PREPARATION AND PRPOPERTIES OF ENERGETIC THERMOPLASTIC ELASTOMERS FROM GAP AND POLY-BAMO

Thomas Keicher, Manuela Dörich, Ulrich Förter-Barth, Carolin Grünfelder, Horst Krause, Uwe Schaller, Sarah Steinert

Fraunhofer Institut für Chemische Technologie ICT, 76327 Pfinztal, Germany
thomas.keicher@ict.fraunhofer.de

ABSTRACT

This work presents the preparation and analysis results of Energetic Thermoplastic Elastomers (ETPEs), which have been prepared from commercial available GAP and Poly-BAMO via chain elongation with difunctional isocyanates and chain extenders. The aim of this work was to evaluate the influence of different chain extenders and a variation of the diisocyante on the melting temperature of ETPEs. Chain extenders that have been evaluated were 1,4-Butanediol (BDO), N,N´-Dimethyl urea (DMU) and Hydrochinone (HC). 2,4-Toluene diisocyanate (TDI) and 1,4-Phenylene diisocyanate (PHDI) have been used as diisocyanates. Twelve compositions have been prepared and analysed by DSC and viscometer. The variations on chain extenders with BDO, DMU and HC did not show any significantly improvement in melting temperature. All ETPEs with high Glycidylazide polymer (GAP) content of 65 % and chain extenders showed decreasing viscosity and softening before the melting temperature. The ETPEs with GAP contents of less than 50 % did not show this softening behaviour. When oligomeric Poly-BAMO-urethanes have been used for chain elongation two samples have shown higher melting points of 86 and 87 °C at DSC and only slightly decrease of the viscosity and softening before the melting temperature even with high GAP content of 65 %. PHDI did not show any significantly influence on the melting point.

INTRODUCTION

Modern solid gun and rocket propellants consist of an elastomeric binder and particulate solid energetic compounds. The binder immobilizes the solid fillers and fixes a defined geometrical shape for the propellant geometry which influences the combustion behaviour. During the combustion the binder acts as fuel. Classical binders are from cast-cured type which means that they are processed by addition of a curing agent such as isocyanates. After adding the curing agent to the formulation the propellant mixture has to be cast into its final shape within a short period of time (pot life time). This restriction is a disadvantage for the use of these materials. An alternative processing method is offered by Thermoplastic Elastomers (TPEs). For processing, in principle they are heated above their melting point, then the solid fillers and additives are added and homogenized. Following the compositions are extruded, injection moulded or pressed to get the desired geometry and then allowed to cool down below the melting point for solidifying. Another technique is the use of solvents for processing.

In this case the TPEs are dissolved and mixed with the solid fillers. After evaporation of the solvent the composition returns to its solid but elastic mode and builds a granular product which can be further processed by pressing.

Most TPEs are block copolymers of type $(AB)_n$ structure, where A and B are the hard and the soft segments respectively. The physical properties of TPEs are due to their composition of hard blocks and soft blocks. The hard segment (glassy or semi crystalline at room temperature) gives its thermoplastic behaviour, whereas the soft segment (rubbery at room temperature) gives the elastomeric behaviour. At room temperature the polymer chains of the hard blocks built inflexible hard domains by reversible interaction such as dipole-dipole interactions, hydrogen bonding, etc. The hard blocks act like curing agents in cast cured binders so crosslinking the elastomeric blocks. On heating above the melting temperature or dissolving in a solvent, the interactions of the hard blocks are overcome and the binder becomes liquid for processing operations.

The following Figure 1 shows a schematic model of TPEs.

