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Study on the Influence of Melt Processing on Segmented Polyurethanes Morphology

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Summary: A study on thermoplastic polyurethanes (TPU) is described. The investigation focuses on morphology of TPU parts depending on processing conditions and its relation with mechanical and thermal properties. It was found that TPU materials present different crystalline structures depending on chemical composition and melt processing conditions during part manufacturing. Due to that fact, strong variations in mechanical and tribological properties are expected.

Keywords: micromechanical behaviour; morphology; processing conditions; thermoplastic polyurethane; viscoelastic properties

Introduction

Thermoplastic polyurethanes are elastomeric copolymer materials. One block of polymer chain consists of long and flexible polyester or polyether diol and is usually amorphous. This is the so called soft segment responsible for the elastomeric character of polymer.

The second block of the copolymer is formed by the reaction of diisocyanates with low-weight diol or triol chain extender and its so-called hard segment (Figure 1). Because of the polar nature of urethane group hard segments are able to create physical intermolecular associations resulting in phase separation, which has direct influence on domain structure and lead to different types of crystalline morphology. The created network structure is thermally reversible but provides a cross-linked nature (hydrogen bonding), besides that the hard segments are also playing the role of reinforcement.

Each TPU has a melting temperature range above which it is fluid, suitable for processing by methods and equipment commonly used for thermoplastics. Below the melting temperature range TPU is solid, flexible, elastic material often very competitive to replace chemically cross-linked thermoset rubber of similar hardness and resistance to mechanical loading and environmental conditions.[1,2]

The state of the art according to literature, as well as experience, presents that the morphology of the TPU part is not taken into consideration at all. It is well known that the structure of macromolecules is responsible for the first reaction of the material in response to stress. The structure is directly linked with the micromechanical process of deformation and fracture, and in dependence on the real local morphology, most of the micromechanical processes are highly localized. It need to research the structure development and to understand it's consequences. Therefore every study on the mechanical properties should be coupled with a detailed investigation on morphology.[3–5]

The morphology for given material can be influenced by several physical factors such as the crystallization temperature, the cooling profile or the thermal history of the sample. Also it is known that the crystalline memory can be erased by melting the polymer at a sufficiently high temperature for a certain period of time, and due to that fact it is strongly related

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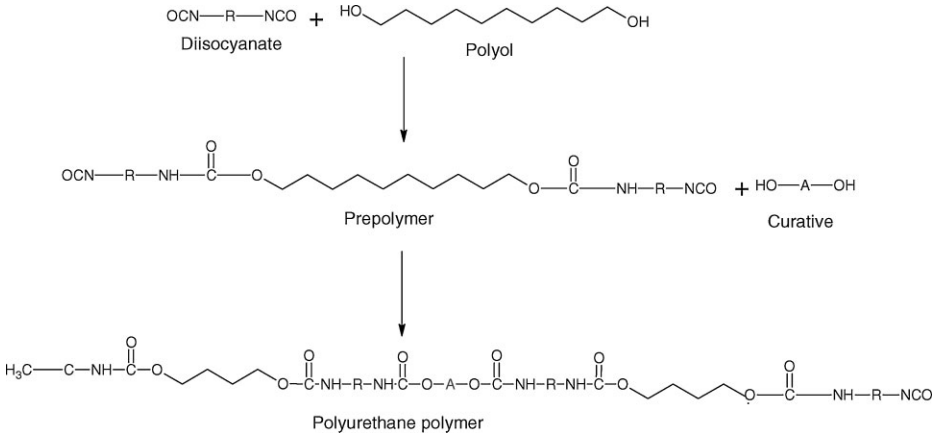

Figure 1.
Formation of polyurethane pre - polymer and chain extension of a polyurethane polymer.

to the processing conditions during TPU manufacturing.[6–8]

Based on preliminary experiments, it is confirmed that the processing conditions influence the polymer structure, and structural variations at different manufacturing parameters are observed. Better understanding of those structures and mechanisms of their transformations have a key role in basic understanding and improving the viscoelastic and termomechanical properties of polymer materials and to decreasing predispositions to failure.

In this work, the morphology of commercially available TPU material was investigated and compared with simulations of the processing conditions done on the raw TPU material.

