

CHARACTERISATION AND THERMAL DECOMPOSITION STUDIES OF A HYDROXY TERMINATED POLYETHER (HTPE) COPOLYMER AND BINDER FOR COMPOSITE ROCKET PROPELLANTS

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ABSTRACT

Propellants based on cross-linked Hydroxy Terminated Polyether (HTPE) binders are being used as alternatives to Hydroxy Terminated Polybutadiene (HTPB) compositions. HTPE propellants have similar mechanical properties to HTPB propellants but they give a less severe response in 'slow cook-off' tests for IM compliance. In an attempt to gain a better understanding of the behaviour of HTPE propellants we have synthesised and characterised an HTPE pre-polymer and a range of binder network samples with different NCO:OH equivalence ratios. The synthesis of a random copolymer of ethylene oxide (EO) and tetrahydrofuran (THF) was carried out through cationic bulk polymerisation. HTPE copolymers with different EO/THF group ratios and different molecular weights were synthesized and characterised by a range of techniques. HTPE binder network samples were prepared with and without plasticizer and cured using different NCO:OH equivalence ratios. Desmodur N-3200 was used as a curing agent and *n*-BuNENA as an energetic plasticizer. The thermal decomposition of the HTPE binder network samples were studied by heating the materials at a rate of 6°C per hour and periodically removing them from the oven for surface examination using interferometric surface measurements, scanning electron microscopy (SEM) and microphotography. Their thermal decomposition behaviour was investigated by Gas Chromatography-Mass Spectrometry (GC-MS), Differential Scanning Calorimetry (DSC) and Fourier Transform Infra-red (FTIR) Spectroscopy. Similar analyses were performed on HTPB pre-polymer and binder network samples and the results were compared with those obtained for the corresponding HTPE samples.

1. INTRODUCTION

Recently, a new family of rocket propellants designed to fulfil IM requirements has emerged. They are based on cross-linked Hydroxy Terminated Polyether (HTPE) binders and are being used in certain composite rocket propellant formulations as alternatives to HTPB. Although HTPE has been described as a new type of binder¹, polyether binders have been used in formulations since the mid-1950s,² prior to the development of HTPB propellants. They are also called HTPE propellants, developed as less sensitive replacements for HTPB/AP propellants currently used in several tactical missile rocket motors³. It is claimed that one advantage of HTPE propellants is that they give a less severe response than HTPB propellants in 'slow cook-off' tests for IM compliance⁴. In this paper we report a study aimed at understanding the behaviour of HTPE propellants, particularly in slow cook-off, for the purposes of which we have synthesised and characterised an HTPE pre-polymer and a range of binder network samples with different NCO:OH equivalence ratios. These copolymers were characterised to determine molecular weight, molecular structure, glass transition temperature (T_g), melting temperature (T_m), impurities and density using a range of analytical techniques. HTPE binder network samples were prepared with and without energetic plasticizer and cured with the poly isocyanate, Desmodur N-3200 (generously supplied by Bayer), using *n*-BuNENA as an energetic plasticizer and 2-NDPA as a stabiliser. Samples containing plasticizer are referred to as "gumstock". The thermal decomposition of

the HTPE binder network samples was studied by heating the materials at a rate of temperature increase of 6°C per hour and periodically removing them from the oven for surface examination using interferometric surface measurements, scanning electron microscopy (SEM) and microphotography. Their thermal decomposition behaviour was investigated by Differential Scanning Calorimetry (DSC) and Fourier Transform Infra-red (FTIR) Spectroscopy. Similar analyses were performed on a sample of HTPB R45M prepolymer supplied by Roxel UK and the results were compared with those obtained for the HTPE.

2. EXPERIMENTAL

Fourier Transform Infrared spectroscopy was performed using a Bruker FTIR spectrometer, model Vector 22, with Optic User Software (OPUS) version 3.1. A thin layer of sample was placed between two sodium chloride plates. Proton and carbon-13 nuclear magnetic resonance spectroscopy was performed using a Bruker DPX 250 spectrometer. Deuterated chloroform (CDCl_3) was used as a solvent and tetramethylsilane (TMS) as reference. Size exclusion chromatography (SEC) was performed using a Viscotek SEC pump, model VE 1121, with a Waters 2410 Refractive Index Detector (RID) and a set of two 5 μm PLgel Mixed-C 300x7.5 columns and a 5 μm PLgel 100 Å 300x7.5 mm column. The SEC system was controlled via a PC running Waters Millennium software. THF stabilised with BHT (250 ppm) was used as an eluent and polyethylene glycol standards were used for calibration. Viscosity data were obtained using a Brookfield Viscometer model RVDVE-230, connected to a small sample adapter of 8 ml volume capacity, model SC4-21/13R/RP