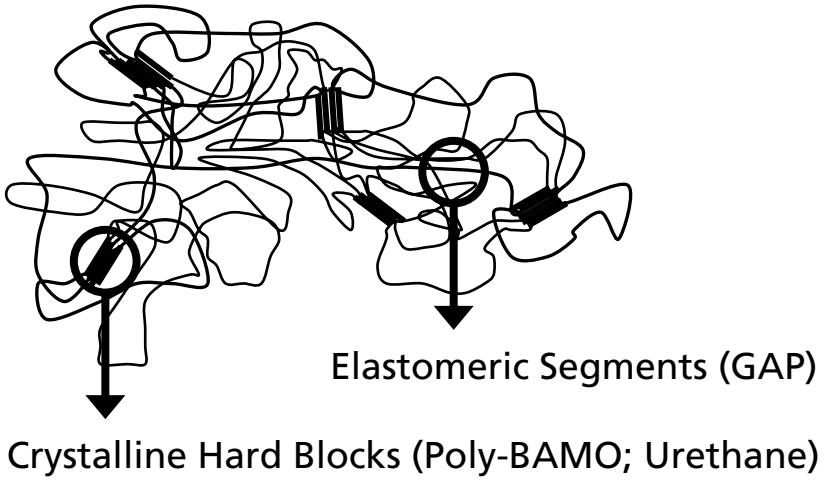

Figure 1: Schematic structure model of TPE

Energetic TPEs are processed like conventional TPEs with an additional advantage as they have energetic substituents like nitro- ($-NO_2$), nitramino- ($-NNO_2$), nitrate ester ($-ONO_2$), difluoramino ($-NF_2$) or azido groups ($-N_3$). Nitro- and nitramino-groups in binders give poor mechanical properties and high glass transition temperatures. The nitrate ester group offers a good oxygen balance however the long term stability and the low self ignition temperature appears as disadvantages. The difluoramino group is hazardous chemistry for synthesis and additionally the combustion products (HF) are toxic. Therefore we choose the azido group for energetic substituents. Azido groups are not as bulky and polar as nitro- or nitramino- groups which influence negatively the mechanical properties and also decompose exothermically very quickly at temperatures above 190 °C evolving nitrogen. The most popular energetic azido binders are GAP, Poly-AMMO and Poly-BAMO. Poly-BAMO is solid at room temperature and it melts at temperatures between 50 to 70 °C. Additionally it is very energetic due to its high nitrogen content (50 wt%) from the azido groups and therefore it is the most common

hard block that is used in ETPEs. Unfortunately Poly-BAMO is not commercial available and has to be synthesized. One popular soft block that is used is GAP because of its low viscosity ($2.4x10^3$ cps at 25 °C), positive heat of formation (+ 957 kJ/kg) and its low glass transition temperature (Tg = -48 °C) [1]. GAP is commercial available and this fact also favours GAP for its use as soft block in ETPEs.
This work presents the preparation of ETPEs from commercial available GAP and from Poly-BAMO. With these precursors ETPEs can be prepared via chain elongation of energetic polymers (GAP, Poly-BAMO) with difunctional isocyanates.
In our former work [2] this route proved to be a very useful method because it allows easy scale up and the properties of the ETPEs can be influenced in a wide range.
J. Sanderson [3] and B. Wardle [4] published a special procedure to get copolymers with high molecular weights and high melting points. The synthetic method uses isocyanate chain linking/extension. A mixture of crystalline and amorphous hydroxyl terminated difunctional polyethers are end capped with TDI. The polymers are then linked and chain extended with a suitable diol normally BDO or with an oligomeric urethane. The reaction is carried out in an inert solvent with a catalyst at ambient temperature.

The following Figure 2 shows the synthesis of the ETPEs.