The properties were examined by light microscopy, scanning electron microscopy and combined with data obtained from DSC measurements.

Experimental Part

Material

As the example and documentation of morphological behavior, a standard TPU O-Ring (94 Shore A) based on MDI as hard segment was investigated. The TPU virgin material used for systematic morphology investigation is commercially available grade, based on MDI as hard segment and caprolactone with HQEE chain extender as a soft segment and has the same hardness.

DSC Studies

DSC studies of TPU samples were carried out on DSC 821^e, Mettler – Toledo device. In order to receive comparable results all samples were prepared with the same procedure. Cylindrical specimens of Ø3 mm were punched from part and thin, flat slices of mass $5 \pm 0{,}1$ mg were prepared using microtome. Ready samples were placed in DSC 40 µl aluminum crucible, sealed by aluminum lid with hole on the top for degassing, and put in the device. Specimens were heated in the temperature ranges 30–270 °C, cooled down and heated one more time, each dynamic segment was separated by 2 minutes of isothermal conditions. Measurement was carried out with heating rate of 20 K/min in nitrogen purge gas atmosphere with gas flux of 60 ml/min. During DSC measurement sample melt and crystallize again, due to that fact TPU processing conditions simulations at 230 °C and 270 °C were performed and created morphologies were investigated step by step.

Light Microscopy Investigations

A Zeiss Axioplan 2 light microscope, equipped with AxioCam digital microscope

camera was used to observe morphology of TPU samples. The specimens for investigation were sectioned with automatic rotary cryo-microtome Leica RM 2165. The slice thickness was set on 10 μm and they were cut at about −100 °C. To be able to observe complete cross-section, low magnifications were applied. Light microscopy was performed in order to have an overview of present material structures and to determine area for more detailed investigations by mean of SEM.

SEM Investigations

Morphology of raw and processed TPU was observed by scanning electron microscope type LEO Gemini 1525. Structural investigation using SEM requires several steps of preparation.

First, all samples were flattened using microtome and then immersed in DMF for 20 minutes for selective etching. The same etching conditions were applied to all of specimens. Hard and soft segments of TPU material are different sensitive to etching agent, due to that fact it is possible to remove part of matrix and make different structures, present in bulk material, visible. Before investigations surface of the samples was pre-treated by sputtering Au/Pt using sputter-coater Bal-Tec type Med 020 in order to make non-metallic sample electrically conductive. The conductive layer was applied with use of argon gas under vacuum conditions (5×10^{-2} mbar) and small electric field around 20 mA. After pre treatment the remaining structures were examined.

SEM was used to confirm the presence of spherulites, globular structures, aggregates and to investigate its size.

Results and Discussion

At the first step preliminary morphology investigations of commercially available MDI based TPU part processed in standard conditions and out of specification were done by light microscopy.

The visual investigation was performed on the cross section of the part in polarized light. The micrographs present various structures depending on the processing conditions of each part. Parts manufactured according to standard parameters at temperatures below 260 °C (part A) shows inhomogeneous morphology, consisting of crystalline and transparent areas. The part processed out of specification, at temperatures above 260 °C (part B) is completely transparent, which means that there are no visible crystalline domains present. Both of the investigated parts are exactly the same material manufactured only with different processing temperatures.

The pictures below present magnifications of the morphology visible in half 1 and half 2 of the part A investigated by light microscopy and compared with SEM micrographs.

The sample morphology in half 1 of the part present crystalline structure with spherulite diameter amounting to 20 μm, which is confirmed by SEM. Half 2 on micrograph investigated with higher magnifications does not show big size spherulitic structures just residual small size domains. In order to confirm observations done by light microscopy and to investigate melting behaviour of different types of present on the picture domains, DSC measurements of parts were taken. Due to the fact that in part A two different structures were observed, both parts were divided into two parts, half 1 and half 2 (Figure 2) and for each of them DSC measurements were conducted respectively.

