The influence of montmorillonite and bentonite addition on thermal properties of polyurethanes based on aliphatic polycarbonate diols

J. Pavličević [a,*], M. Špirkova [b], A. Strachota [b], K. Mészáros Szécsényi [c], N. Lazić [d], J. Budinski-Simendić [a]

[a] Faculty of Technology, Department of Materials Engineering, Bulevar Cara Lazara 1, 21000 Novi Sad, Serbia
[b] Institute of Macromolecular Chemistry AS CR v.v.i., Department of Polymer Networks and Mechanical Properties, Heyrovskeho Sq. 2, 16200 Prague 6, Czech Republic
[c] Faculty of Sciences, Chemistry Department, Trg Dositeja Obradovića 4, 21000 Novi Sad, Serbia
[d] Institute of General and Physical Chemistry, Studentski trg 12, 11000 Belgrade, Serbia

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ABSTRACT

Segmented polyurethanes based on hexamethylene-diisocyanate, aliphatic polycarbonate diol and 1,4-butanediol as chain extender were prepared in a bulk by one-step procedure. The structure of elastomeric materials obtained in the form of films and sheets was varied eighter by polycarbonate diol type or chain extender content. The organically modified particles of montmorillonite and bentonite were used as reinforcing fillers. The glass transition temperatures of prepared hybrid materials were determined by modulated differential scanning calorimetry MTDSC. Thermal stability of obtained materials has been studied by thermogravimetry coupled with DSC from an engineering perspective to determine service temperature of prepared elastomeric composites.

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1. Introduction

Due to the wide range of compositions possible, polyurethanes have found extensive use in numerous commercial applications such as coatings, foams, adhesives, sealants, synthetic leathers, membranes, elastomers as well as in many biomedical applications. Although these materials contain repeating urethane groups, other moieties such as urea, ester, ether and aromatic may also be present in the structure. The flexibility available in the selection of raw material components such as di-/tri-isocyanates, polyols, as well as chain extenders have made it possible to custom tailor the properties to a large extent [1]. A correct design of the segmented polyurethane structure becomes crucial as it provides the desired properties that meet customers' needs. The mass fraction, molecular mass, polydispersity of hard and soft segments, as well as manufacturing conditions are affected on morphological factors, such as degree of hard/soft macro- and micro-phase separation, crystallinity, and domain size. All these factors define properties, such as hardness, stiffness, tensile strength, and clarity of materials [2]. The high polar nature of the urethane linkages is responsible for the thermodynamic micro-heterogeneous phase separation and often in combination with the crystallization of both segments leads to the formation of hard and soft domains, which in turn regulates the behavior of materials [3]. Soft segments are generally derived from polyether or polyester polyol, whereas diisocyanate via conversion to urethane linkage NHCOO forms the hard segment. The aliphatic segmented polyurethanes are very promising materials due to their suitable end-use properties, and hence, they can be used for various applications [4–6]. Manufacturing of polyurethanes is often based via crosslinking of network precursor (prepolymer) prepared in the first step. The urethane linkage is a result of the reaction between an NCO group from isocyanate component and hydroxyl group OH from polyol. If a stoichiometric excess of isocyanate is used, the resulting urethane chains are NCO terminated and the product is called NCO terminated precursor. In general, these materials derive their specific properties from the thermodynamic incompatibility of the polymer segments and their consequent micro-phase separation on a length scale comparable to the dimensions of the chain segments. Hard segment packing is affected by some structural factors: the isocyanate size and symmetry; the chain extender length and functionality, the polyol type, molecular mass, and functionality [7]. Other factors influencing the phase separation are crystallinity, and tendency for soft segment–hard segment hydrogen bonding [8]. In industry, considerable attentions have been devoted to new polycarbonate-based polyurethane elastomers due to their improved mechanical performances [9] and their better anti-hydrolyzation and anti-oxidation properties compared to

* Corresponding author. Tel.: +381 214853742; fax: +381 21450413.
E-mail address: jelenapavlicevic@gmail.com (J. Pavličević).

