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Preparation and Evaluation of the Dynamic Mechanical Properties of Condensation Nonisocyanate Polyoxybutylene Urethane Films

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The present study investigates the dynamic mechanical (DMA) properties of condensation nonisocyanate polyurethanes (NIPUR) containing different hard segments (HS) content. NIPUR films were prepared by reacting phenol sulfonic acid with urea and formaldehyde with a molar ratio of 1:1:2. Obtained films were submitted to different thermal treatments prior to DMA testing. The FTIR and DMA results confirmed linear and segmented structures of obtained films with phase separation between HS and SS (soft segments). The obtained films have shown a wide range of utilization temperature as expressed by the glass transition temperature of SS and the melting temperature of HS. The decomposition of all tested NIPUR films took place at temperatures above 150 °C, confirming their high thermal resistance. The elasticity plateau of annealed samples at 160 °C increased in flatness and breadth.

Keywords: nonisocyanate polyurethanes, dynamical mechanical properties, FTIR, phase transitions.

1. INTRODUCTION

Polyurethanes are characterized by versatile structures which could be adjusted by properly choosing the relevant polyols and diisocyanates. They are widely used in many areas such as in automotive industry, medical applications, building and construction, coating materials, furniture as well as footwear [1, 2].

However, due to the toxic nature and high price of isocyanates, more environmentally friendly and less expensive polyurethanes are synthesized without isocyanates. Nonisocyanate polyurethanes (NIPUR) have attracted increasing attention because of improvements observed in the thermal and chemical resistance as well as water absorption over conventional polyaddition polyurethanes [3 – 14].

Most of the conducted studies were concerned with the preparation of NIPUR using carbon dioxide and diamines [3 – 6]. Endo et al. [4] used a polyaddition method to synthesize NIPUR using carbon dioxide, bisepoxide and diamine. Their results demonstrated that the hydroxyl groups in the side chains of polyurethane could be further transformed to yield NIPUR with very interesting properties. However, Diakoumakos and Kotzev [5] used cyclocarbonate resin and diamines to prepare NIPUR. The chemical structure and molecular weight of amines influenced the reactivity of amines toward cyclocarbonate terminated dendrimer. Wilkes et al. [6] carried out the reaction of carbonated soybean oil with carbon dioxide in the presence of tetrabutylammonium bromide as catalyst at 110 °C to produce NIPUR. The characterization of the obtained NIPUR confirmed the network character of all obtained materials, as well as the dependence of the mechanical and dynamic properties on the type and stoichiometry of the amines used.

Soybean oil has been extensively used in combination with diamines for the preparation of nonisocyanate polyurethanes [7 – 9]. Javni et al. [7] prepared NIPUR by reacting carbonated soybean oil with different diamines. The reaction of epoxidized soybean oil with carbon dioxide led to the formation of polyurethanes with a higher crosslink density and higher tensile strength.

Most recently, other natural components such as vegetable oils, or chitosan were used to prepare polyurethanes [10, 11]. To overcome the numerous discrepancies observed between results presented in the literature, rheometry technique was used to optimize the synthesis conditions (time and temperature) to produce NIPUR exhibiting optimal properties [12].

The need to prepare ecologically friendly polyurethanes has always been a challenge for polymer scientists [13, 14]. Segmented condensation nonisocyanate polyurethanes were already prepared by using phenol sulphonic acid, formaldehyde and urea and tested for their physical properties such as water vapor sorption and desorption as well as tensile strength [15]. Such obtained NIPUR elastomers exhibited segmented structures analogous to the conventional polyaddition diisocyanate based polyurethanes. The oligoether carbamates constituted the flexible (soft) segments while the rigid (hard) segments were formed from urea, phenol sulphonic acid and formaldehyde.

The objective of the present work was to investigate the effect of hard segments content and thermal treatment conditions on the dynamic mechanical properties of nonisocyanate polyurethanes synthesized by the condensation method.

