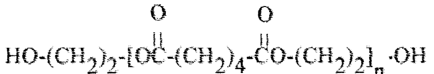
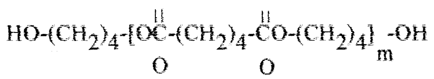
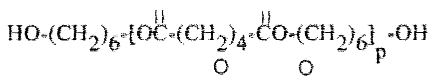
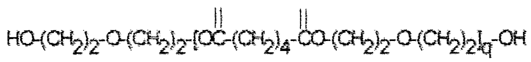
Table 1
Polyester diol oligomers; structure and characteristics. Symbols of polyurethane methacrylates

No.	Type and structure	Symbol prepolymer/ polyurethane methacrylate	C_{OH} (mg KOH g^{-1})	I_{OH} (mg KOH g^{-1})	M_n
1	 $HO\text{-}(CH_2)_2\text{-}[O\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_4\text{-}\overset{\overset{O}{\|}}{C}O\text{-}(CH_2)_2]_n\text{-}OH$	PEU/PEUMA	56.2	2.6	1964
2	 $HO\text{-}(CH_2)_4\text{-}[O\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_4\text{-}\overset{\overset{O}{\|}}{C}O\text{-}(CH_2)_4]_m\text{-}OH$	PBU/PBUMA	56.74	4.5	1978
3	 $HO\text{-}(CH_2)_6\text{-}[O\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_4\text{-}\overset{\overset{O}{\|}}{C}O\text{-}(CH_2)_6]_p\text{-}OH$	PHU/PHUMA	63.83	1.5	1778
4	 $HO\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_2\text{-}[O\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_4\text{-}\overset{\overset{O}{\|}}{C}O\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_2]_q\text{-}OH$	PDEU/PDEUMA	55.85	3.7	2005

have been synthesized in aqueous medium, by unconventional methods. On the other hand, the relatively easy polymerization of liquid acrylic polyurethane oligomers, by UV light or electron beams [26] which runs with crystallinity conservation of polyesteric chains [27], represents another convincing proof of the special both technical and scientific interest.

They are usually synthesized in a two-step process [28]. An excess molar concentration of a diisocyanate reacted with a polyether or a polyester diol (number-average molecular weight is in the range 1000–3000) to form an isocyanate-terminated prepolymer in bulk or in the solvent. The prepolymer is then polymerized to form a poly (urethane-urea) [PUU] with an aliphatic diamine such as ethylenediamine or propylenediamine in the same solvent. If the polymerization reaction rate is significantly reduced by any methods, then the bulk polymerization reaction without any solvents becomes practical, affording a convenient and economical route.

The microphase separation of the urethane segments, which is governed mainly by the soft segment length and type, is a key parameter to control the mechanical properties of the polyurethane acrylates [29–35].

Utilizing the above results of the model reactions, a more systematic study was made in this paper by using isocyanate-terminated prepolymer prepared from an excess molar concentration of 4,4′-methylenediphenyldiisocyanate (MDI) and a series of polyester diol and hexamethylene diamine in excess and methacrylic acid.

Four polyurethanes with either internal ester groups were prepared and their IR spectra were resolved. Polymers containing methacrylate pendant groups may undergo crosslinking reactions under suitable conditions and can obtain protective films and finish materials for leather industry.

In this investigation, comb-like methacrylated polyester polyurethanes, based on a series of polyester soft segments, 4,4′-methylene diphenyl diisocyanate, hexamethylene diamine hard segments were studies. The synthesis reactions were possible to synthesise polyurethane containing pendant methacrylic groups. The soft segments were varied and their effects on the ultimate tensile properties, thermal response and morphology of these materials were investigated.

2. Experimental

2.1. Materials

A series of four polyesters diol oligomer samples with molecular weight of about 2000 with the structure and characteristics presented in Table 1 were investigated.