the traditional polyurethanes [10,11]. The aliphatic polycarbonate polyurethane can be used for industrial parts, building materials, sports goods, medical equipment [7,12,13], and even artificial tissues [14]. According to publication of Tetsushi et al. [15] new types of polycarbonate diols, which are liquid at room temperature, are easy for handling, and improved in flexibility and chemical resistance when changing to polyurethane, compared with conventional commercially available (solid at laboratory conditions) polycarbonate diols. Dispersing nanometer-scale inorganic particles in a polymer networks offers the potential of creating new materials, the properties of which arise from the synergies between the components. Using polyhedral oligosilsesquioxane nanobuilding blocks can be used to create a wide variety of hybrid materials, where precise control of nanostructures and properties is required. In polyurethane/polyhedral oligosilsesquioxane nanohybrids, the degradation temperatures are shifted toward higher temperatures that can be determined using thermogravimetry [16]. The polymer nanocomposites based on minerals with a layered structure that are used as fillers are systems containing reinforcing elements in the form of plates approximately 1 nm thick with different ratios of the length to the crosssection size [17]. It was shown that the rigid amorphous fraction of the polyurethanes increases with increasing volume fraction of organically modified montmorillonite [18]. The knowledge of thermal properties and the interplay of the constituents' phases make it possible to manufacture polyurethane materials having properties combinations that are better than those found in other polymeric materials, specifically biodegradable elastomeric materials with high stiffness and tear resistance [19]. Upon thermal excitation, the covalent bonds in polyurethane chains undergo complex vibration and rotation within their local space. With further excitation, these bonds can break to form a variety of fragment radicals or small molecules, which may further mutually recombine or undergo further fragmentation [20]. Ultimately, the resulting fragments may be vaporized, diffused out, or carbonized. The decomposition process ends with the loss of all volatile material and with the formation of char that does not change further above the char temperature. A number of investigations have been made to determine the effect of the chemical structures of chain extender on the thermal stability of polyurethanes. The chain length, molecular volume, functionality and the conformational arrangement can influence hard segment packing, crystallinity and thus the thermal stability of the hard domains. This paper presents our results on thermal stability investigation of polycarbonate-based segmented polyurethanes which structure has been varied either by polycarbonate diol type or aliphatic chain extender content. The additional goal has been focused to the influence of organically modified montmorillonite and bentonite on the thermal properties of hybrid materials obtained in the form of films and sheets.

2. Experimental

2.1. Materials

The primary materials were polycarbonate macrodiols with molecular mass ca. 1000 (PCDL T5651 and T4671), kindly provided by Asahi Kasei Chemical Corporation. All characteristics of macrodiols were given by the supplier. For PCDL T5651: OH value: 111.4 mg KOH/g; water content: 0.0052 wt.%; viscosity at 50 °C: 1619 mPa. For PCDL T4671: OH value: 109.9 mg KOH/g; water content 0.0072 wt.%; viscosity at 50 °C: 2388 mPa. The hexamethylene-diisocyanate (HMDI), 1,4-butane diol (BD) and the catalyst, dibutyltin dilaurate (DBTDL), all Fluka, were used. The catalyst solution was prepared in oil Marcol (20%). As fillers, organically modified montmorillonite (Cloisite®15A produced by

Southern Clay Products, Inc.) and organically modified bentonite (Bentonite for organic systems, BO, Fluka) were used.

2.2. Polyurethane film preparation

The films were prepared by one-step technique. The ratio of NCO and OH groups, called isocyanate index ($r = $[NCO]/[OH]) was kept constant: 1.05. In this contribution, the ratio of OH groups from polycarbonate diol and chain extender ($R = $[OH]$_{diol}$/[OH]$_{extender}$) was eighter 1 or 10. Catalyst concentration, c_{DBTDL}, was 0.05 m/m%. One serie was prepared without chain extender. The chain extender (1,4-butane diol) mixed with catalyst was added to diol, and the reaction system was degassed. In the final step, diisocyanate was put to the reaction vessel. Then, the reaction mixture was degassed again, in order to remove the residual bubbles. Such prepared reactive system was spread on polypropylene sheet. The constant layer thickness (500 μm) was obtained using a ruler. Prepared samples were kept in an oven under nitrogen atmosphere at 90 °C for 24 h. The filled samples were obtained by the same procedure, except that the filler particles were left to be dispersed in polycarbonate diol over the night.

2.3. Polyurethane sheet preparation

The chain extender and catalyst were placed into the reaction vessel containing diol and blended at room temperature. After that, the reaction mixture was degassed during 5 min. Hexamethylene-diisocyanate was added as the last component. Finally, reactive system was placed to the teflon molds. The molds were transferred to an oven and left there at 90 °C during 24 h. The thickness of prepared sheets was 2 ± 0.1 mm.

2.4. Modulated differential scanning calorimetry

Thermal behavior of chosen samples was estimated by modulated differential scanning calorimeter (MTDSC, Q1000 TA Instruments). The measurements were done in sealed aluminum pans from −80 to 200 °C with a heating rate of 3 °C/min. The sample masses were about 3 mg. A purge gas was nitrogen. The instrument was calibrated using an indium standard. A modulation period was 40 s with modulation temperature amplitude of ±0.5 °C. MTDSC results were obtained from the first scan.

2.5. Thermogravimetry coupled with differential scanning calorimetry (SDT analysis)

Thermal stability of the synthesized materials was determined by thermogravimetry instrument coupled with DSC (SDT Q600 TA Instruments). The measurements were performed from room temperature to 500 °C in flowing nitrogen atmosphere (100 cm³/min), with a heating rate of 20 °C/min and sample masses of about 3 mg, employing open alumina crucible and a corresponding empty referent crucible.