2. EXPERIMENTAL

2.1. Materials

The following chemicals were used in the present study:

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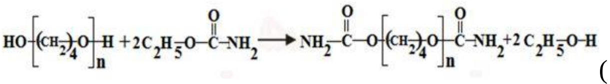
- Phenol sulfonic acid as 65 percent water solution (Sigma Aldrich Chemie GmbH Riedest Steinheim, Germany),
- Polytetramethylene glycol (PTMG 1000) with a molecular weight of 1000 (Du Pont Co. München, Germany),
- Formalin with concentration 34 – 37 percent (“Zakłady Azotowe”, Tarnów, Poland),
- Urea and ethyl urethane (“POCh”, Gliwice, Poland),
- Tetrabutoxy titane (Schuchardt München, Germany).

2.2. Synthesis of dicarbamate

Oligooxybutylene dicarbamate was obtained by reacting polyoligooxybutylene diol with ethylene urethane (molar ratio = 1:1.24) and using toluene as the solvent. Water was removed from the reacting mixture by azeotropic distillation and finally the catalyst (Tetrabutoxy titane) was incorporated. The transesterification reaction was conducted at azeotrope boiling temperature according to the following reaction [16]:



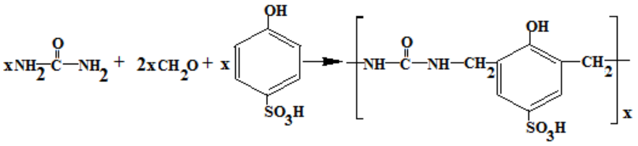
$$HO\!-\!\left[(CH_2)_4O\right]_n\!-\!H + 2C_2H_5\!-\!O\!-\!\overset{O}{\overset{\|}{C}}\!-\!NH_2 \longrightarrow NH_2\!-\!\overset{O}{\overset{\|}{C}}\!-\!O\!-\!\left[(CH_2)_4O\right]_n\!-\!\overset{O}{\overset{\|}{C}}\!-\!NH_2 + 2C_2H_5\!-\!O\!-\!H$$

(1)

The temperature of 130 °C (connected with entire removal of ethanol) was chosen as criterion to the reaction completion. Toluene and the excess of ethylene urethane were removed by distillation under vacuum. The reaction yield was estimated on the basis of estimated hydroxyl number, which approaches zero for complete reaction.

2.3. Preparation of oligomers containing hard segments

First, a 65 % aqueous solution of phenol sulfonic acid was introduced in a 500 ml four-neck round bottom flask equipped with a reflux condenser and a mechanical stirrer followed by a solution of urea in formalin at such a speed that the reaction temperature did not exceed 50 °C (temperature at which an unfavorable decomposition of sulfonic groups might take place, leading to additional reactions in the flexible segments). The molar ratio of phenol sulfonic acid, urea and formaldehyde was 1:1:2. The following reaction was expected to take place:



(2)

The obtained oligomer was designated as UPF and was used as hard segments (HS) for the synthesis of NIPUR films.

2.4. Preparation of polyurethane films

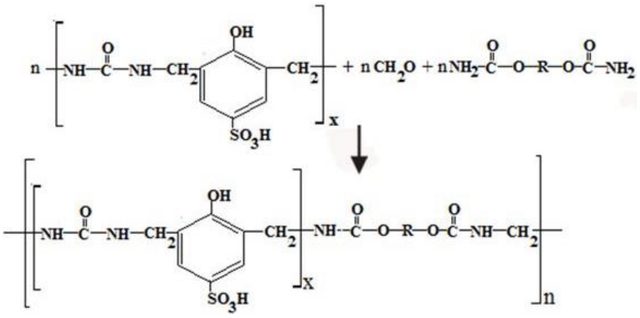
Polyurethanes containing different amounts of hard segments (0.8, 0.9, 1.0 and 1.5 moles), oligooxybutylene dicarbamate (oligomers with soft segments) and formaldehyde were prepared by polycondensation reaction (obtained compositions are shown in Table 1). The components were mixed at room temperature for approximately 5 min until complete homogenization of the mixture, then poured into a glass mould to obtain thin films having 4 mm of thickness.