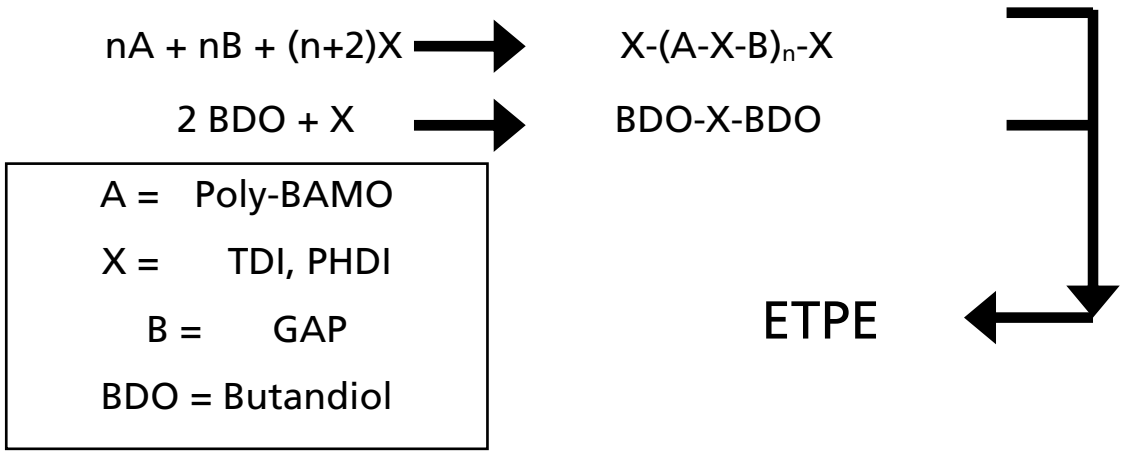

Figure 2: Synthesis of the ETPEs

RAW MATERIALS AND ANALYSIS EQUIPMENT

The ETPEs were prepared from commercial available GAP-Diol from SME France with the following analytical data.

Table 1: Analytical data of GAP-Diol

Molecular weight measured by GPC (in THF)			
Mw	Mn	PDI	Mp
3946 g/mol	2455 g/mol	1.61	2939 g/mol
Equivalent weight per mole OH-groups			
1180 g/mol			

Poly-BAMO has been synthesized from the commercial available starting material Tri-bromo-pentaerythritol via a three step synthesis, following in generally some published methods [5] [6] [7]. The following Table 2 shows the analytical data for the Poly-BAMO.

Table 2: Analytical data of Poly-BAMO

<table>
<tr><td colspan="4">Molecular weight measured by GPC (in THF)</td></tr>
<tr><td>Mw</td><td>Mn</td><td>PDI</td><td>Mp</td></tr>
<tr><td>8766 g/mol</td><td>3428 g/mol</td><td>2.56</td><td>8770 g/mol</td></tr>
<tr><td colspan="4">Thermal analysis by DSC</td></tr>
<tr><td colspan="2">Melting point</td><td>Decomposition temperature</td><td>Heat of decomposition</td></tr>
<tr><td colspan="2">78.5 °C
(peak max)</td><td>247.15 °C
(peak max)</td><td>2316 J/g</td></tr>
<tr><td colspan="4">Equivalent weight per mole OH-groups</td></tr>
<tr><td colspan="4">3250 g/mol</td></tr>
</table>

2,4-Toluene diisocyanate (TDI; T39853), 1,4-Phenylene diisocyanate (PHDI; 262242), Boron trifluoride diethyl etherate (216607), Dibutyl tin dilaurate (D22; 291234), Hydrochinone (HC; H9003) and N,N´-Dimethyl urea (DMU; 15450) has been used as received from chemical supplier Aldrich. The chain elongation agent 1,4-Butanediol (BDO) and the solvent Dichloromethane (DCM) was purified by drying and distillation prior to use.

Differential scanning calorimetry (DSC) was done to measure the glass transition temperatures. The measurements were performed on a TA instruments Q 1000 using aluminium pans. Scans were carried out on each sample at scan rates of 5 °C/min, under nitrogen flux, in the -80 to 20 °C range. Thermal gravimetric analysis was done TGA Q 5000, TA Instruments

The viscosity measurement was done by a rotational rheometer (Physica Rheometer MCR 501).

PREPARATION OF THE ETPE

For the preparation of the ETPEs the published methods of Sanderson [3] and Wardle [4] has been modified. The classical chain extender that has been used is BDO. Besides this we also used the chain extenders HC and DMU. TDI is the most used diisocyanate in ETPEs. In this work we used TDI and additionally PHDI in one specific composition. The aim for these variations was to increase the melting temperatures of the ETPEs and also to reduce the necessary content of Poly-BAMO which is not commercial available. The use of the chain extender DMU was due to the expected additional intermolecular hydrogen bonding interactions that would increase the melting temperature of the final ETPE. The highly symmetrical 1,4 substituted PHDI and HC should give an increase of crystallinity and higher melting temperatures.

The reaction was carried out in Dichloromethane (DCM) and the reaction was promoted by the catalyst Dibutyl tin dilaurate (D22).