3. Results and discussion

3.1. Polycarbonate-based polyurethane structure

Segmented polyurethanes have chains composed of alternating low glass transition (soft) segments and more rigid polar hard segments which soften much above room temperature. The morphology of prepared segmented polyurethanes is influenced by structure of chains given in Fig. 1.

The hard domains in obtained polyurethane samples consist of segments formed from hexamethylene-diisocyanate (HMDI) and chain extender (1,4-butanediol), while the soft segment is based on

$$\cdots NHCOO \longrightarrow (CH_2)_6 \longrightarrow NHCOO \longrightarrow \underset{chain}{polycarbonate} \longrightarrow NHCOO \longrightarrow (CH_2)_4 \longrightarrow NHCOO\cdots$$

HMDI   1,4-BD

Fig. 1. The structure of polyurethane chains synthesized from polycarbonate diol, hexamethylene-diisocyanate (HMDI) and 1,4-butanediol (1,4-BD).

polycarbonate diol component. The hard domains generally exhibit a degree of order or semicrystalline structure that is able to reinforce the material. The presence of an amorphous region inside the hard domains may constitute a weak part. It is known from the literature that for hybrid materials based on montmorillonite or bentonite, the spacing between these layers is of the order of few (2–3) nanometers prior dispersion of polymer. Hence the hybrid materials are called polymer clay nanocomposites [21]. Clays are very often used after surface-modification (usually with an organic ammonium salt) in order to enhance compatibility between the matrix polymer and the clay. Such clays are termed as organoclays [22]. The replacement of inorganic cations by organic onium ions on the gallery surfaces of smectite clays not only serves to match the clay surface polarity with the polarity of the polymer, but it also expands the clay galleries. Depending on the charge density of clay and the onium ion surfactant, different arrangements of the onium ions are possible. It has been shown that small addition of layered silicates, in particular, brings an increase in the thermal stability and improvement of the mechanical characteristics of the polymer [23]. In this case, in order to achieve the maximum effect exerted by the introduced inorganic filler on the properties of the polymer matrix, it is necessary to provide a complete exfoliation or intercalation of silicate structures into individual layers [24]. Polar adsorbates (water, alcohols, amines) are capable of incorporating into the structure of these minerals with an increase in the distance between layers up to their delamination. This specific feature of clay minerals has predetermined their wide usage as fillers for polymer composites [25]. During recent years, organically modified montmorillonite has been widely investigated in the development of polymeric materials. This type of filler for polymer composite preparation is a member of smectice clay group. The clay structure comprised of tetrahedral layers of silica sandwiching octahedral layers of alumina. On a whole, the structure looks like nearly parallel layers of silica held by alumina pillars [26,27] (see Fig. 2a). The other most frequently used clays are bentonites. They belong to the aluminosilicate group with 2:1 type layers in which exchangeable cations like Na^+ and Ca^{2+} can fill spaces between the layers (see Fig. 2b). These cations can be replaced by organic cations like quaternary ammonium salts by chemical treatments, producing an organophylic clay (generally called organoclay) with much higher compatibility with the polymer [28].

3.2. MTDSC analysis

Modulated differential scanning calorimetry provides not only the same information as conventional DSC, but also gives some unique information on chain dynamics due to the additional dynamic heating rate [29]. Thus, it is reasonable to expect much more information on chain thermal movements by this method. Thermal transitions observed in polyurethanes include the glass transition and crystalline melting of soft segments, and multiple endotherms associated with hard segment domains. Typical thermal curves of total specific heat flow versus temperature for one unfilled sample and filled samples with montmorillonite and bentonite are presented in Fig. 3. The values of T_g, marked in Fig. 3, were determined by middle point method.

Three transitions can be clearly observed: one is the glass transition of soft segments at $-32\,^\circ C$; the second transition is located at about 40–60 $^\circ C$, and the third, multiple endotherms, between 100 and 160 $^\circ C$. The degree of miscibility between hard and soft segments depends on their respective lengths and their mutual affinity, mainly as a consequence of their ability to establish hydrogen bonding interactions between hard and soft segments, which strongly depend on segments' chemical composition, and also on the hard segment content [30]. The existence of multiple endotherms might be associated with the starting of physical crosslink disruption and can be a result of domain sizes, or different degrees of order in the crystalline structure [31,5]. Addition of organoclays resulted in a non-significant shift of the endothermic peak at about 46 $^\circ C$, but has the influence on the melting process of hard segments. The non-reversing specific heat flow signals versus temperature for investigated polyurethane materials in the form of the sheets are shown in Fig. 4, giving a clearer picture of the three transitions compared with Fig. 3. For further understanding of the hard domains transition nature, the reversing signals of heat capacity versus temperature for prepared samples are presented in Fig. 5.
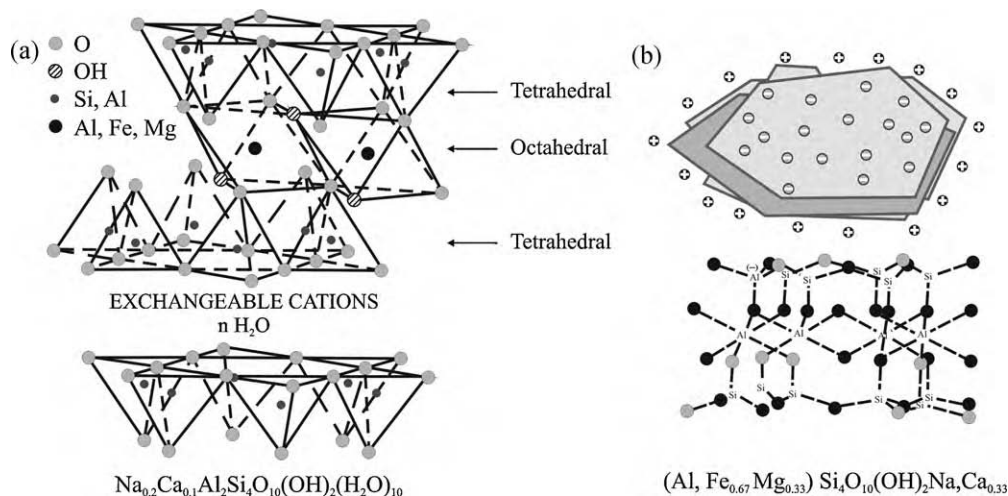