To determine glass transition temperature (T_g) and melting temperature (T_m), differential scanning calorimetry (DSC) was performed using a Mettler TA4000 thermal analyser equipped with a TA processor TC-11 and a DSC 30 measuring cell. Sample weights were around 8 to 18 milligrams. Samples were heated at a rate of 2°C per minute from -100°C to +100°C. The copolymer and binder network thermal decomposition characteristics were studied by DSC and thermogravimetric analysis (TGA). TGA was performed using a Mettler thermo balance model TG 50, using the same analyser as DSC. Sample masses were around 14 to 18 milligrams and they were heated at a rate of 10°C per minute from 30°C to +600°C under a nitrogen atmosphere. DSC and TGA systems were controlled via a PC using a STARe, version 8.1x for Windows® 2000 and Windows® XP from Mettler Toledo software.

In order to study the surface behaviour of the HTPE binder network samples, before and after they were slowly heated, interferometric 3-D surface profile analysis was performed using a MicroXam surface mapping microscope, with a lens of 1.25. The microscope was controlled via a PC running the MapVue EX version 6.51 surface mapping software. Scan lengths of 15 μm to 70 μm and a magnification of 25.3 were used. The surface topography was described by the statistical descriptor “surface roughness, R_a ”.

3. HTPE SYNTHESIS AND CHARACTERISATION

The synthesis of a random copolymer of ethylene oxide (EO) and tetrahydrofuran (THF) was carried out through cationic bulk polymerisation⁵ under sub-zero temperature conditions using ethylene glycol (EG) as a proton reservoir and tetrafluoroboric acid diethyl ether complex as a catalyst. Details of the HTPE copolymer synthesis have been published previously,⁶ and a comprehensive study of the mechanism of formation and kinetics of the process and of copolymer composition in the presence of diols has been conducted by Bednarek and

Kubisa.^{7,8,9} By changing the concentration of ethylene oxide (mass flow of EO) and the temperature, the structure of the copolymer can be modified to synthesise a copolymer with different [THF]/[EO] ratios, to give a random copolymer as shown in Figure 1, where R corresponds to an ethylene oxide unit when ethylene glycol is used as initiator⁵ and y , n and m are dependant on the reaction conditions.

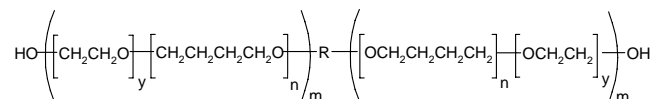


Figure 1. EO/THF Copolymer Structure

Quantities of each reagent were changed over a series of experiments in order to obtain copolymers with different THF/EO ratios, different molecular weights and thus different chemical, physical and mechanical properties. The experimental temperature was maintained at around -42°C . Polymerisation started when EO gas was added through a stainless steel needle immersed in the reaction solution.

3.1. FTIR and NMR Spectroscopy Results and Discussion

From the FTIR spectrum presented in Figure 2A, three main sets of absorption peaks can be observed. The peak at 1117 cm^{-1} is assigned to an aliphatic ether, i.e. $-\text{CH}_2\text{-O-CH}_2-$, the shoulder at 2860 cm^{-1} is assigned to the $-\text{CH}_2\text{CH}_2-$ groups from THF and EO and the peak at 3470 cm^{-1} is assigned to a primary alcohol group, i.e. HOCH_2- . The spectrum is in good agreement with that presented by Zhiping *et al*¹⁰, indicating that it corresponds to that of a hydroxy terminated copolymer of THF and EO.

^{13}C NMR spectra obtained from the copolymer samples were compared against the spectra presented by Bednarek and Kubisa⁷ and by Zhang Jianguo *et al*¹¹, and ^1H NMR spectra were compared against those of Zhiping and Quinwey¹² and Bednarek and Kubisa⁵. Agreement was good. Figure 2B shows a typical ^{13}C NMR spectrum. Quantitative analysis to determine the [THF]/[EO] ratio, presented in Table 1, was based on the integral ratio of the THF and EO groups present in the HTPE copolymer chains, as obtained from ^1H NMR spectra.