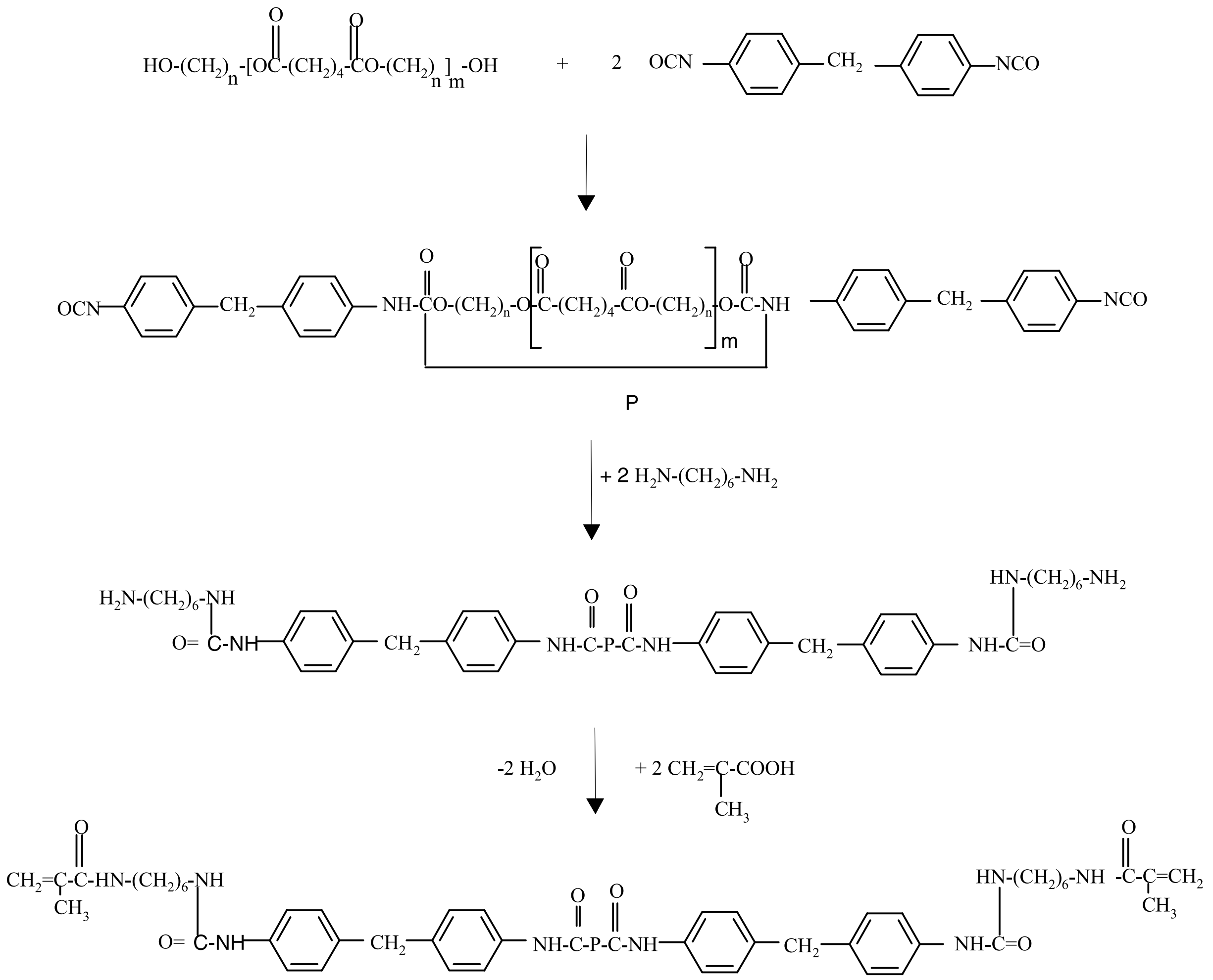
The sample were:

- 4,4′-diphenylmethane diisocyanate (MDI); mp 42–44°C, $d = 1.180$; bp = 200°C/5 mmHg; Merck, was melted at 60°C, filtered using hot funnel and stored at 0–4°C until use;
- 1,6-hexamethylene diamine: mp = 42–45°C; bp = 204–207°C; Merck, used without further purification;
- methacrylic acid: mp = 13°C; bp = 139°C; $n_D^{20} = 1.4202$; $d = 1.051$, Merck, was distilled at reduced pressure and the middle portions were stored at 0–4°C until use;
- dimethylformamide, purified and dried by vacuum distillation on 4,4′-MDI, bp = 153°C; $n_D = 1.4295$.

2.2. Preparation of poly(urethane-urea-methacrylate)s

The polymers were synthesized in a multi-step reaction as shown in Scheme 1.

Segmented polyurethanes of hard-segment content and of various soft-segment molecular weights were used in this study. The hard-segments consist of 4,4′-diphenylmethane diisocyanate and hexamethylene diamine and methacrylic acid. The soft-segments are various hydroxyl-terminated poly(esters).



Scheme 1.

The poly(ester-urethane) prepolymers were prepared in a melt using 20 g (0.01 mol) poly(ester)diols and 5 g (0.02 mol) 4,4′-diphenylmethane diisocyanate. The prepolymers diisocyanate 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 to the flask and melted in an oil bath at 120–130°C and deshidratation for 2 h at 2 mmHg. Then 5 g (0.02 mol) of 4,4′-diphenylmethane 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 was introduced 2.3 g (0.02 mol) hexamethylene diamine in 160 ml dimethylformamide. To ensure the complete dissolution, it was added slowly, and mechanically stirred, to the prepolymer diisocyanate and the reaction mixture was stirred for 2 h. Then 1.7 g (0.02 mol) methacrylic 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%.

The chemical structure of the polyurethane methacrylate material was varied by changing the poly(ester)diol.

Films from the synthesized polymers have been obtained on glass plate by thermal treatment at 120°C for 2 h. During the solvents removal, the double bonds polymerization occurs at a film of polyurethane methacrylate with urea and an amide structure is formed. Cured film samples were used for tensile testing and thermal study.

2.3. 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.