Fig. 2. The structure of organically modified clays: (a) montmorillonite and (b) bentonite.
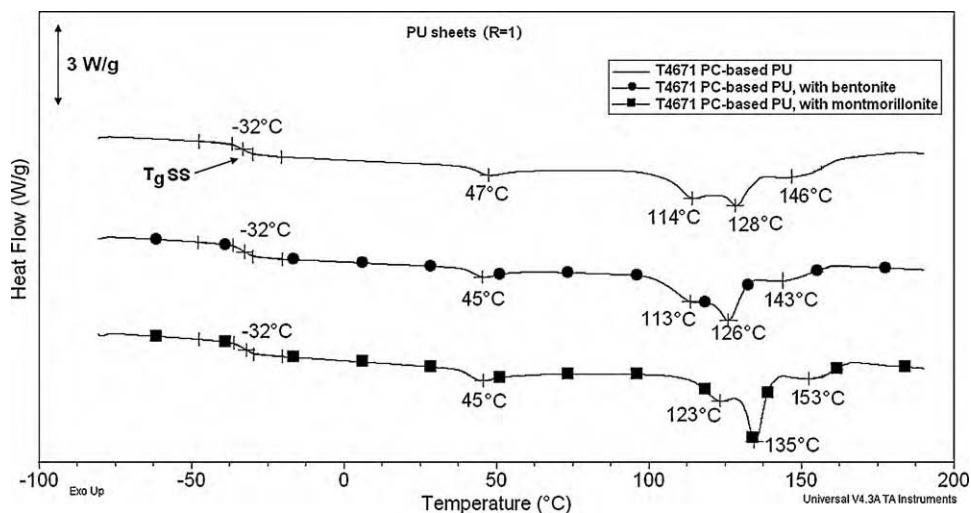
Fig. 3. Thermal curves of total specific heat flow versus temperature for polyurethane sheets based on polycarbonate diol T4671 and different nanofillers, at a heating rate of 3 °C/min.
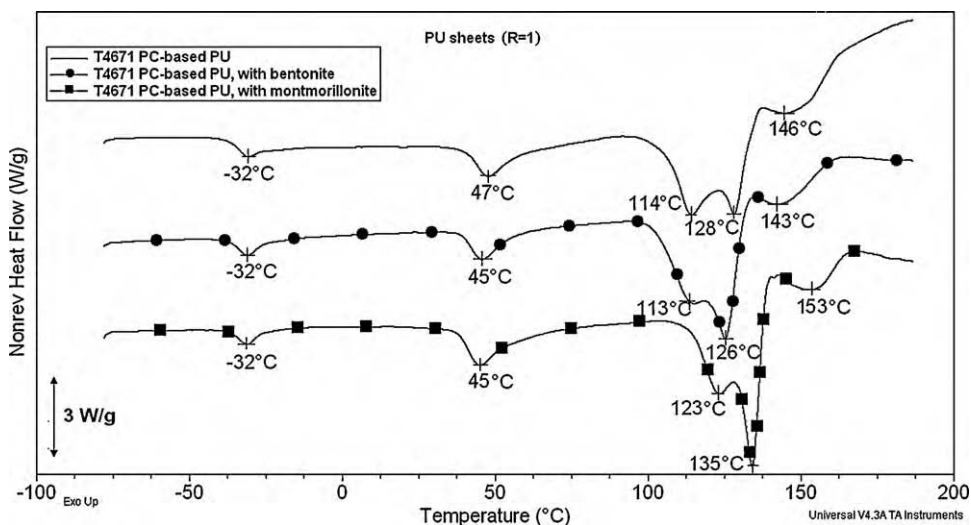
Fig. 4. Non-reversing heat flow signals versus temperature for polyurethane sheets based on polycarbonate diol T4671 and different nanofillers, at a heating rate of 3 °C/min.
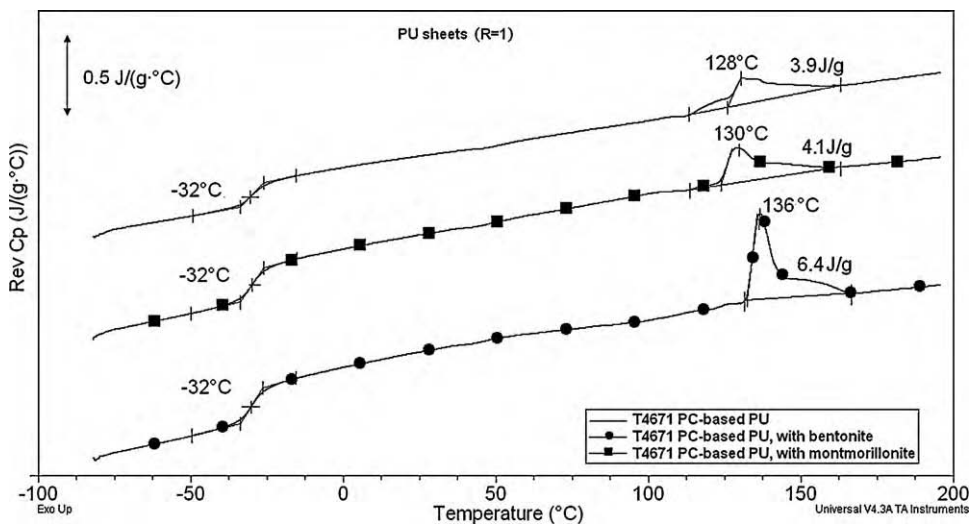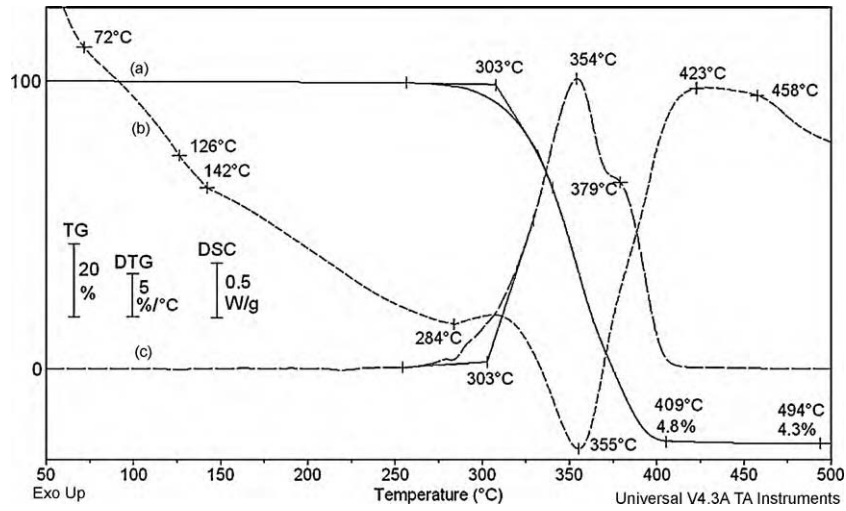
Fig. 5. Reversing signals of heat capacity versus temperature for polyurethane sheets based on polycarbonate diol T4671 and different nanofillers, at a heating rate of 3 °C/min.