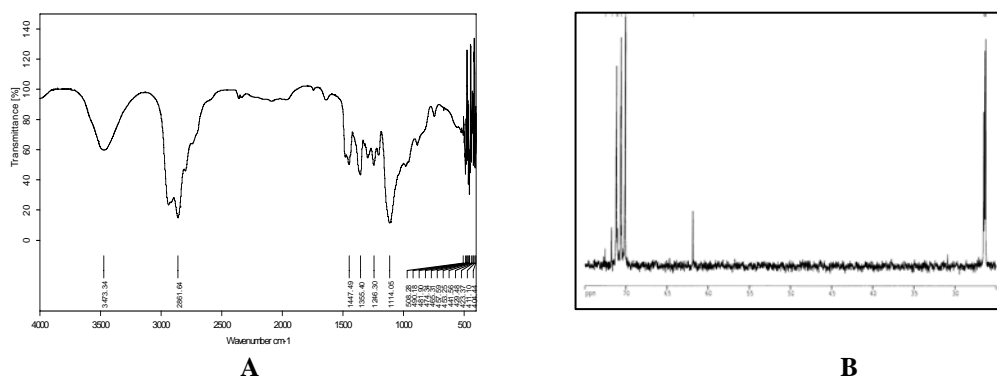


Figure 2. (A) FTIR spectrum of HTPE copolymer (B) Typical ^{13}C NMR spectrum

3.2. SEC and GC-MS Results and Discussion

SEC was used to determine HTPE molecular weights, polyethylene glycol standards being used for calibration. The results of the determinations of number average molecular weight (M_n) are presented in Table 1. The by-products from the copolymerisation of THF and EO

were observed in GC-MS and from small peaks in the low molecular weight region of the SEC chromatograms. It was found that they were mainly tetramers, trimers and dimers with molecular weight around 204, 132, 116 and 88 corresponding to THF₁-EO₃, EO₃, THF₁-EO₁ and EO₂ respectively. The cumulative percentage of these components was found to be less than 3% in all samples.

3.3. Relationships Between Mn, THF/EO Ratio and Tg Results and Discussion

The relation between Mn and Tg is presented in Figure 3A, with information on HTPB also included.

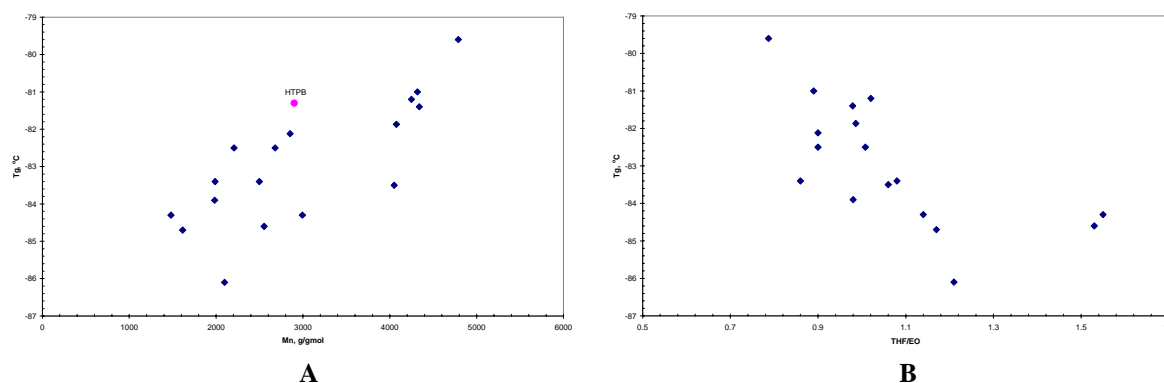


Figure 3. (A) Mn versus Tg and (B) Tg versus THF/EO ratio

It can be seen that HTPB shows a higher Tg than the HTPE copolymers with a similar or higher Mn. In general terms, for the HTPE copolymers there is a slight trend towards a higher Tg as Mn is increased. However, it can be seen that in some cases copolymers having similar molecular weights have a different Tg, e.g. E8 in comparison to E12. This difference can be explained by the difference in copolymer chain structure as can be seen in Figure 3B. As the THF/EO ratio increases, i.e. the number of THF groups in the polymer chain increases relative to the number of EO groups, Tg decreases. These results are consistent with what is observed for Poly THF and Poly EG. Poly THF has a Tg of 82.5°C for a Mn of 2000 while for Poly EG the Tg is -58.3°C for a Mn of 1000⁵.