The obtained polyurethane films containing 17 wt.%, 19 wt.%, 21 wt.% and 32 wt.% of hard segments (HS) were subjected to a two steps thermal treatment. In the first step, all prepared films were treated at 50 °C for 2 h. However, in the second step, additional thermal treatments were carried out at 135 °C for 15 min as well as at 160 °C during 10 min.

Table 1. Composition and thermal treatment of NIPUR films

Segments content, %		Thermal treatment conditions			
soft	hard	Temperature, °C	Time, min	Temperature, °C	Time, min
83	17	50	120	–	–
		50	120	135	15
		50	120	160	10
81	19	50	120	–	–
		50	120	135	15
		50	120	160	10
79	21	50	120	–	–
		50	120	135	15
		50	120	160	10
68	32	50	120	–	–
		50	120	135	15
		50	120	160	10

The reaction was initiated by using a stoichiometric amount of formaldehyde (Scheme 3). Polyurethanes films containing different amounts of HSs and SSs as well as thermal treatment conditions were submitted to dynamical mechanical testing as well as spectroscopic analysis.



(3)

2.5. Dynamic mechanical measurements and structure analysis

The DMA tests were performed using a DMA analyzer MK II Rheometric Sciencific with head B/S 500. NIPUR samples having 10 mm in width and 5 mm of gauge length were subjected to single-bending mode with a frequency of 1 Hz at temperatures between – 100 °C to + 200 °C and heating rate of 2 °C/min.

Fourier transform infrared (FTIR) spectroscopy was performed on selected NIPUR samples using a Perkin Elmer spectrometer (Model 1650).

3. RESULTS AND DISCUSSION

3.1. Dynamic mechanical properties

The dynamic mechanical analysis (DMA) was carried out to evaluate the variations of storage modulus and logarithm decrement tanδ of the prepared polyurethane films. The DMA analysis showed significant differences in NIPUR structure induced by the presence of HSs. We can observe different transitions associated with the soft segments (SS) in the low temperature range and with the hard segments (HS) in the high temperature range. It should be pointed out that the lower and upper limits of NIPUR films utilization can be represented by the glass transition temperature of SS and the melting temperature of HS, respectively. It is well accepted that, the soft segments contribute to the polyurethanes high extension as well as its elastic recovery, while the hard segments enhance their strength and elastic modulus.

The variation of storage modulus and tanδ of polyurethane films containing different amounts of HS and subjected to heat treatment (referred to as annealing) only at a temperature of 50 °C during 2 h is shown in Fig. 1 and Fig. 2, respectively. It was already demonstrated that the thermal treatment has a significant effect on the morphology and the properties of segmented conventional polyurethanes. Indeed, specific changes were confirmed in the hard segments crystallinity and domains rearrangement.

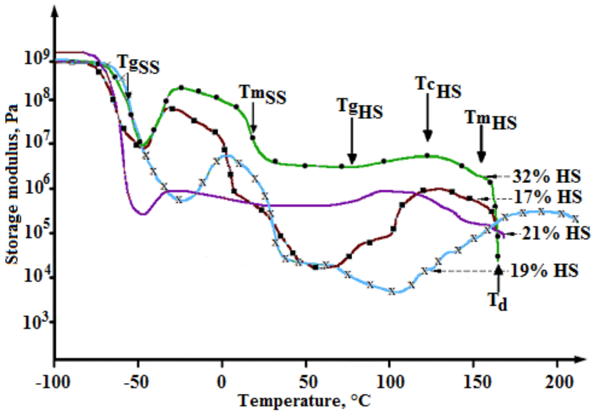


Fig. 1. Effect of temperature on the storage modulus of polyurethane films containing different amounts of hard segment (HS) thermally treated at 50 °C for 2 h

As examples, the different transitions temperatures of NIPUR films containing 32 % HS are indicated by arrows. It can be noted that the thermal treatment did not affect significantly the glass transition temperature of SSs. Furthermore, the glass transition temperatures of soft segments (T_{gSS}) were in the range from – 55 °C to – 58 °C, thus confirming that NIPUR films exhibited a quite high frost resistance.