The ETPEs were prepared from two solutions in which the components were diluted and reacted for a certain time after which the solutions have been combined to finalize the reaction. These two solutions were prepared in variations to evaluate the influence of three different preparation approaches.

Variation 1: Sample 1 to 6

Solution 1: GAP + Poly-BAMO + TDI (excess; Rf = 1.5)
Solution 2: Chain extender BDO or DMU + TDI (deficit; Rf = 0.5)

Variation 2: Sample 7 to 10

Solution 1: GAP or Poly-BAMO + TDI (excess; all TDI for the final composition)
Solution 2: Chain extender GAP or HC

Variation 3: Sample 11 to 12

Solution 1: GAP + some Poly-BAMO + TDI (excess; Rf = 1.5)
Solution 2: Chain extender Poly-BAMO + TDI or PHDI (deficit; Rf = 0.5)

EXPERIMENTAL – PREPARATION OF ETPES

The components given in following Table 3 are dissolved in DCM (as 5 wt% solution) and stirred at room temperature. The reaction progress was monitored via IR spectroscopy (decreasing or disappearance of the isocyanate band). After the reaction

Table 3: Preparation details for ETPEs

Sample	Solution 1			Solution 2	
	GAP [wt%]	Poly-BAMO [wt%]	TDI [wt%]	BDO [wt%]	TDI [wt%]
1	60.0	27.6	7.5	2.5	2.4
2	60.0	20.5	9.7	5.0	4.8
3	65.0	22.4	7.7	2.5	2.4
4	65.0	15.3	9.9	5.0	4.8
5	60.0	27.5	7.5	DMU 2.5	2.5
6	65.0	22.2	7.8	DMU 2.5	2.5
7	65.1	21.7	10.0	HC 3.2	
8		51.1	4.4	GAP 44.5	
9		51.1	4.4	GAP 44.5	
10		51.1	4.4	GAP 44.5	
11	65.0	0.5	5.1	Poly-BAMO 29.0	0.4
12	65.0	0.5	5.1	Poly-BAMO 29.0	PHDI 0.4

was finished (normally after around 48 hours) solution 1 and solution 2 were combined and stirred until the reaction has been finished (no isocyanate band left at IR spectra).

After the reaction was finished, the solvent was evaporated and the solid products have been washed with methanol. The products were characterized by viscometer measurements, DSC and TGA. The following tables give the preparation details and the results from DSC analysis.

Table 4: DSC results from ETPE´s

Sample	Tg (DSC) Mid-point [°C]	Melting point (DSC) onset [°C]	Melting point (DSC) max. [°C]	DSC Decomposition energy [J/g]	TGA Mass loss 1. step [%]
1	-30.3	73.3	78.3	2359	41.24
2	-29.1	71.1	77.8	2200	40.65
3	-28.5	72.7	73.9	2300	41.16
4	-26.0	71.5	75.2	2013	41.20
5	-31.5	72.6	77.0	2388	40.46
6	-30.3	72.1	77.4	2373	40.15
7	-29.9	68.5	69.1	2277	5.02 + 37.00
8	-44.6	69.1	77.3	2651	40.80
9	-45.3	68.0	76.3	2623	40.40
10	-39.5	68.0	77.3	2616	40.70
11	-36.6	86.3	91.6	2538	40.00
12	-35.5	87.1	89.8	2509	40.00

The DSC results show that the melting points of the ETPE´s are between 68 to 87 °C and the glass transition temperatures (Tg) are between -26 to -45 °C. The Tg´s for samples 1 to 7 are all between -26 to -30 °C but the samples 8 to 12 showed lower Tg´s between -35.5 to -45 °C. Samples with low Tg´s are prepared with low amounts of diisocyanates which lead to low contents of urethane bonds in the ETPEs. Urethane bonds and their hydrogen bonding decrease the flexibility of the ETPE chains and increase the Tg.