Table 1. Properties of HTPE Copolymers

Sample Number	[THF]/[EO], n	Mn	Tg, (°C)	Melting Point, (°C)	Melting Heat, (J g ⁻¹)	Viscosity (mPas)	Density, (g cm ⁻³)
E7	0.98	1984	-83.9	-16.5	36.2	508	--
E8A	1.53	2553	-84.6	-1.8	56.9	--	1.028
E8	1.55	2993	-84.3	-2.2	52.6	1485	--
E9	1.08	1988	-83.4	-7.8	44.60	807	1.029
E11	1.01	2206	-82.5	-8.4	44.40	--	1.035
E12	0.9	2853	-82.1	-10.0	41.30	1338	1.043
E13	0.84	2680	-82.5	-11.0	44.20	1043	--
E14	0.86	2498	-83.4	-15.0	38.10	703	--
E15	1.14	1481	-84.3	-9.9	48.40	--	--
E18	1.17	1615	-83.5	-11.9	36.00	--	--
E19	1.06	4050	-86.1	-10.8	39.00	1825	--
E24	0.79	4789	-80.8	-14.1	32.3	3785	1.042
E25	1.03	4249	-82.4	-3.9	37.5	2938	--
E26	0.99	4076	-82.4	-8.5	37.2	2350	1.042
E27	0.98	4340	-81.6	-7.0	38.3	2796	1.036

3.4. Density and Viscosity Results and Discussion

Density data (Table 1) allows some conclusions to be drawn about the relationship between copolymer structure, molecular weight and density. For THF/EO ratios more than or less than one, the trend is for the density to decrease as the molecular weight increases. This is in agreement with results presented by Bednarek and Kubisa⁵. On the other hand, for ratios very close to one, the trend is for the density to increase as Mn increases.

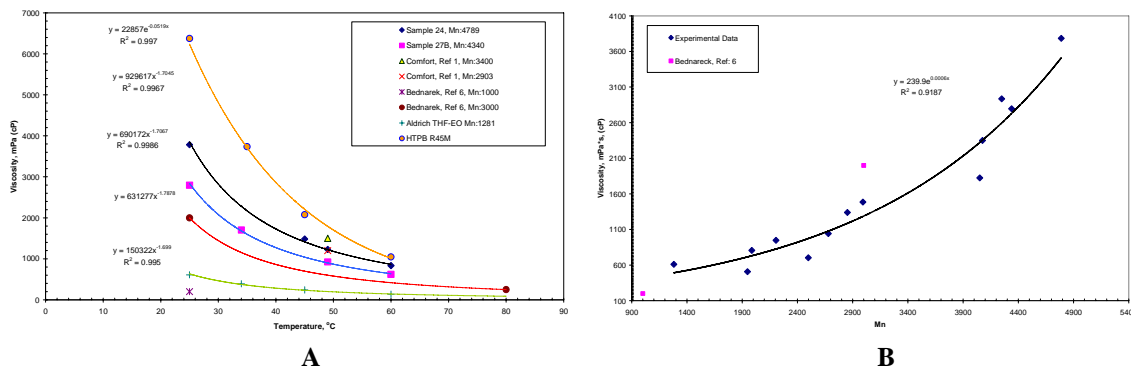


Figure 4. Viscosity versus Temperature for different Mn and THF/EO ratios

The relation between viscosity and temperature for four samples is presented in Figure 4A and B together with information presented by Bednarek⁵ and Comfort¹. The viscosity trend increases with increasing Mn and decreases with increasing temperature. Also, it can be observed that the viscosity figures for all samples, regardless of molecular weight, tend to coalesce above 80°C.

3.5. Thermal Analysis Results and Discussion

DSC and TGA analysis was performed on two samples of HTPE copolymer and on one of HTPB R45M (Figure 5A and B). HTPE samples E9 and E13, with Mn of 1988 and 2680 and THF/EO equivalence ratios of 1.08 and 0.84 respectively, were studied. From the DSC thermogram (Figure 5A), it can be seen that, for HTPE samples, no thermal events occur before the onset at around 360°C. In contrast, onset of exothermic decomposition of HTPB polymer begins at 377°C. According to Tingfa,¹³ and Gupta and Adhikari,¹⁴ this first stage in the decomposition of HTPB corresponds primarily to depolymerisation, new bond generation by cyclization and crosslinking of material that has not undergone depolymerisation.