Fig. 6. The simultaneous (a) TG, (b) DTG and (c) the corresponding DSC curve of the polyurethane elastomer based on macrodiol T5651, for $R = 1$. Heating rate was 20 °C/min.
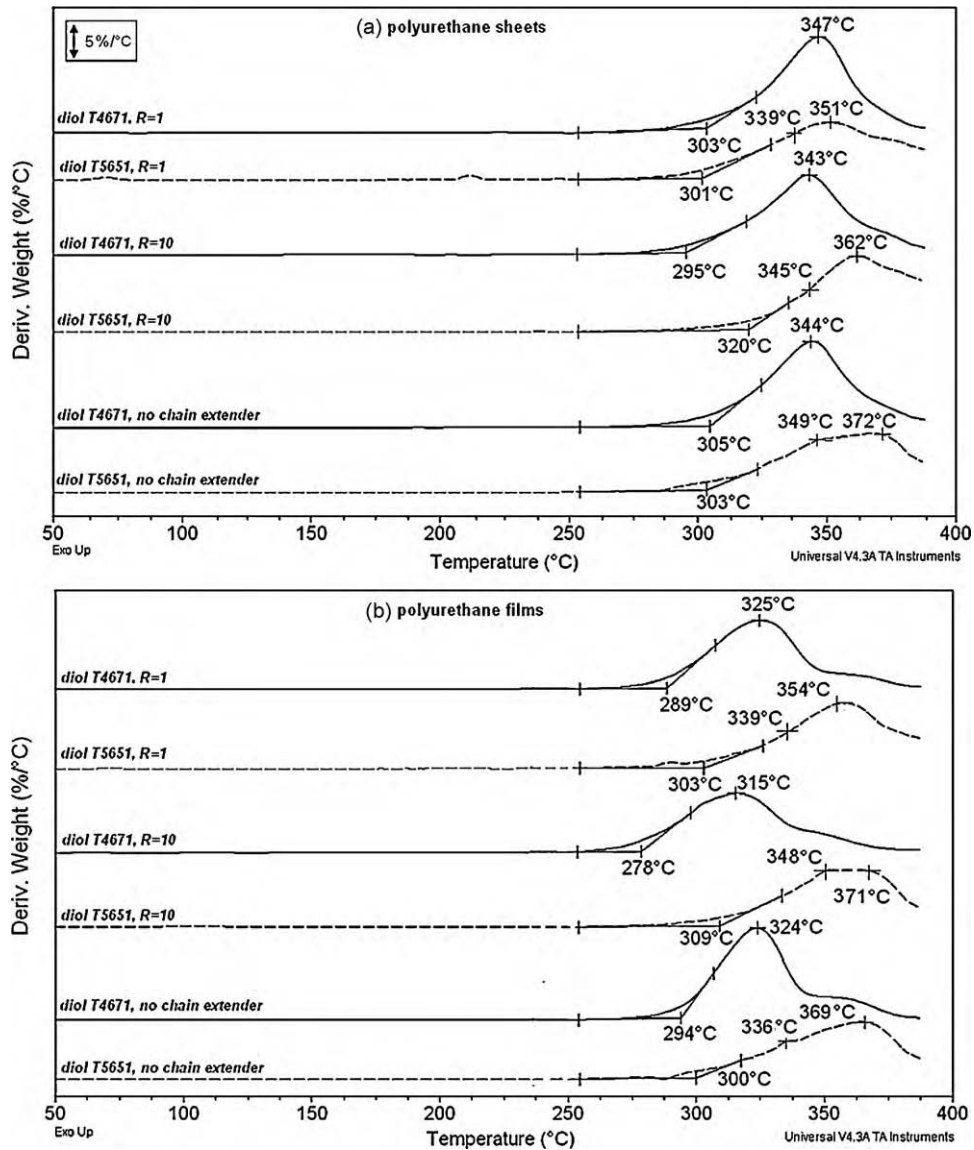