The majority of melting points measured by DSC (onset) are around 70 °C. The variations on chain extenders with BDO (2.5 % or 5.0 %), DMU and HC did not show any significantly improvement in melting temperature. Only samples 11 and 12 show higher melting points of 86 and 87 °C. These samples have been prepared from Poly-BAMO which had already reacted with diisocyanate to build oligomeric Poly-BAMO-urethanes (solution 2). These oligomeric Poly-BAMO-urethanes might have higher tendency for crystallisation in the ETPE than randomly separated the Poly-BAMO units between the GAP segments. Any influence of PHDI on the melting point cannot be seen

from DSC results. ETPEs in formulations should have melting points of at least 80 °C. Therefore sample 11 and 12 seem to be favourable for formulation work.

The following Figure 3 shows the results from measurements of viscosity on samples 1 to 6. All curves show clear a decreasing viscosity already before the main melting step. The difference between the viscosities (firmness) of the solid samples is around 5.00 E+05 Pa s. All ETPEs with high GAP content of 65 % show decreasing viscosity and softening before the melting temperature. A second factor that favours such softening behaviour is the high content of chain extender BDO. Sample 4 shows the lowest viscosity due to a high GAP content and a high BDO content. The viscosities of the melted samples are very similar at around 100 Pa s which allows easy processing of propellants.