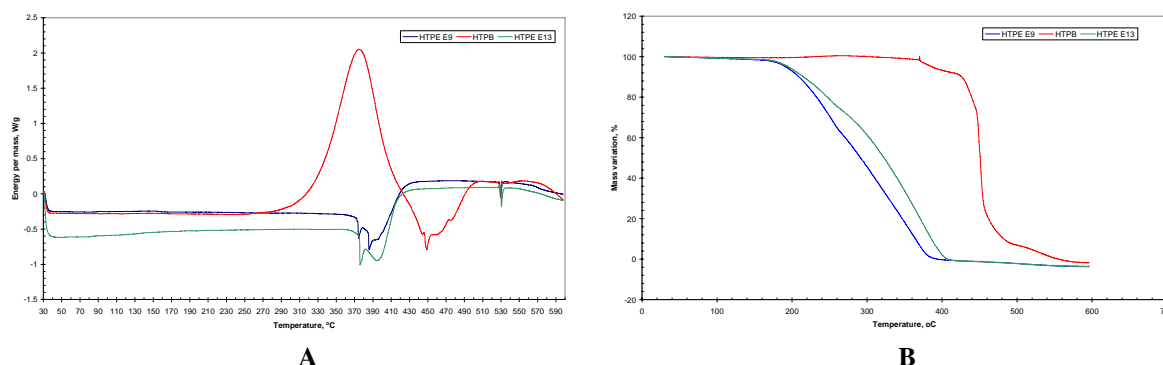


Figure 5. DSC (A) and TGA (B) results for HTPE copolymers and HTPB

HTPE TGA traces (Figure 5B) indicate a constant rate of weight loss, with an onset at approximately 169°C for E9 and at approximately 174°C for E13. When the TGA traces of the HTPE copolymers are compared with that of HTPB, differences can be seen in the onset decomposition temperature and the curve gradient. The onset decomposition temperature is

considerably lower for HTPE copolymers than for HTPB, the difference being around 146°C. Secondly, the curve gradient for HTPB shows a different rate of weight loss, which is consistent with that stated by Tingfa.¹³ While three stages around 377°C, 423°C and 446°C can be observed in the HTPB TGA thermogram, the HTPE samples show only one relatively smooth rate of weight loss.

4. HTPE AND HTPB SLOW HEATING TEST

In order to understand the behaviour of binder network and gumstock under slow heating, different samples made from copolymer HTPE E27 and polymer HTPB R45M, both cured with Desmodur N-3200, were prepared. *n*-BuNENA and di-*n*-octylsebacate (DOS) were used as plasticizers for HTPE and HTPB samples, respectively. Samples were poured into a mould and, after curing, small flake shape samples were cut. The samples were then placed into a head space vial previously flushed with nitrogen in order to have an inert environment during the slow heating process. Taking into account the HTPE and HTPB propellant cook off ignition temperatures of 133°C and 233°C respectively, reported by Atwood *et al*¹⁵ and Chan and Turner¹⁶, samples were placed into a controlled oven, and the temperature increased from ambient up to 297°C at a rate of 0.1°C per minute (6°C per hour). The samples were removed from the oven at 100°C, 150°C, 240°C, 280°C and 297°C. FTIR, SEM, Surface profile and DSC analysis were performed. Binder networks made from HTPE and HTPB were called 17NE27 and 1NHTPB, and they had a NCO:OH equivalence ratio of 0.90 and 0.89 respectively. Gumstocks made from HTPE and HTPB were called 5GE27 and 3GHTPB and they had a NCO:OH equivalence ratio of 0.88 and 0.86 respectively.

As can be seen for HTPE binder network and HTPE and HTPB gumstock samples in Figure 6, Figure 7 and Figure 8 as the oven temperature was increased most of the samples follow the same trend in terms of colour changes.