Moreover, the storage modulus and tanδ of the samples were depended on the samples composition. However, samples containing minimum and maximum amount of HS (17 % and 32 %, respectively) exhibited smaller values of tanδ associated with smaller decrease of the modulus values. It should be pointed out, that the properties variations were much smaller than those obtained for samples with equimolar amounts of HS (21 % HS) or samples based on nearly equimolar HS content (19 % HS). The increase of the tanδ height for these samples indicates the relative ease of the soft chains motion under this particular heat treatment conditions. However, the broadening of the glass transition and decrease of peak height implies large distribution of the relaxation times and greater restriction of the soft segments chain mobility by the hard phase. Polyurethane soft segment chains with higher mobility reached high elasticity state with high arrangement (paracrystalline) state at about – 20 °C, regardless of their preparation conditions. It was confirmed that, the mobility of polyurethane chains was seriously restricted by the increasing amount of bulky HS compounds.

The increase of storage modulus following the glass transition observed for soft segments in all tested samples, could arise from a possible flexible chains reorganization. This phenomenon occurred at 0 °C for samples containing 19 % HS and at about – 30 °C for the rest of the samples. Petrović et al. [13] explained the increase in storage modulus by the nonequilibrium state of the material and its densification (volume shrinkage) at low temperature. However, Kojio et al. [17] attributed the increase of storage modulus to the crystallization of the soft segments during the heating process beyond their glass transition.

The most important increase of storage modulus in the elastic state was ascribed to sample with highest HS content (32 % HS), while the lowest modulus increase was assigned to sample with equimolar amounts of HS (21 % HS). This latter was characterized by a quite large high elasticity plateau, which defines the temperature range where the material could be used safely. The storage modulus increase occurring at higher temperature for sample with 19 % HS, might be due to specific interactions with hard segments.

Furthermore, it can be observed that the soft segments melt between 0 °C and 20 °C. The tanδ of polymer film samples containing 19 % HS did not appear within the test temperature range, due to possible sudden variation of elasticity which took place during this transition. The crystallization was accompanied by an increase of tanδ with increasing HS content within the prepared samples. The melting took place with decreasing storage modulus as well as tanδ of NIPUR films in the temperature range 125 °C – 170 °C. Obviously, the mobility of polyurethane chains was significantly disturbed by the hard segments compounds.

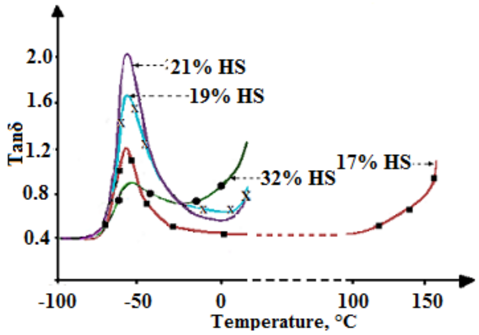


Fig. 2. Effect of temperature on the tanδ of polyurethane films containing different amounts of hard segment (HS) thermally treated at 50 °C for 2 h

From tanδ of polyurethane films treated at 50 °C (Fig. 2), it can be confirmed that the transitions of all tested samples took place almost at the same temperature (around – 56 °C). The height and broadness of tanδ provided an indication about the degree of arrangement and freedom of soft chains mobility. NIPUR film containing 21 % HS exhibited the highest peak (tanδ = 1.66) and the sample with 32 % HS the lowest peak (tanδ = 0.48). The high value of logarithm decrement is generally explained by the high value of loss modulus which is in turn associated with a significant amount of loss energy during the transition. One can add that this peak was broader in comparison with other peaks, specifying the slow transition process of this sample.

As far as the HSs are concerned, it can be noted that the transition from the glassy to the rubbery state took place only in polymer samples containing 17 and 19 % HSs in the typical temperature range between 50 °C and 100 °C, as for commercial PURs [1].