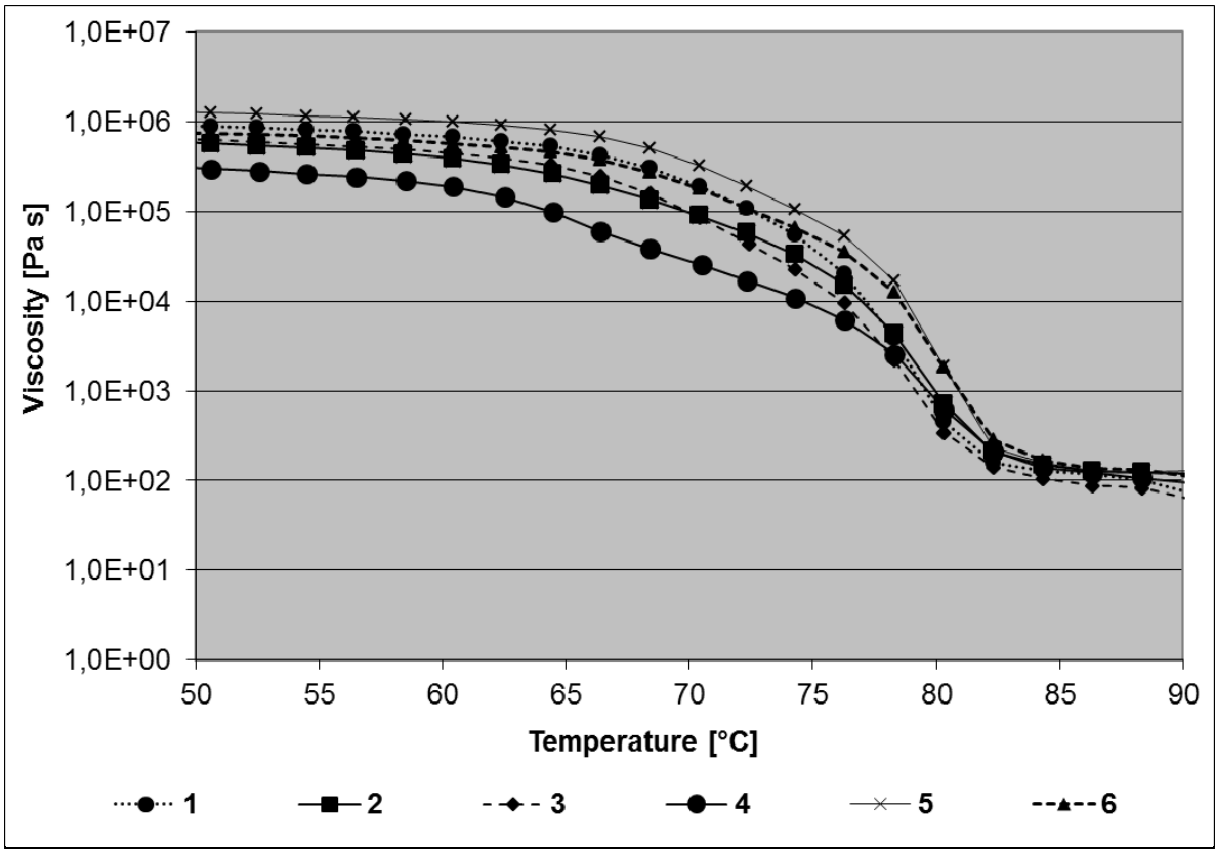

Figure 3: Viscosities of ETPE samples 1 to 6

The following Figure 4 shows the results from measurements of viscosity on samples 8 to 10. In contrast to the former sample series (sample 1 – 6) these ETPEs show a sharper melting point. The viscosities of samples 8 to 10 do not decrease up to temperatures of 70 °C. In the temperature range between 70 to 85 °C the viscosities drop to 100 Pa s and in case of sample 10 even down to 10 Pa s. The reason for this behaviour is not clear. In principle all three samples should give the same results because they have exactly the same composition and have been prepared with the same procedure.

The following Figure 5 shows the results from measurements of viscosity on samples 11 and 12. Sample 11 shows a slightly decreasing viscosity up to 72 °C, followed by a