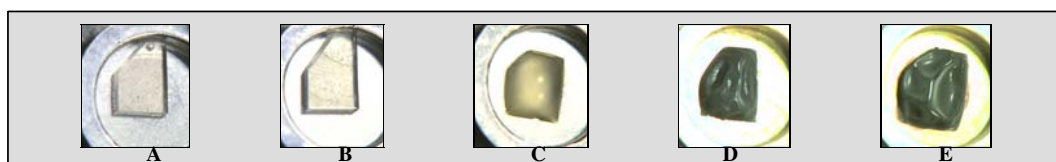


Figure 6. Samples 17N27B after slow heating trial up to: (A) 100°C, (B) 150°C, (C) 240°C, (D) 280°C and (E) 295°C.

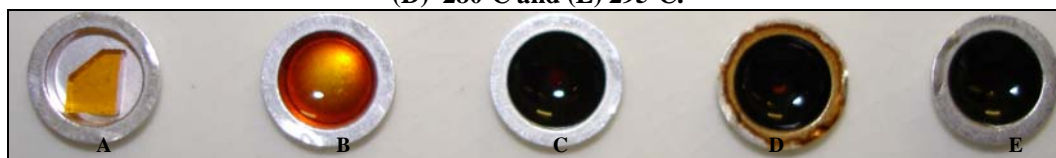


Figure 7. Samples HTPE 5G27B after slow heating trial up to: (A) 100°C, (B) 150°C, (C) 200°C, (D) 240°C and (E) 200°C

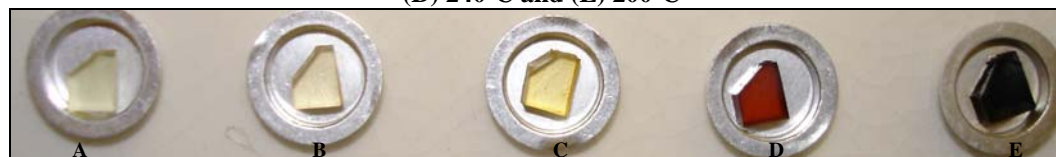


Figure 8. Samples 1NHTPB after slow heating trial up to: (A) 100°C, (B) 150°C, (C) 200°C, (D) 240°C and (E) 297°C.

Despite the fact that HTPE and HTPB were cured with the same curing agent, the slow heating behaviour in terms of shape was completely different. In fact, while both HTPB samples retained their shape throughout the heating process, HTPE gumstock samples lost their shape and became liquid around 150°C, and the HTPE binder network became softer at around 240°C. The softening process is possibly a result of breaking of the hard segment links or of the HTPE copolymer chains. A similar softening behaviour in HTPE propellants aged at 71°C, was reported by Rice and Neidert¹⁷, however the curing agent used was not specified. In contrast, HTPB samples become harder and more brittle during slow heating, which according to Ahlblad *et al*¹⁸ is due to the formation of a secondary network produced by a oxidative crosslinking. Therefore, if any softening due to hard segment scission occurs in HTPB, it is possibly in competition with the hardening due to formation of the secondary network.

4.1. Surface Profile and SEM Analysis

In order to study the surface behaviour of the HTPE and HTPB samples, interferometric 3-D surface profile analysis were performed. Figure 9 and Figure 10 show the hybrid map for the surface profile of HTPE binder networks and HTPB gumstock heated up to different temperatures.

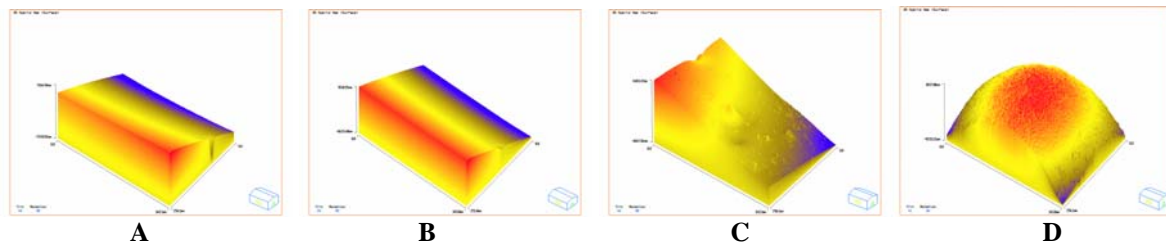


Figure 9. Surface hybrid map of HTPE binder network sample heated up to: (A) 25°C, (B) 100°C, (C) 150°C and (D) 240°C.