The tanδ peak denotes very well the end-use temperature where polyurethane begins to soften. Furthermore, it is well known and that Tg of soft segments is used as shape recovery temperature for shape memory materials such as segmented polyurethanes [18]. If the identification of the glass transition temperatures of the soft segments remained unambiguous, that of hard phase was more difficult to define, most probably due to the relatively important stiffness of hard segments as well as their restricted mobility. Similar findings were already reported in other studies [19]. These main arguments motivated to concentrate the analysis of tanδ data to lower temperatures.

The results of the storage modulus and tanδ of NIPUR samples containing different amounts of hard segments (17 %, 19 %, 21 % and 32 % HS) which were treated at 50 °C for 2 h and then annealed at 135 °C for 15 min, are shown in Fig. 3 and Fig. 4, respectively. In general, the phase transitions of elastomers are characterized by glass transition temperatures of the soft segments in the temperature range between – 55 °C and – 58 °C. The increase in the values of tanδ correlated with an increase of HS content between 17 % and 21 % HS.

The thermal treatment of the oligomers formed during the first stage (2 h at temperature 50 °C), followed by 15 min at temperature135 °C allowed the preparation of segmented polyurethanes having the best mechanical properties. Moreover, it can be observed that soft segments crystallization occurred at temperatures between – 10 °C and – 25 °C. It was confirmed that the samples containing the lowest HS content (i.e. 17 % HS) crystallize at lower temperatures in comparison with samples containing 19 %, 21 % and 32 % HS.

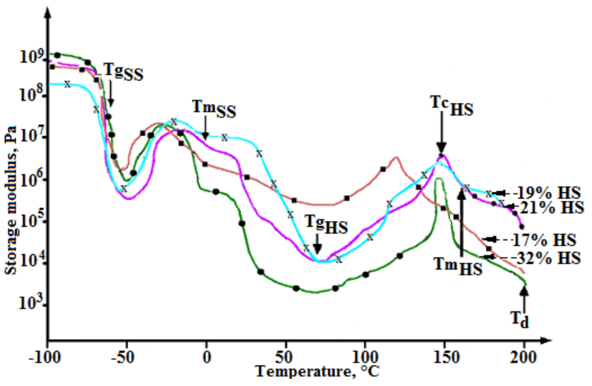


Fig. 3. Effect of temperature on storage modulus of polyurethane films with different hard segment content and thermally treated at 50°C for 2h and annealed for 15 min at 135°C

However, films containing 32 % HS exhibited the highest Tg value (Fig. 4), whereas the storage elastic modulus values were not significantly affected by HS content in NIPUR samples. The variations were in the range 20 Pa – 225 Pa and could be related to the low degree of hard and soft segments domain mixing as reported in literature [20]. It is well known that the hard segments are stiff and their mobility which is associated with the variation of the storage modulus, does not change much even after the transition.

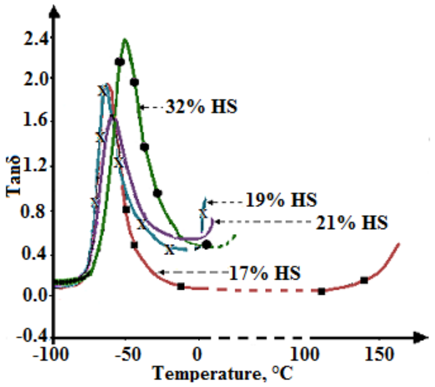


Fig. 4. Effect of temperature on tanδ of polyurethane films with different hard segment content and thermally treated at 50 °C for 2 h and annealed for 15 min at 135 °C

It has already been confirmed that the samples with 21 % HSs (i.e. films with equimolar HSs and SSs) exhibited the highest tensile strength in relation with other NIPUR samples containing 17 %, 19 % and 32 % HS [16]. Zhang and Huang [21] attributed the significant improvement of tensile strength to microphase separation that existed between the SSs and HSs. Moreover, the tensile strength of samples heated at 50 °C for 2 hours and additional 15 min at 135 °C was about 120 % higher than that of samples heated only at 50 °C for 2 hours.