Fig. 7. DTG curves of polyurethane samples based on different macrodiols and different ratio of OH groups in the form of (a) sheets and (b) films. Heating rate was 20 °C/min.

It can be seen that there are only two clear change transitions, the first at around −32 °C and the second one between 115 and 160 °C, respectively, and there is no obvious change at about 40–60 °C. These results illustrate that the change at −32 °C is evidence for the glass transition of soft segment and the other ones are transition of hard domains. It is also notable that the addition of the organoclays had no significant effect on the glass transition of soft segments. The endothermic peak position and its area, observed at above 125 °C increased with addition of organically modified bentonite and montmorillonite nanoparticles. It is concluded that the transition of such structured hard domains is like an order–disorder transition. The thermal event located at 40–60 °C (Figs. 3 and 4) may likely be a result of annealing treatment. From the above discussion, it is proposed that the endothermic behavior located at 40–60 °C is not a micro-phase-domain transition, but is the relaxation of chain segments in the diffused interface between soft and hard segment phases [32].

3.3. Thermal stability of filled and unfilled elastomers

The mechanism of thermal decomposition of polyurethanes is an important phenomenon from both of fundamental and technological perspective. Investigation of degradation processes allows us to improve the design of the structure and to determine the optimal conditions for its processing. The decomposition of polyurethanes occurs as a result of a multitude of physical and chemical changes and is not dominated by a single process. Using a setup for simultaneous TG and DSC measurements enables us to study the structural changes and the thermal decomposition at the same time. An example of such an experiment is presented in Fig. 6 showing the TG/DTG and DSC curves for elastomers based on macrodiol T5651. TG/DTG curves show that up to about 300 °C, the polymeric material is chemically stable. The corresponding DSC curve up to the decomposition temperature shows one endotherm at ca. 70 °C, two endothermic peaks between 115 and 160 °C, and one endotherm in the temperature range of 250–295 °C. In the temperature range from 250 °C to the onset temperature only a small mass loss is observed in TG curve (<2%). The endothermic effect in the temperature range from 250 to 295 °C can be prescribed to the departure of volatile clathrate compounds and/or to the low temperature degradation of side chains. It also may be related to the evaporation of prop-2-enenitrile, the fragment of free diisocyanate component, added in a slight excess (≈5%) to the reaction mixture.