NMR spectroscopy was utilized and the samples were analyzed in DMSO on a C 80-HL type High Resolution NMR Instrument, at room temperature using tetramethylsilane as an internal standard.

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

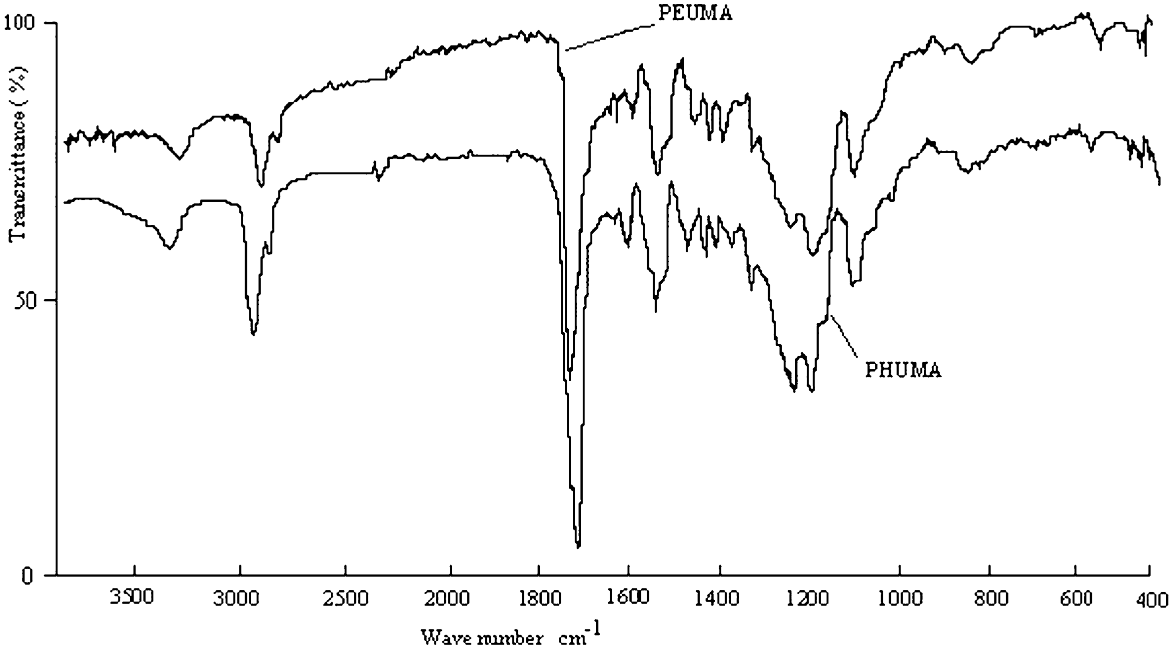


Fig. 1. IR spectrum of PEUMA and PHUMA.

100N cell and an extension rate of 10 mm min^{-1}. Measurements were taken at 25°C. All samples were measured five times and the averages were obtained.

Thermogravimetric analyses were performed on a DERIVATOGRAF MOM apparatus (Hungary) in a temperature range from 0–600°C. The heating rate was 12°C min^{-1} in air atmosphere and sample size was 50 mg.

Thermally stimulated depolarization currents (CSDT). The polymer specimens of, approximately, 0.4-mm thick were disk shaped, moulded from melted polymer. Polymer films about 0.2-mm thick were prepared by casting polymer on clean glass plates. After removal from the support, the films were dried in vacuum for two hours at 60°C. Samples with 12 mm in diameter were provided with vacuum evaporated silver electrodes of circular form ($\varnothing = 10$ mm). The thermal cycles of polarization and depolarization of samples consisted of the following steps. A sample with a polarization field E_p up to 50 kV cm^{-1} was warmed up to the polarization temperature T_p, which was maintained for a polarization time $t_p = 5$ min; after cooling to 200 K using liquid N_2, E_p was removed and the sample was short-circuited for 5 min. In order to eliminate the rapid depolarization currents; then the depolarization was recorded at a heating rate of 3.5 kV min^{-1}.

3. Results and discussion

3.1. IR study

Four poly(urethane-methacrylate)s were prepared according to Scheme 1.

In both the model polymers the morphological changes are fundamentally important for the IR study; therefore, investigation on the effect of thermal history is primarily required. All IR spectra polymers were examined in the –NH and –C=O absorption regions. With typical spectra for polyurethanes based on an aromatic (MDI), three regions are of interest: the –NH stretch absorptions (3500–3000 cm^{-1}), the CH_2 stretch absorptions (3000–2700 cm^{-1}) and the carbonyl vibrations (1750–1650 cm^{-1}).

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 peak is located at about 2980–2990 cm^{-1} in the spectra (Figs. 1 and 2), which is characteristic of hydrogen-bonded NH groups, and –C=O absorption bands centred at 1740 cm^{-1}.

There are two regions in the IR spectrum that can be useful for the determination of the phase separation degree as follows: 3500–3000 cm^{-1}, which includes the hydrogen-bonded N–H stretching vibration and the free N–H stretch, and 1750–1650 cm^{-1}, which includes carbonyl symmetric stretching vibrations. The intensity of the peak at 1740 cm^{-1} in comparison to other ones within the carbonyl band suggests the extent of the microphase separation.