The arrangement of flexible segment occurred between – 9 °C to – 30 °C and was accompanied by a small increase of storage modulus values from $8 \cdot 10^6$ Pa to $5 \cdot 10^7$ Pa. For samples with minimum (17 % HS) and maximum hard segment (32 % HS) content, we observed separate melting and flow phenomena, which were accompanied by variations in elastic modulus values. The melting of hard segments taking place at temperatures between 120 °C and 170 °C was accompanied by a decrease of storage modulus values. The decomposition of the tested polymers occurred at temperatures above 170 °C and was not significantly affected by HS content, except for annealed films which exhibited generally lower decomposition temperatures. This might be related to rearrangement of the polymer chains after the annealing process.

The storage modulus and tanδ of polyurethane films containing different amounts of hard segment and thermally treated at 50 °C for 2 h and annealed at 160 °C during 10 min are shown as a function of temperature in Fig. 5 and Fig. 6, respectively. The different thermal treatments including the annealing process (15 min at 135 °C and 10 min at 160 °C) were conducted in order to determine the optimum conditions for the synthesis of NIPUR films with a defined structure leading to optimum properties. The heating of condensation NIPURs at temperatures below the melting temperature and above the glass temperature of HSs led to the increase of the degree of crystallization of these latter, thus affecting positively the end-use properties of new polyurethane-urea products. Moreover, it was observed that the annealing of NIPUR samples by using the highest temperature (160 °C) during 10 min resulted in the decrease of their decomposition temperature, which was associated with their earlier degradation as already observed during the treatment process. Moreover, the elasticity plateau of annealed samples increased in flatness and breadth.

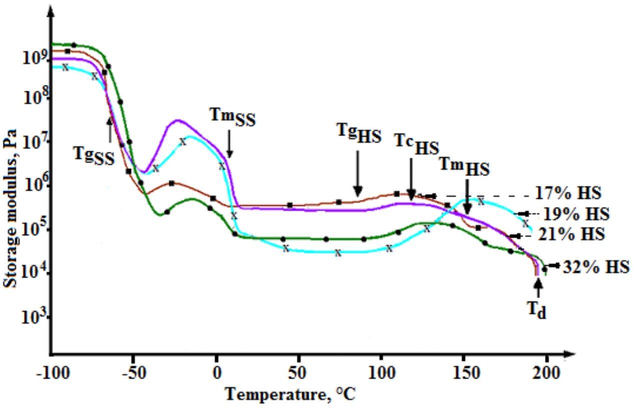


Fig. 5. Effect of temperature on storage modulus of polyurethane films with different hard segment content and thermally treated at 50 °C for 2 h and annealed for 10 min at 160 °C

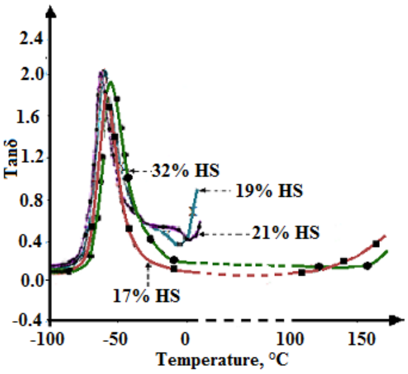


Fig. 6. Tan δ of polyurethane films with different hard segment content and thermally treated at 50 °C for 2 h and annealed for 10 min at 160 °C

It seems that the flexible chain reorganization took place for most of the samples obtained from equimolar amounts of SS and HS segments (21 % HS). However, it should be mentioned that the glass transition was not distinct for all tested samples. Interestingly, it can be observed that the values of the storage modulus changed regularly and similarly for all tested NIPUR samples, including a relatively large elasticity plateau which indicates a wide temperature range for material utilization. Moreover, all tested samples showed crystallization of hard segments between 120 °C and 150 °C and melting at approximately 160 °C. However, there was no clear dependence between these temperatures, the NIPUR compositions and the conditions of their preparation. It should be mentioned that both the glass transition and softening of hard segments took place slowly. Only the hard segment crystallization process occurred faster and was associated with a sudden drop of storage modulus.