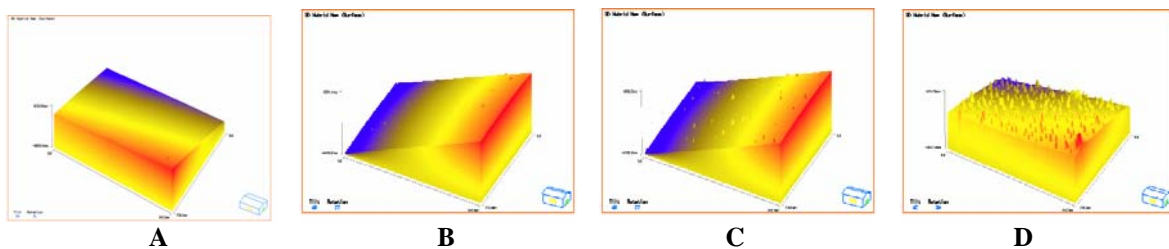


Figure 10. Surface hybrid map of sample HTPB gumstock heated up to: (A) 100°C, (B) 100°C, 150°C and (D) 240°C

Samples surface roughness was measured before and after the heating process and the percentage in Ra change was plotted and is presented in Figure 11.

As can be seen from Figure 11, initially all binder network samples, either from HTPE or HTPB polymers, showed increased roughness with increasing temperature. However, for the HTPB sample heated up to 240°C, a decrease in roughness with temperature can be observed. The initial behaviour of the HTPE gumstock is similar, although the increase in roughness is negligible and at temperatures over 100°C the sample becomes liquid. HTPB gumstock behaves in a completely different way from HTPE. In fact, contrary to initial expectations, the

surface roughness decreases instead of increasing. This behaviour was also observed in the HTPB binder network sample.

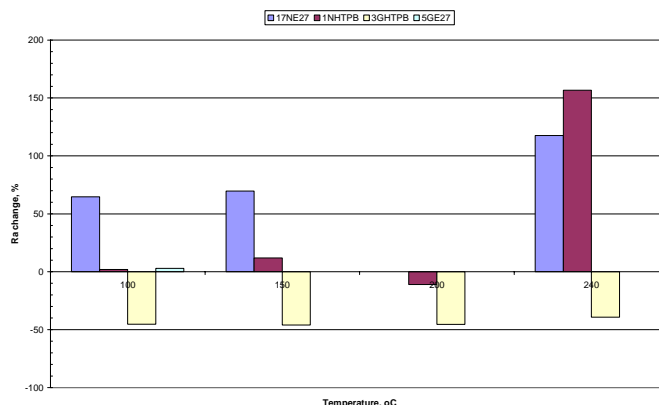


Figure 11. Percentage change in Ra for samples: binder network HTPE 17NE27 and HTPB 1NHTPB and gumstock HTPE 5GE27 and HTPB 3GHTPB.

The degree of decrease in surface roughness suggests that there is a liquid phase migration to the surface, this can be appreciated clearly in Figure 10D and in the SEM photographs taken of the HTPE and HTPB samples in Figure 12.

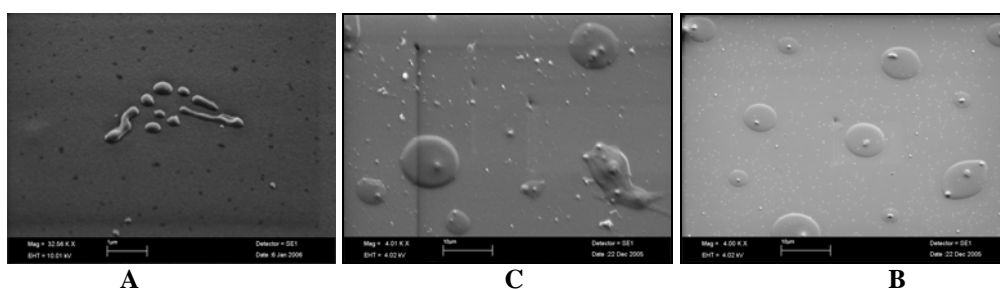


Figure 12. SEM photograph of sample: (A) HTPE binder network heated up to 150°C (32560x), (B) sample 1NHTPB and (C) sample 3GHTPB heated up to 240°C (4000x).

The surface roughness in the SEM photographs is not evident but a well defined pattern of flat semi-spheres or little domes can be observed on the sample surface. The domes attached to the surface have a measured radius between 0.12µm and 3.8µm. This is an indication that liquid phase material is migrating to the surface during the slow heating process. This liquid is possibly non-cured polymer, plasticiser or products from the chain scission migrating through the binder network or gumstock.