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

After heat treatment at 120°C for 2 h both bands basically remained intact but showed a decrease in the intensity peak at 1605 cm^{-1} and then an increase at 1635 cm^{-1} (Fig. 3).

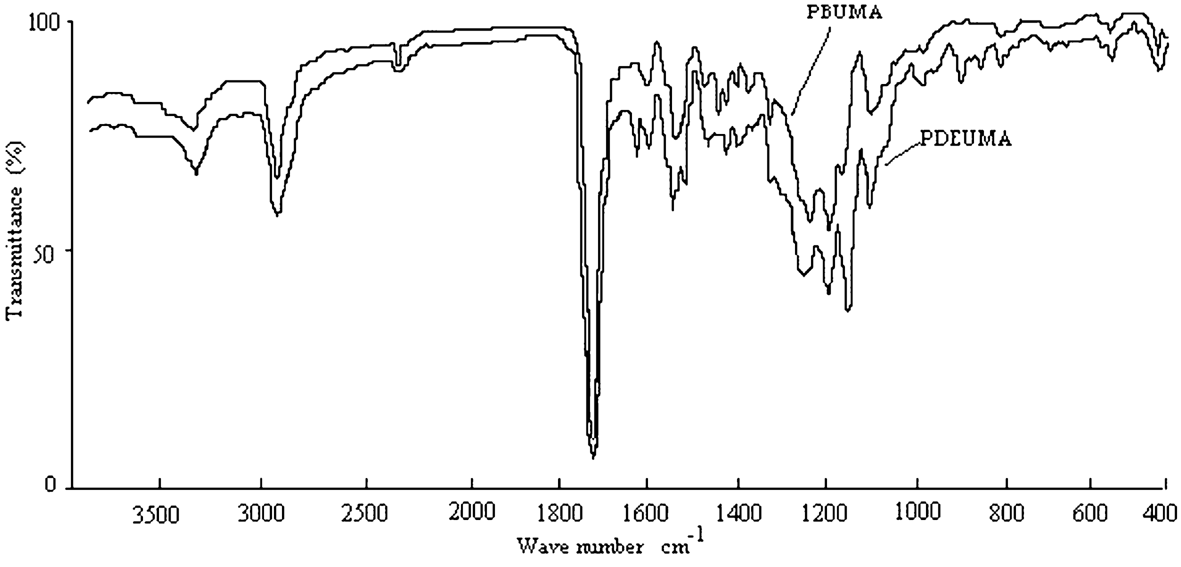


Fig. 2. IR spectrum of PBUMA and PDEUMA.

The absorption band at 1605 cm^{-1} corresponds to symmetrical and asymmetrical –NH deformation vibrations overlaps on C═C band from the aromatic nucleus.

On heating, dehydration of –COO^{-}$^{+}$NH$_3$ may lead to a decrease in the absorption band at 1605 cm^{-1} and an increase in the band at 1635 cm^{-1} characteristic of the carbonyl group of the amide structure (Fig. 3).

A relatively low increase of the band from 1635 cm^{-1}, as a consequence of amide group formation, may be due to the consumption of the double bond C═C of the macromolecular chains ends, derived from methacrylic acid.

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 above may be expressed in the