Part A on the micrographs shows two different types of morphology and these results are confirmed by DSC. The curve received from half 1 of the part presents a strong peak at 240 °C, representing melting of the hard segments, curve coming from investigate second part of the TPU sample shows one peak at 240 °C and a new peak appears at the temperature around 205 °C. Heating of part B gave the same result for half 1 and 2 and presents a residual peak at 240 °C and a well visible peak at around 205 °C. This suggests that during processing of the part in the temperatures above 260 °C, the crystalline domains coming

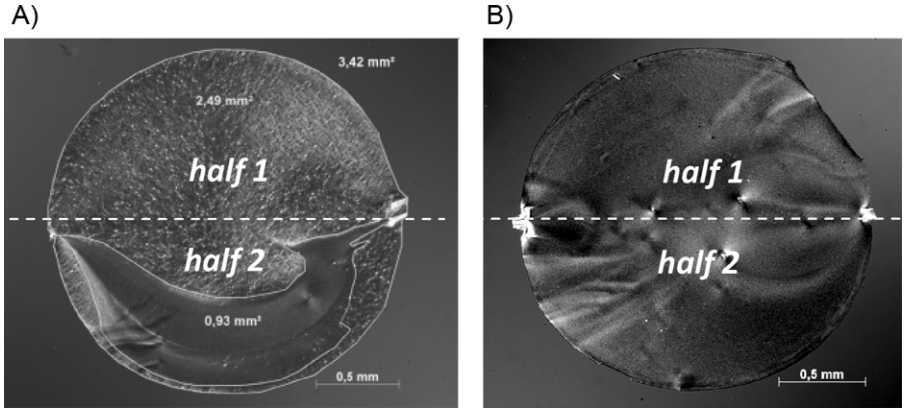

Figure 2.
Micrographs of TPU part, processed with standard conditions (A); processed out of specification (B); transmission light microscope, (Zeiss Axioplan 2), sample thickness: 10 μm.

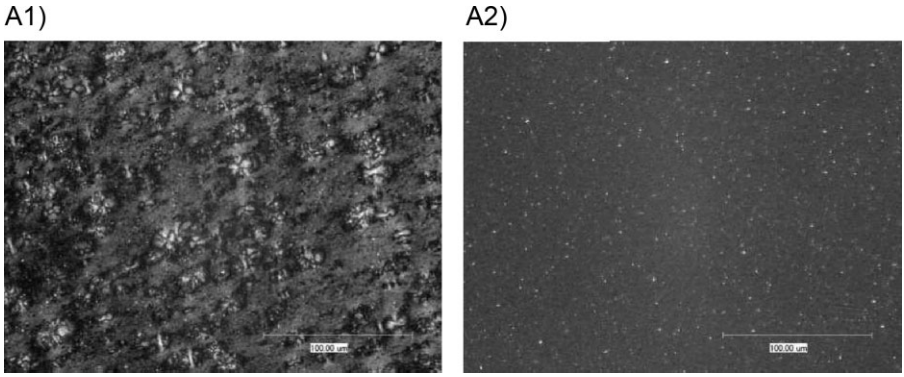

Figure 3.
Micrographs of the crystalline (A1) and transparent (A2) area of TPU part, processed with standard conditions; transmission light microscope (Zeiss Axioplan 2), sample thickness: 10 μm.

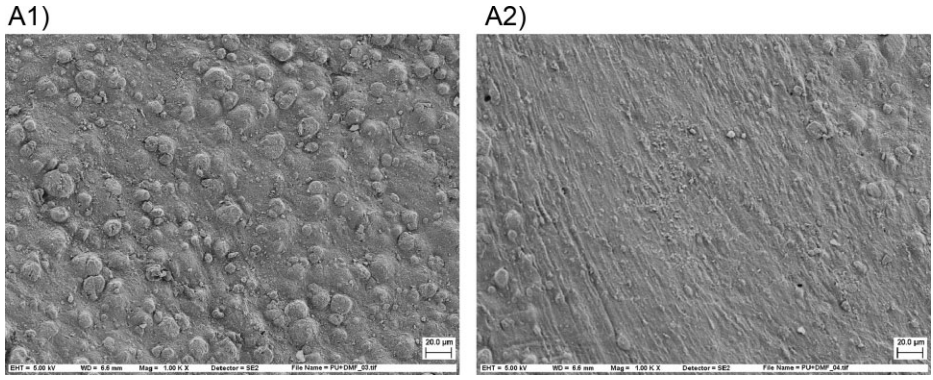

Figure 4.
Micrographs of the crystalline (A1) and transparent (A2) area of TPU part, processed with standard conditions; SEM (LEO Gemini 1525), Au/Pt sputtered (coater Bal-Tec type Med 020), 40 s.