The TG curve refers to one-step process decomposition. As the sensitivity of DTG curves is higher than that of TG ones, in Fig. 7a and b are presented the corresponding DTG decomposition curves for the segmented polyurethane sheets and films, respectively. The inspection of DTG curves refers to multiple processes, taking place simultaneously. The first step is most probably due to degradation of the hard segments, i.e., to the splitting of the urethane bonds [33,34]. The initial decomposition temperature (not shown in Fig. 6) within experimental error is about the same for the polyurethanes based on both macrodiols of almost the same molecular mass, but of different polycarbonate chain constitutions, for $R = 1$ and $R = 10$. The decomposition onsets for the polyurethane sheets based on polycarbonate diol T4671 are $300 \pm 5\,°C$, with the corresponding peak temperatures at $345 \pm 2\,°C$. The film stability is somewhat lower ($T_{onset} = 286 \pm 8\,°C$, with the corresponding peak temperatures at $320 \pm 5\,°C$). The decomposition onsets for the polyurethane sheets based on polycarbonate diol T5651 are $310 \pm 10\,°C$ and the decomposition onsets for the polyurethane films based on same polycarbonate diol are $305 \pm 5\,°C$. DTG curves of polyurethanes based on T5651 macrodiol show at least two superposed DTG maxima in the temperature range of 340–370 °C (up to mass loss of about 25%, see Fig. 7). DTG curves of elastomers made from polycarbonate diol T4671 show broader peak, without separation. It seems that the decomposition mechanism depends on the type of the building units in the macrodiols. On the other hand, the absence of chain extender does not affect essentially the thermal stability of the prepared samples. DSC curves show that the decomposition of all the samples is accompanied by endothermic reactions, probably as consequence of the CO_2 evolution due to different initial cleavage pathways of the urethane linkage as was proposed in polyurethanes based on isophorone diisocyanate, carboxylated polyurethane anionomers or by the degradation of side chains [2,20,35]. The decomposition of the elastomers is almost complete up to 400 °C, with about 5% residue. However, in all prepared unfilled samples in the temperature range of 400–500 °C, an additional mass loss of 0.5% is observed. Practically the process is detectable only in DSC curves showing a board exothermic peak(s) even in a nitrogen atmosphere and may belong to some oxidative processes. They probably result also in CO_2 evolution and may occur in compounds containing oxygen. The amount of the carbonaceous residue around 500 °C is about 4%. The thermal TG/DTG and DSC curves of the polyurethane sheet based on polycarbonate diol T5651 and rein-
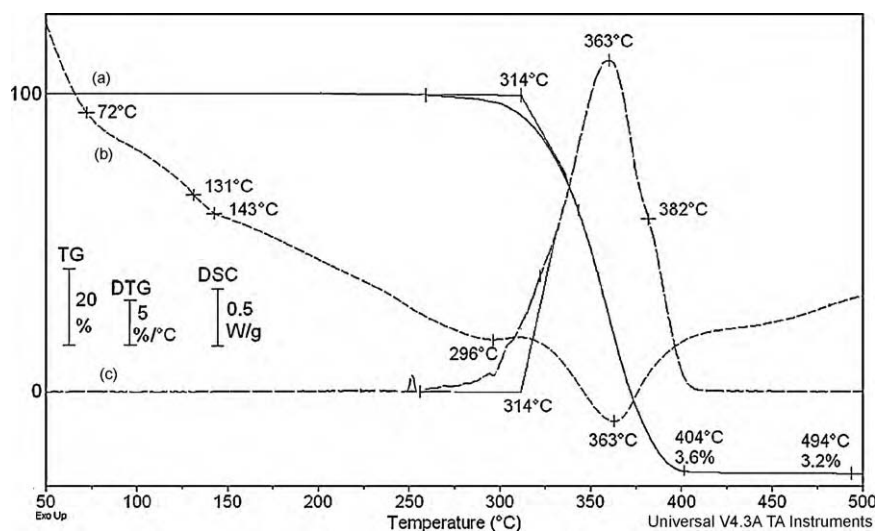