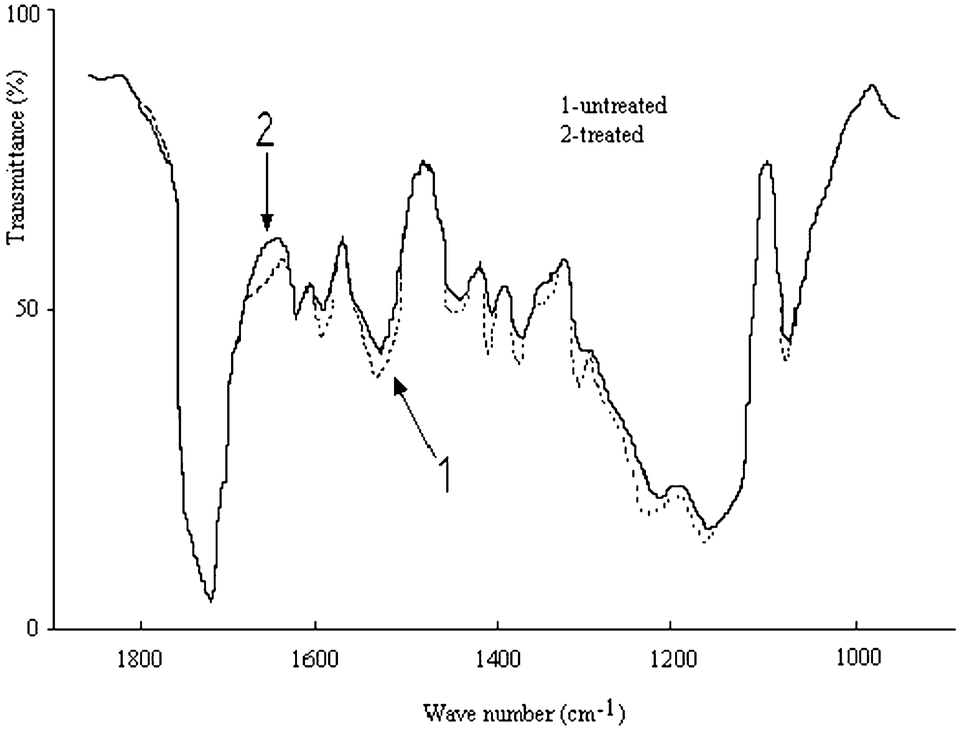


Fig. 3. IR spectrum of PEUMA untreated and thermal treated.

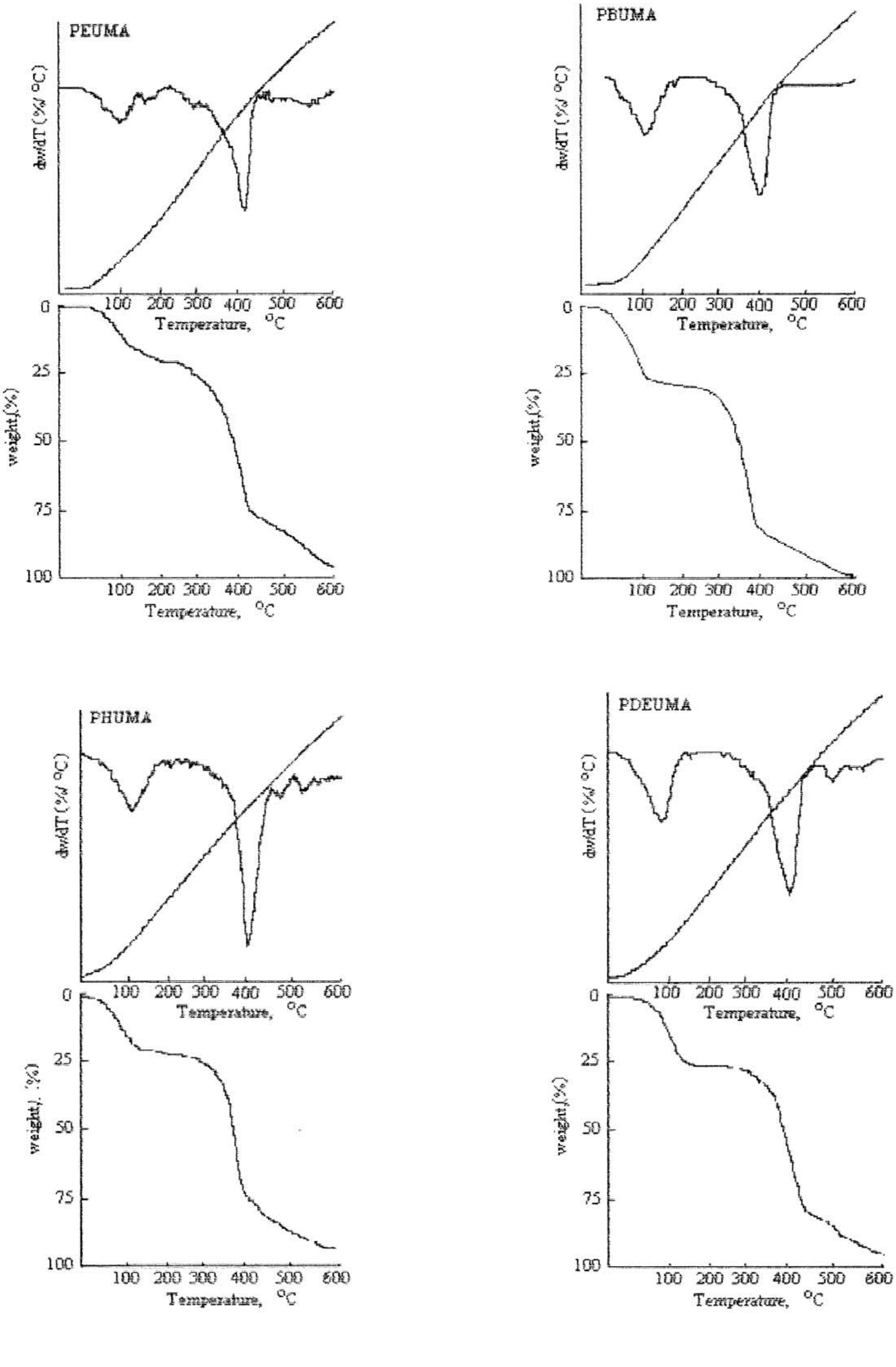
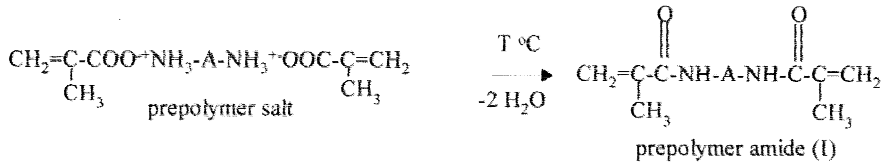
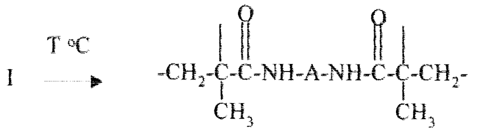