from hard segments disappear and new, different types of structures with lower melting temperature range are created. Part A was processed with standardised processing temperature, and the transparent zone like in part B is present. This can be the result of local overheating coming from e.g. high shear during melt processing.[9,10]

To confirm and understand the mechanism of morphology transformations, an investigation of TPU parts processing conditions was performed on commercially available, MDI based raw material (raw pellets, granules manufactured at T = 230 °C, melted and recrystallized pellets at T = 270 °C) and compared with the manufactured part. First visual and thermal investigation were performed.

The investigated TPU shows different structures depending on the thermal history of the sample. Temperature conditions impact the size, number and shape of structures crystallised from melt. It is observed in raw TPU pellets etched with DMF that two types of globular structures are present in the sample and they different from each other by size and shape. The domains do not fill whole volume but are isolated from each other and contact is present only in some areas (structures are very well visible, the etching agent probably could penetrate the material better due to less compression after synthesis, than in case of granules manufactured in extruder). These spherulites have melting temperatures of 217 °C and 235 °C according to DSC curve. Granular structures type I appear in form of bigger domains and structures type II in from of small domains. Heating of the sample till 230 °C makes significant changes in the structure. Due to the light microscopy spherulites are a little smaller but still dense, SEM shows that two kinds of domains are still existing but the big structures (type I) are already deformed. Heating up raw material till 270 °C changes morphology completely, micrographs present that there are no more present crystalline domains I and II but SEM indicates presence of another third type of very small structures, which melt at temperature of 200 °C.

Figure 8 presents a comparison of heating scans of virgin granules and of the same material after two different processing conditions, the results confirm observations done by SEM. Strong differences in melting behaviour are observed. Melting temperatures for virgin granules amount to 217 °C and 235 °C, whereas material after processing simulations at

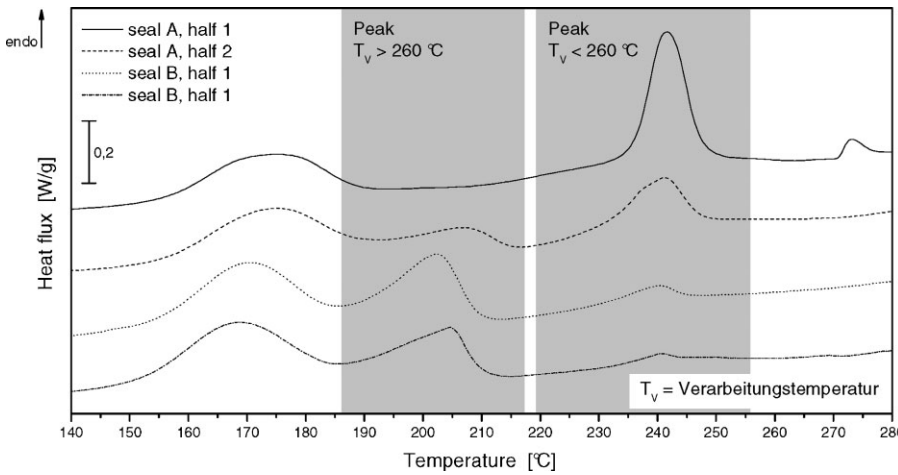

Figure 5.
DSC measurement of TPU part, processed with standard conditions (A) and out of specification (B); 1st heating, heating rate: 20 K/min, gas flux: N_2 (60 ml/min), sample mass: 5,0 ± 0,1 mg.