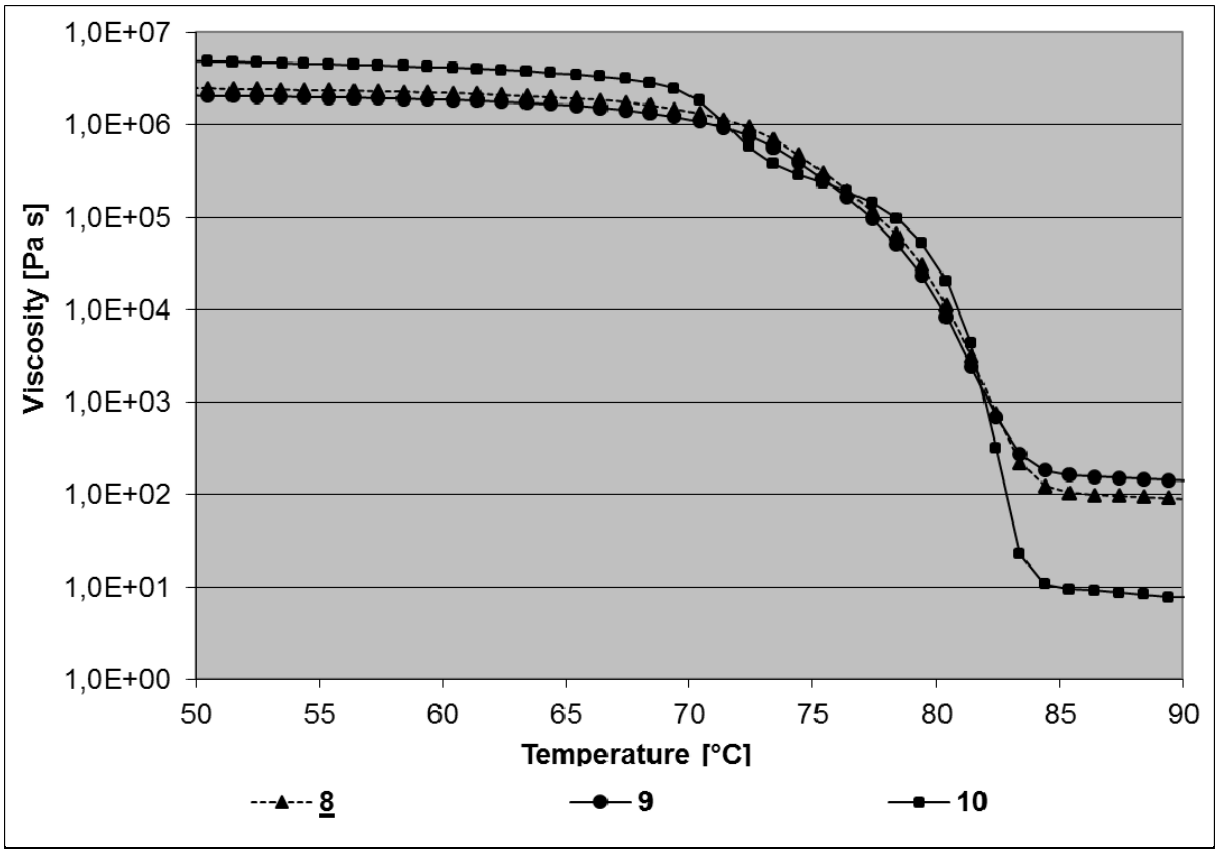

Figure 4: Viscosities of ETPE samples 8 to 10

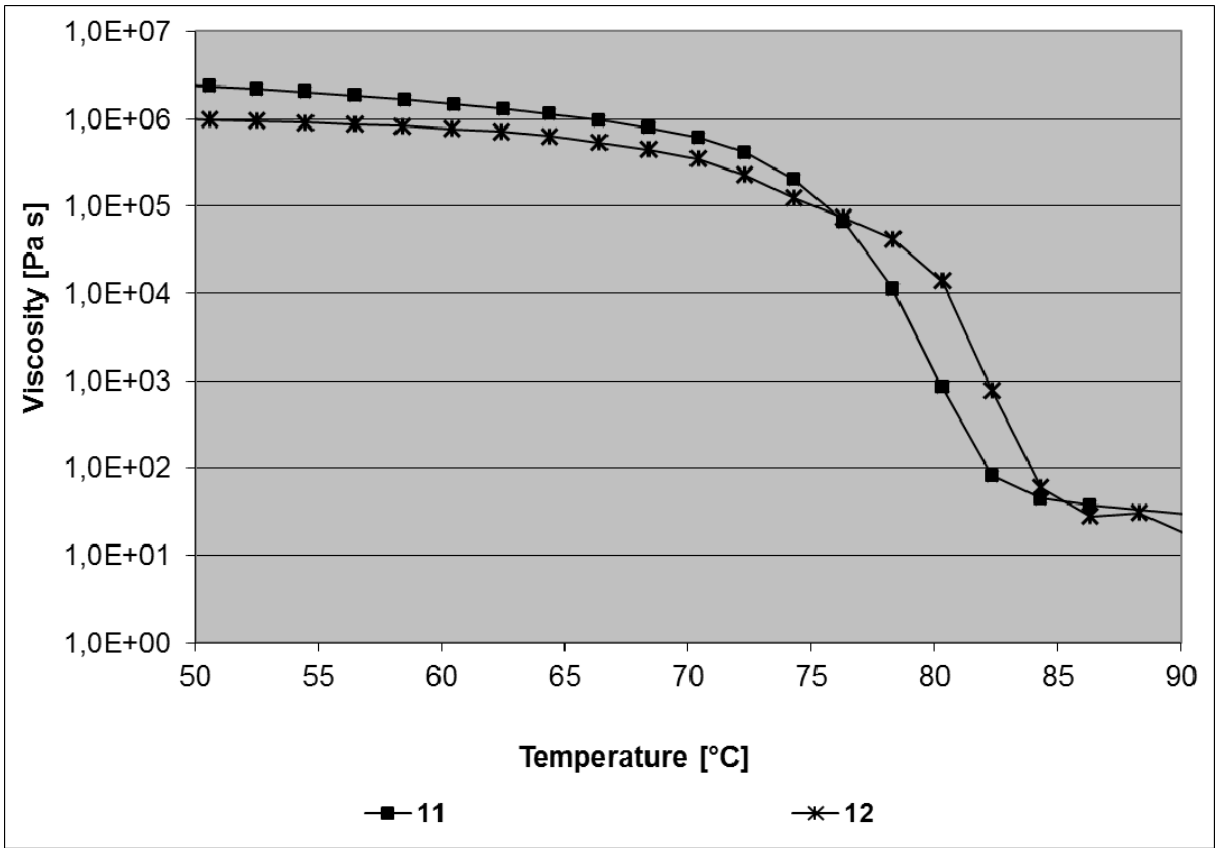

Figure 5: Viscosities of ETPE samples 11 to 12

strong decrease of the viscosity in the temperature range up to 82 °C. Sample 12 also shows a decreasing viscosity up to 78 °C and in the temperature range between 78 to 85 °C the viscosity drops sharply. In melted state both samples show a viscosity of 50 Pa s which allows easy processing of propellants.