Fig. 4. Characterization of polyurethane methacrylates decomposition by TGA.

following equations:

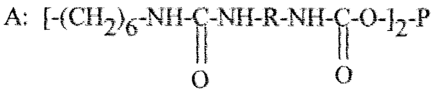


$$CH_2{=}\underset{CH_3}{C}\text{-}COO^{-+}NH_3\text{-}A\text{-}NH_3^{+-}OOC\text{-}\underset{CH_3}{C}{=}CH_2 \xrightarrow[-2\,H_2O]{T\,^{\circ}C} CH_2{=}\underset{CH_3}{C}\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}A\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{CH_3}{C}{=}CH_2 \quad (1)$$

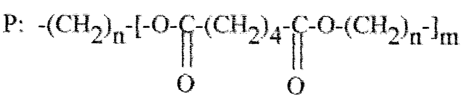


$$I \xrightarrow{T\,^{\circ}C} \text{-}CH_2\text{-}\underset{CH_3}{\overset{|}{C}}\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}A\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{CH_3}{\overset{|}{C}}\text{-}CH_2\text{-} \quad (2)$$

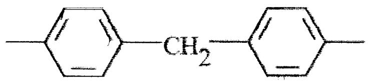
Polyurethane-methacrylate with amide and urea structures:



$$A\text{: } [\text{-}(CH_2)_6\text{-}NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}NH\text{-}R\text{-}NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}]_2\text{-}P$$



$$P\text{: } \text{-}(CH_2)_n\text{-}[\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_4\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}(CH_2)_n\text{-}]_m$$



In polyurethanes, the NH group is characteristic of the hard segment and may be conveniently used to study hard-block orientation. The CH_2 group generally can be used for soft-segment orientation, although methylene groups are also normally present at small concentrations in the hard segment.

A narrow –NH stretching at 3340 cm^{-1} and two sharp –C=O absorption bands at 1740 and 1635 cm^{-1} which, after heat treatment, remained intact, referred to the high crystallization rate. The two –C=O absorptions at 1740 and 1635 cm^{-1} assigned to be disordered and ordered bonded carbonyl absorptions [36],respectively. 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.

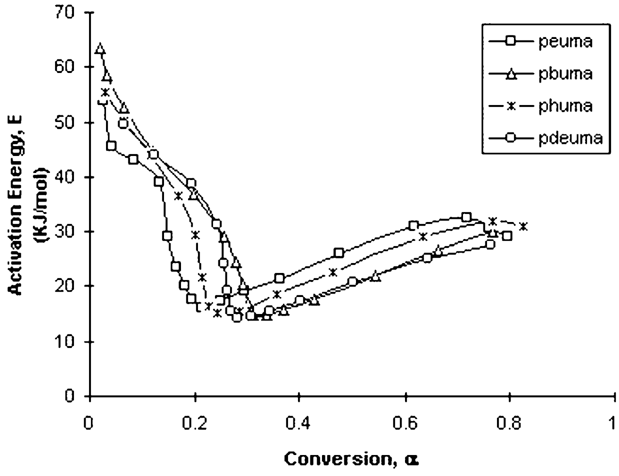


Fig. 5. Activation energy vs. conversion.

3.2. Thermogravimetric studies

Analysis of the thermograms (Fig. 4) by Reich and Levi methods [37] and Coats and Redfern methods [38] leads to the curves showing the activation energy modification as a function of conversion for the four polyurethanes (Fig. 5).

These curves show a decreasing of the activation energy, up to a 20–32% conversion, followed by an increase up to 80–85% conversion. The decreasing in the activation energy of 20–32% may be due to several phenomena, such as:

1. dehydration of the $-COO^{-+}NH_3$ structure (Eq. (1), occurring with water removal and energy consumption;
2. double bond polymerization (Eq. (2), provoked by the thermal effect, accompanied by an energy elimination;
3. transurethanation reactions running with low molecular product elimination and energy consumption (40 kcal mol^{-1}) [39].

Processes 1 and 2 being prevalent, the overall phenomenon is accompanied by a decrease in the activation energy. All these processes occur between 120 and 140°C. Also, Fig. 4 show that, in the case of PEUMA, the activation energy decreases up to 20%, while for PBUMA it decreases up to 32% and for PHUMA up to 26%. These different results may be caused by transurethanation reactions, running with a higher yield at polyurethane acrylates, synthesized with PEA.