Fig. 8. The simultaneous (a) TG, (b) DTG and (c) DSC curves of the polyurethane nanocomposite sheet, based on polycarbonate T5651 and 1 wt.% of montmorillonite filler. Heating rate was 20 °C/min.
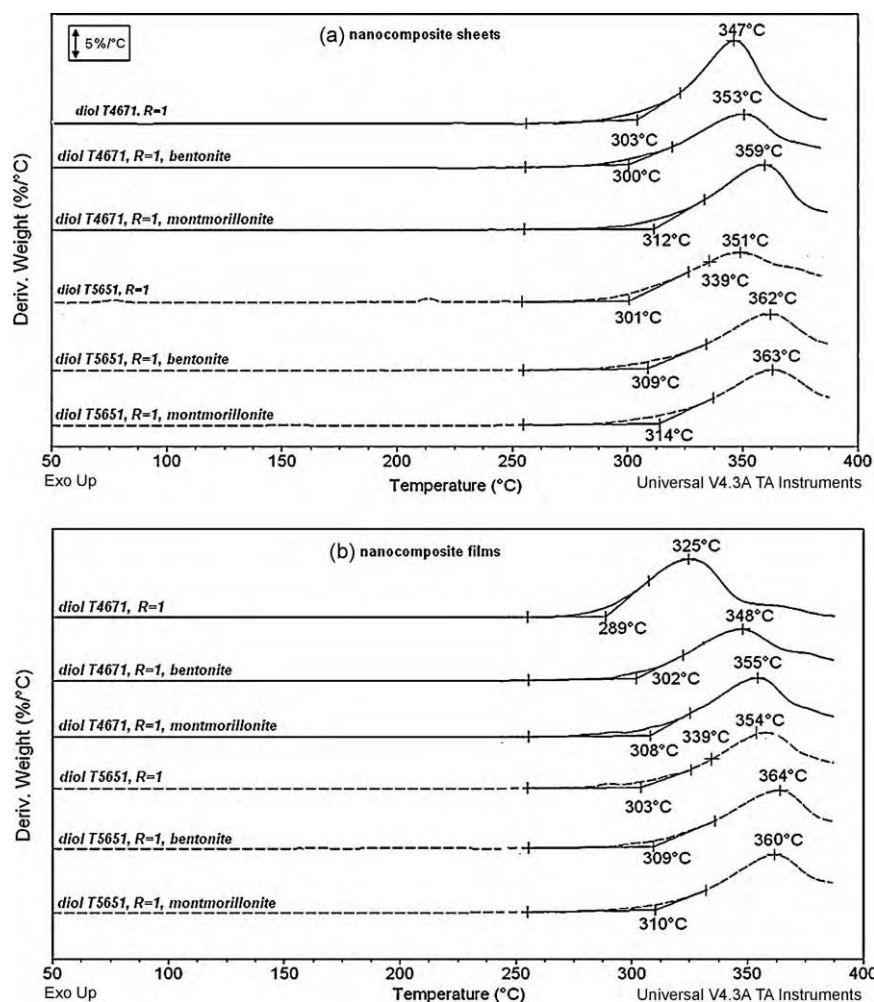
Fig. 9. DTG curves of elastomers based on polycarbonate diols with different chain structure (T5651 and T4671) and organically modified montmorillonite and bentonite obtained in the form of (a) sheets and (b) films. Heating rate was 20 °C/min.

forced with 1 wt.% of montmorillonite nanoparticles are presented in Fig. 8.

The intensity of the exothermic reactions above 400 °C is lower in the elastomers with filler. In spite of the fact that montmorillonite does not suffer any thermal change in the whole measured temperature range, the residue is less by about 1% compared to the mass of the residue of the unfilled sample. The lower residue is in accordance with the higher speed of the decomposition in the temperature range of 300–400 °C (see DTG peaks in Figs. 6 and 8). The influence of filler on the thermal behavior of the prepared hybrid materials was investigated for samples with $R = 1$. The corresponding DTG curves are presented in Fig. 9a and b. The thermal stability of the filled samples is a little bit higher for both sample forms. For obtained polyurethane nanocomposite sheets, the decomposition onsets (see Fig. 9) are 307 ± 7 °C with the corresponding DTG peak temperatures at 358 ± 3 °C. The stability of polyurethane hybrid materials in the film form is somewhat lower, with decomposition temperatures at 306 ± 4 °C and corresponding DTG peak temperatures at 356 ± 8 °C. The two-step decomposition of the polymers containing different constitution units partially vanishes. The course of the curves is much more alike, referring to a more uniform decomposition mechanism. On the basis of DTG curves it may be concluded that addition of clay particles with layered structure stabilizes polyurethane materials and, in this case, the thermal decomposition is less influenced by the sample form. Similar stabilization effect was observed in different kinds

of polyurethanes reinforced with organically modified montmorillonites [36,37].

4. Conclusions

One of the objectives of this research was to demonstrate the effect of the addition of modified clay particles to a polyurethanes on the thermal stability of polyurethanes based on hexamethylene-diisocyanate, aliphatic polycarbonate diol and 1,4-butanediol. On the basis of MTDSC results, thermal transitions observed in the polyurethanes include the glass transition of soft segments, relaxation of chain segments in the diffused interface between soft and hard segment phases, and multiple endotherms associated with hard segment domains. The glass transition temperature of soft segments for all samples is about −32 °C. On the basis of DTG results, it can be concluded that the absence of chain extender does not affect essentially the thermal stability of the prepared samples. On the other hand, it seems that the decomposition mechanism depends on the type of the building units in the macrodiols. The decomposition and the corresponding peak temperatures of the samples containing montmorillonite or bentonite particles are shifted to slightly higher temperature compared to that of unfilled samples. Addition of 1 wt.% of fillers stabilizes the structure of polyurethane materials, and, in this case, the thermal stability is less influenced by sample form preparation.

Acknowledgements

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