CONCLUSIONS

The aim of this work was to evaluate the influence of different chain extenders and a variation of the diisocyante on the melting temperature of ETPEs. Twelve compositions have been prepared and analysed by DSC and visosimeter. The variations on chain extenders with BDO (2.5 % or 5.0 %), DMU and HC did not show any significantly improvement in melting temperature. All ETPEs with high GAP content of 65 % and chain extenders showed decreasing viscosity and softening before the melting temperature. The ETPEs with GAP contents of less than 50 % did not show this softening behaviour. When oligomeric Poly-BAMO-urethanes have been used for chain elongation the samples (11 and 12) have shown at DSC higher melting points of 86 and 87 °C and only slightly decrease of the viscosity and softening before the melting temperature even with high GAP content of 65 %. PHDI did not show any significantly influence on the melting point.

LIST OF ABBREVIATIONS

BDO - 1,4-Butanediol

DCM - Dichloromethane

DMU - N,N´-Dimethyl urea

DSC - Differential scanning calorimetry

ETPE - Energetic thermoplastic elastomer

GAP - Glycidylazide polymer

GPC - Gel permeation chromatography

HC - Hydrochinone

HF - Hydrofluoric acid

Mn - Number average molecular weight

Mp - Peak molecular weight

Mw - Weight average molecular weight

PDI - Polydispersity index Mw/Mn

PHDI - 1,4-Phenylene diisocyanate

Poly-AMMO - Poly-(3-azidomethyl-3-methyl-oxetane)

Poly-BAMO - Poly-(3,3-bis(azidomethyl)-oxetane)

Rf - Molar ratio isocyanate groups/hydroxyl groups

TDI - 2,4-Toluene diisocyanate

Tg - Glass transition temperature

TGA - Thermal gravimetric analysis

THF - Tetrahydrofuran

TPE - Thermoplastic elastomer

LITERATURE

[1] Y. Murali Mohan, M. Padmanabha Raju, K. Mohana Raju; Synthesis Spectral and DSC Analysis of Glycidyl Azide Polymers Containing Different Initiating Diol Unit, Journal of Applied Polymer Science, Vol. 93, 2157-2163, 2004

[2] A.M. Kawamoto, Th. Keicher, H. Krause, J.A. Saboia Holanda; Synthesis and Characterization of Energetic ABA-Type Thermoplastic Elastomers for Propellant Formulations, 37th International Annual Conference of ICT, Energetic Materials; Insensitivity, Ageing, Monitoring; 27-30 June, 2006, Karlsruhe; Germany, 136/1-136/11

[3] A.J. Sanderson and W. Edwards; Synthesis of Energetic Thermoplastic Elastomers Containing Oligomeric Urethane Linkages; US Patent 6815522B1 (2004);

[4] J. Sanderson and B. Wardle; The Synthesis and Combustion of High Energy Thermoplastic Elastomer Binders, 32nd International Annual Conference of ICT, Energetic Materials; Ignition, Combustion and Detonation; 03-06 July, 2001, Karlsruhe; Germany, 9/1-9/7

[5] (a) A.J. Sanderson, W.W. Edwards; Method for the Synthesis of Energetic Thermoplastic Elastomers in Non-halogenated Solvents; US Patent 6997997B1 (2006); (b) A.J. Sanderson, W.W. Edwards; Synthesis of Energetic Thermoplastic Elastomers Containing Oligomeric Urethane Linkages; US Patent 6815522B1 (2004)

[6] A.A. Malik, G.E. Manser, R.P. Carlson, T.G. Archibald; Solvent-Free Process for the Synthesis of Energetic Oxetane Monomers; US Patent 5523424 (1996)

[7] (a) R.B. Wardle, W.W. Edwards, J.C. Hinshaw; Method of Producing Thermoplastic Elastomers Having Alternate Crystalline Structure such as Polyoxetane ABA or Star Block Copolymers by a Block Linking Process; US Patent 5516854 (1996); (b) T.G. Archibald, R.P. Carlson, A.A. Malik, G.E. Manser; Preparation and Polymerization of Initiators Containing Multiple Oxetane Rings: New Routes for Star Polymers; US Patent 5663289 (1997)