With conversion values of over 32%, the activation energy beings to increase, probably because of the primary chemical bond splitting, occurring with an energy consumption. This trend is usually attributed to a decrease in the free volume and mobility due to the bonding of soft segments to 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 to providing dimensional stability and to stop cold flow in the uncured materials. The effect of restricting segmental motion in a three-dimensional network by chemical crosslink

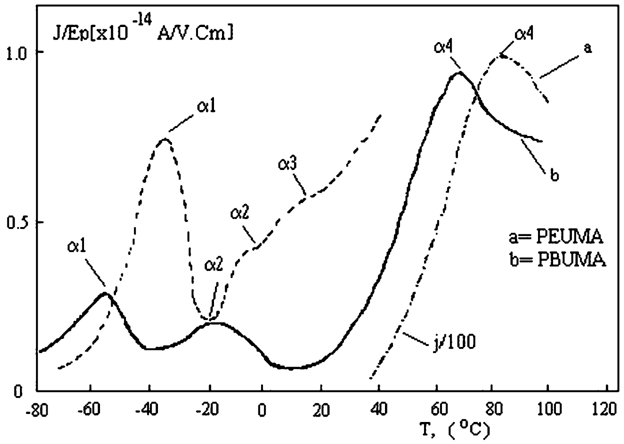


Fig. 6. TSDC spectra of polyurethane methacrylates (PEUMA, PBUMA).

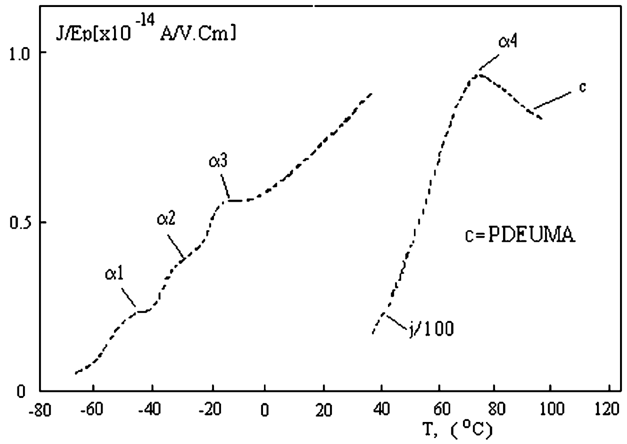


Fig. 7. TSDC spectra of polyurethane methacrylates (PDEMA).

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 their melting temperature.

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

In Figs. 6 and 7, the TSDC spectra of the polyurethane methacrylates based on the above polyesters are shown. The structure of TSDC spectra are complex; besides the α_1 and α_4 peaks assigned to glass transition and melting of the sample, respectively, intermediate peaks called α_2, α_3 were observed.

The intensity and location of the relaxation processes are dependent on the nature of the polyester; α_1 peak intensity decreases and shifts to lower temperature with an increase in methylene sequence length. It was found that the α_1 peak intensity is a linearly increasing function of the polarizing field. These facts support that α_1 peak is due to the glass transition of the sample which involves micro-Brownian motions of the soft polyester segments over the all the macromolecules. One can see that the glass temperature value in polyurethane methacrylates are lower than in corresponding polyesters. This is probably due to the segregation process undergone by the hard segments in polyurethane methacrylates, which diminished the interchains polyester interactions (Table 2).

This is in agreement with the general trends of increasing T_g with decreasing soft segment molecular weight commonly observed for polyurethane block copolymers. This trend is usually attributed to decrease in free volume and mobility due to the bonding of soft segments to rigid urethane blocks and to increased phase mixing at lower polyester molecular weight.

Table 2
The dielectric relaxation characteristics of polyurethane methacrylates

Polyurethane-methacrylates	Peak temperature (°C)					
	γ	α_1	α_2	α_3	α_4	δ
PEUMA	–	−35	−8	10	84	–
PBUMA	–	−54	−16	–	68	–
PDEUMA	–	−43	−30	−12	76	–

The intensity, width and temperature of the α_2 and α_3 peaks were found strongly dependent on the thermal history (polarizing time and temperature) of the sample.

This means that the morphological identity of the sample could be changed during its polarization. In order to explain the appearance of more relaxation processes, it was accepted that besides the main hard and soft phases, having ordered and respectively amorphous structures, some mixed microphases with intermediate structure exist. It is apparent that still some uncertainties remain regarding the number and assignments of these transitions.

3.3. Stress–strain measurements

Physico-mechanical analyses evidence the extent of the supermolecular modifications of polyurethane-methacrylates obtained as a function of their structural modifications.

Stress–strain, modulus and elongation are important for polymer characterization, depending on their structure by varying the polyol and/or diisocyanate molecular weight, as well as variation of double bond percentage, leading to modifications of stress–strain, modulus and elongation [40].

If the amount of hard segments is greater, then higher stress and modulus, and lower elongations result. Reverse effects occur with more numerous and longer soft segments.

The shorter soft segment implies that a higher hardness of polyurethane would be obtained. This result may be due to an increase in polar groups and cohesive energy density. This is because these polar groups, which have a high cohesive force, participate in intermolecular hydrogen bonding and restrict the rotation of polymer segments, resulting in a higher hardness.