3.2. Structure analysis of polyurethane films

Fig. 7 presents the spectra of selected NIPUR films that were obtained under optimum thermal treatment conditions (first stage for 2 h at a temperature of 50 °C, and then 15 min at 135 °C). It is seen that the position of the absorption bands of the different specific functional group was similar for all tested NIPUR samples. Moreover, the linear structure of the obtained polymer films was confirmed, as proved by the stretching of N–H groups appearing at 1368 cm^{-1} as well as the deformation vibration of N–H bonds shown at 1180 cm^{-1} and the resulting urea within –NH–CO–NH–. Furthermore, unquestionable is the existence of numerous CH *stretching* modes of the methylene groups (in the range 1520 – 1444 cm^{-1}) as arising from polytetramethylene glycol of the soft segments.

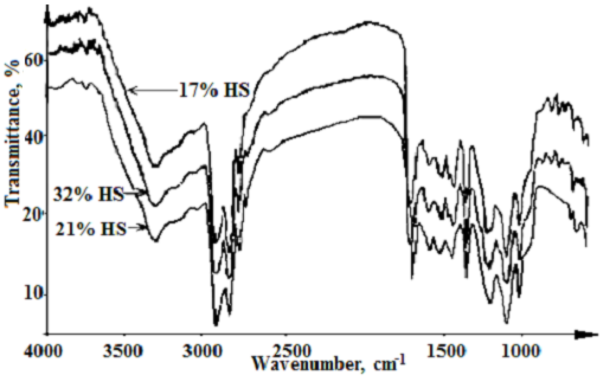


Fig. 7. Infrared spectra of polyurethane films containing different hard segments content

The characteristic absorption peaks are observed at 1710 cm^{-1} for the carbonyl group from urea, 2780 cm^{-1} linked to the C–H stretching vibration of $-CH_2-$ groups from formaldehyde and soft segment. However, the three peaks appearing in the range between 2270 and 2410 cm^{-1} are attributed to urethane groups, while the absorption peak at 2335 cm^{-1} might be due to C=O stretching (bonded) in urethane. The FTIR bands around 1710 $cm^{-1}$are assigned to the vibration of carbonyl groups derived from urea and urethane groups. Furthermore, the presence of a relatively weak absorption band at 1000 cm^{-1} attributed to C–H covalent bonds within $-CH_2OH$ group could indicate the presence of urethane (–N–H) groups and C=C bonds in aromatic rings. Bands from the stretching vibrations of C=O groups in urea and urethane linkage as well as N–H groups are used to analyse the phase separation in segmented polyurethanes [20]. Indeed, hydrogen bonding is known as an important driving force for the phase separation between hard and soft segments.

The sharp and distinct band appearing at ~ 1235 cm^{-1} is attributed to covalent S=O within $R-SO_3X$ groups, the peaks at about 1030 cm^{-1} are due to covalent –C–O groups in C–O–C aliphatic system, while the covalent –C–S sulfur in $R-SO_3X$ connected with aromatic system appear in the range 698 – 705 cm^{-1}. The very intensive and broad band appearing ~ at 2934 cm^{-1} is assigned to –C–H stretching and is connected with aromatic ring. However, the band at 780 cm^{-1} could be due to covalent –N–H bond in urethane group as well as aromatic C=C bonds.

4. CONCLUSIONS

Polyurethanes obtained by condensation reaction of urea, phenol sulphonic acid and formaldehyde exhibited a linear and segmented structure as demonstrated by FTIR and DMA analyses. The hard and soft segments have shown a distinct phase separation, as confirmed by their respective glass transition temperatures. All NIPUR films exhibited a wide range of utilization temperature as expressed by the glass transition temperature of soft segments and the melting temperature of hard segments.

NIPUR sample with equimolar amounts of HS (21 %) was characterized by the largest elasticity plateau specifying a significant temperature range of material utilization. The decomposition of synthesized polymers took place at temperatures above 150 °C independently of hard segments content and thermal treatments, confirming the high thermal resistance of the NIPUR films. Moreover, the elasticity plateau of annealed samples increased in flatness and breadth.

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