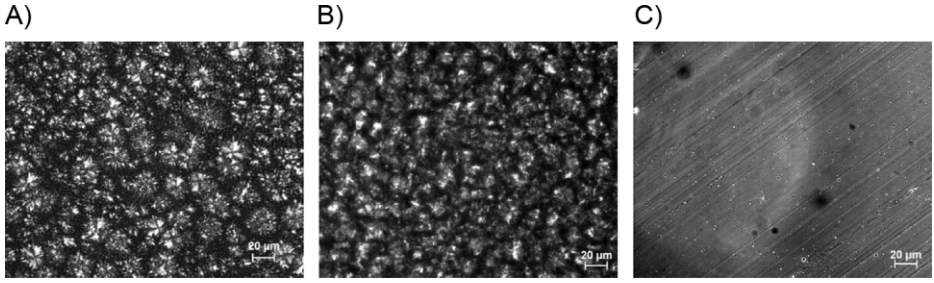

Figure 6.
Micrographs of TPU virgin material before processing (pellets) (A), processed at T = 230 °C (granules) (B), processed at T = 270 °C (melted and recrystallized pellets) (C); transmission light microscope (Zeiss Axioplan 2), sample thickness: 10 µm.

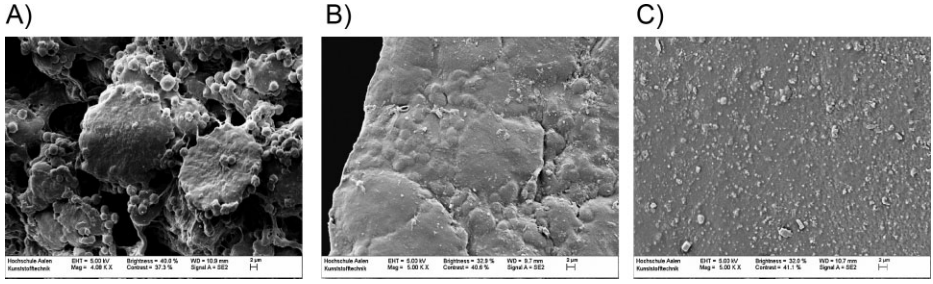

Figure 7.
Micrographs of TPU virgin material before processing (A), processed at T = 230 °C (B), processed at T = 270 °C (C); 20 minutes etching in DMF; SEM (LEO Gemini 1525), Au/Pt sputtered (coater Bal-Tec type Med 020), 20 mA, 40 s.

230 °C shows dominant melting peak at 239 °C. Heating scans of material heated till 270 °C presents melting peak at around 200 °C.

It is observed that different thermal loadings of TPU raw material makes changes in morphologies of hard segments crystallites. The treatment of virgin granules with

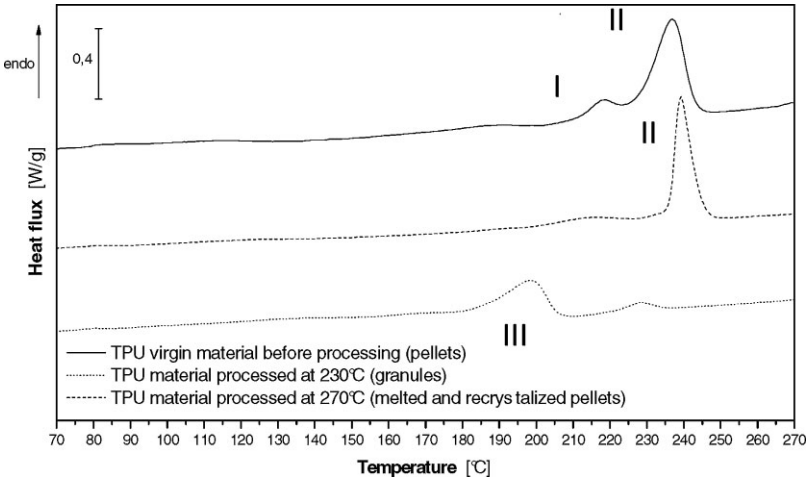

Figure 8.
DSC measurement of TPU virgin materials processed with different conditions; 1st heating, heating rate: 20 K/min, gas flux: N_2 (60 ml/min), sample mass: 5,0 ± 0,1 mg.