The results of physico-mechanical measurements are presented in Table 3, evidencing that an increase of the

Table 3
Tensile properties of polyurethane methacrylates

Symbol	Modulus value ($cN\ mm^{-2}$) a_1 10%	F/S (break) ($cN\ mm^{-2}$)	Elongation at break (%)
PEUMA	2.139	59.219	34.7
PBUMA	1.941	46.193	48.73
PHUMA	1.705	41.26	64.28
PDEUMA	0.905	13.904	28.36

methylenic group number of the saturated polyesters employed leads to a lower tensile strength, while an increasing methylenic group number from 2 to 6, leads to decreasing of the tensile strength from 59 to 41 $cN\ mm^{-2}$, which may be explained by decreasing concentration of the ester groups on the macromolecular chain.

An ester group develops an intermolecular force of 3.9 $kcal\ mol^{-1}$, while a $-CH_2-$ group, only 0.68 $kcal\ mol^{-1}$. The same thing cannot be observed, in the case of elongation at breaking, it increases from 34.7 to 64.28%, being evidence.

Effective moduli at 10% elongation are presented in Table 3 (a_1); lower moduli for polyurethane-methacrylates based on PEA, may be observed, compared with the PBA and PHA based one. For example, in the case of PBA- based polyurethane-methacrylates, the modulus value is almost two times greater (Table 3).

This fact, can be explained by the formation of hydrogen bonds ($NH\ldots O=C<$) with a much higher frequency in the case of PBA and PHA, may be explained by the transplanar structure formed [41].

Therefore, with an increase of the applied stress, for the PEA-based polyurethane-methacrylates, there is an increase of the forces impeding deformation, by the rearrangement of the macromolecules.

In the monomeric unit of tetramethylene, only hydrogen atoms are attached to the main chain. The high molecular symmetry and the chain segment mobility make it partially crystalline at room temperature.

The three phase possible in the system include an amorphous polyesters phase, a crystalline polyester phase and a hard domain composed of urea urethane methacrylate segments [42].

Because the crystalline regions play a similar role to crosslinks in improving mechanical properties, the tensile properties of crystallizable material are superior to non-crystallizable material. The influence of molecular weight on the ultimate tensile properties of the soft segment is larger than that of the previously studied factors, especially at low molecular weight. It is clear that, the content of the soft segment increases, if the content of hard-segment domains and the crosslinking density decrease. Varying the polyester soft segment molecular weight affects the tensile properties of the methacrylated polyurethanes and the crosslinked materials.

In segment polyurethanes, the mechanical properties were generally accredited to the result of a pseudo-cross-linking effect [41] resulting from the hard-segment aggregation. The hard-segment domain generally exhibits a different degree of order or semicrystalline structure, which was considered to be able to reinforce the hard segment domain and, in the case of polyurethane-methacrylates, added a crosslinking effect of the double bonds.

Nevertheless, the amorphous region has never been studied in the literature. However, the presence of an amorphous material may constitute the weakest part inside the hard-segment domain. Catastrophic failure of the pseudo-crosslinking may start from this region. Since physical aging would densify and strengthen the hard-segment domain from the weakest point, the mechanical properties of the polyurethane may be improved by proper control of the physical aging.

This present study may provide possibilities of enhancing the mechanical property of the polyurethane-methacrylate material.

4. Conclusion

Radiation and thermal sensitive polyurethane methacrylate materials have been synthesized and effects of soft segment molecular weight, hard segment type and thermal crosslinking have been investigated. In general, these materials exhibit physical properties similar to those of linear segmented polyurethanes rather than conventional thermal or radiation-cured oligomer based on polyurethane methacrylates.

The stresses and strains at break observed in this study are closer to the values of conventional linear urethane block copolymers. This is not surprising due to the structural similarities between the methacrylated polyurethanes described here and their linear counterparts, and low concentration of methacrylate groups.

An increase in polyester segment molecular weight leads to higher soft segment crystallinity a longer polymer chain between crosslink sites in the cured materials and a smaller hard domain content. Soft segment crystallinity results in yielding behavior being observed in the stress–strain curves. Longer chain lengths between crosslinks produce higher elongations at break and lower mechanical moduli. The curing process increases the urethane acrylate domain rigidity and decreases the soft segment crystallinity. These factors enhance the tensile strength of the cured materials.

The $C=O$ absorption patterns from the as reacted and heat-treated samples were compared and deconvoluted into the constituent peaks. Generally, a heat-treated sample possesses a broader peak as compared to an as reacted one. The resulting crystalline structures subsequently melted into a nematic mesophase.

Analysis of the thermograms leads to the curves which evidence a decrease of the activation energy up to a 20–32%

conversion, followed by an increase. Decreasing activation energy may be due to dehydration of the $-H_3N^{+-}OOC-$ structure and the polymerization of the double bond.

Since the amorphous hard segment region is the weakest part of the polyurethane acrylate hard phase, densifing the amorphous hard segment region by proper physical raising crosslinking, greatly reinforce the hard phase integrity and thus greatly improve the mechanical properties of the polyurethane materials.

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