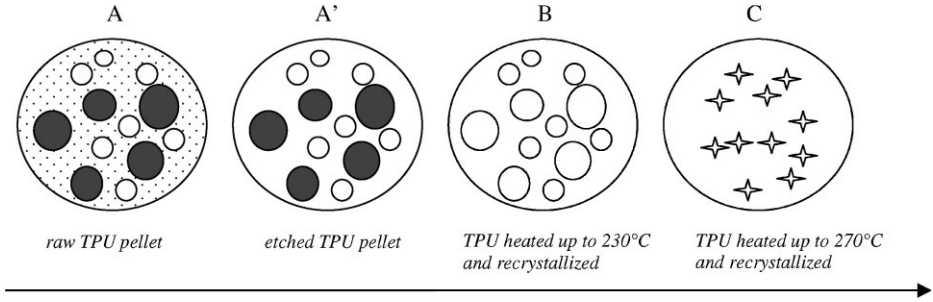

Figure 9.
Model of suspected morphology transformations in TPU during thermal loading; big cylindrical domains represent crystalline structure type I, small cylindrical domains represent crystalline structure type II and asteroids represent crystalline structure type III (Figure 8).

low temperatures (T = 230 °C) presents increase of hard segments type II which can be result of annealing of not melted hard segment crystallites and shows also decrease of HS type I which can be a possible recrystalization of type I into type II crystalline domains. Sample after higher thermal loading (T = 270 °C) melts in lower melting range and it is probably result of transformations of crystalline domains I and II into third different crystalline type. According to these observations (Figure 6 and Figure 7) simple model of morphology transformations was prepared (Figure 9).

Conclusion

According to visual and thermal investigation the resulting morphology of thermoplastic polyurethane elastomers strongly depends on thermal conditions applied during processing. In the TPU parts investigated in this work two different morphologies were visible. Due to processing simulations performed on a virgin material the content of different crystallite types were detected depending on the maximum thermal load. Virgin material contains crystallites type I and II. If material is processed at temperature near 230 °C high content of crystallites type II could be observed, applying higher temperatures to the material destroy structures type I and II and a new domain with lower melting temperatures seems to be present. Combining different investigation methods there is a need to clarify the nature and development mechanism of existing structures.

[1] C. Rader, R. Fuest, J. Dick, *Rubber Technology*, Hanser, Münich **2001**, 239–281.
[2] A. Frick, A. Rochman, Characterization of TPU - elastomers by thermal analysis (DSC). *Polymer Testing*, *23*, **2004**, 413–417.
[3] J. Foks, G. Michler, Electron - Microscopical Investigation of the Morphology of Segmented Polyurethanes. *Journal of Applied Polymer Science*, *31*, **1986**, 1281–1291.
[4] G. Michler, Micromechanics of Polymers. *Journal of Macromolecular Science, Part B: Physics*, *38*, **1999**, 787–802.
[5] M. Z. Yue, K. S. Chian, Mechanical Properties and Morphology of Thermoplastic Polyurethane Elastomer with Pol(vinylidene fluoride) Blends. *Journal of Applied Polymer Science*, *60*, **1996**, 597–603.
[6] P. Supaphol, J. Spruiell, Crystalline Memory Effects in Isothermal Crystallization of Syndiotactic Polypropylene. *Journal of Applied Polymer Science*, *75*, **2000**, 337–346.
[7] G. Pompe, A. Pohlers, P. Pötschke, J. Pionteck, Influence of Processing Conditions on the Multiphase Structure of Segmented Polyurethanes. *Polymer*, *39*, **1998**, 5147–5153.
[8] E. Govorcin, V. Rek, A. Sendijarevic, K. C. Frisch, DSC Study of Morphological Changes in Segmented Polyurethane Elastomers. *Journal of Elastomers and Plastics*, *32*, **2000**, 162–181.
[9] A. Frick, A. Rochman, Einfluss der Herstellbedingungen auf die Morphologie und Gebrauchseigenschaften von Hydraulikdichtungen aus TPU Tagungsbuch: ISC Internationale Dichtungstagung Stuttgart 5.-6. **2004**, p. 524–531.
[10] A. Frick, A. Rochman, P. Fleszar, Moderne, Qualitätsprüfungen für Formdichtungenin: Untersuchung und Anwendung von Dichtelementen Essen: Vulkan **2005**, p. 253–259.