4.2. FTIR Analysis

As stated before, during the slow heating process, samples made from HTPE became soft and liquid. FTIR analyses were performed on these samples and their spectra compared with the initial ones.

As can be seen from Figure 13B, the addition of the energetic plasticizer *n*-BuNENA does not have a strong effect on the infra red spectrum in comparison with the binder network (Figure 13A), probably because almost all the groups from *n*-BuNENA are absorbing in the same region than the cured copolymer due to the similar nature of the components. However, the peaks at around 1639cm⁻¹, 1515cm⁻¹ and 1460cm⁻¹ are magnified due to the absorption of the *n*-BuNENA groups in the same region as the main groups of the cured copolymer.

HTPB binder network, the event is an exothermic one and is possibly due to reaction of the newly formed groups with the polybutadiene double bonds. On the other hand, in both binder network samples, exothermic decomposition peak at around 377°C can be seen. In HTPE itself, decomposition is not apparent at this temperature (Figure 5A), so it appears that segments derived from the curing agent are responsible for this decomposition event. In fact, as can be seen in Figure 5A and B, the thermal behaviour for both uncured polymers is completely different at around 377°C. While the HTPE copolymer shows an endothermic peak, the HTPB polymer shows an exothermic peak which, according to Tingfa *et al*¹³, is primarily due to depolymerisation and new bond generation by cyclization and crosslink reactions. The exothermicity; calculated by extending the baseline just before the DSC onset, is considerably lower in HTPE samples, 82 Jg⁻¹, than in HTPB sample, 802 Jg⁻¹. This is possibly due to the heat contribution from the reaction of the double bonds.

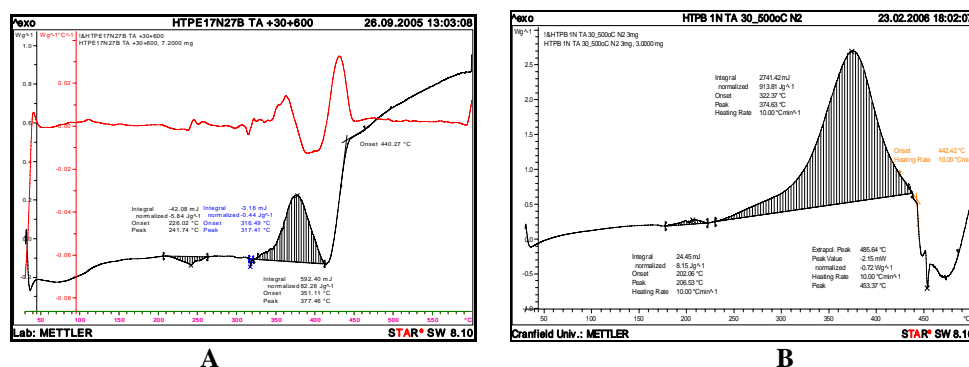


Figure 14. DSC thermogram binder network sample: (A) HTPE 17N27B and (B) HTPB 1N

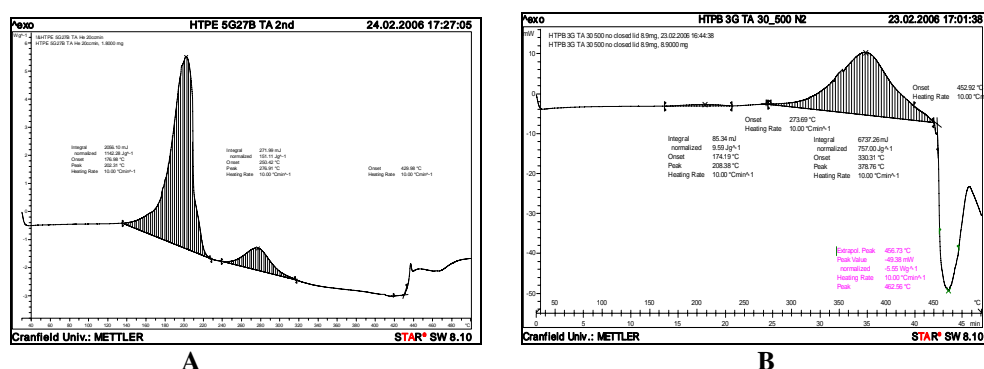


Figure 15. DSC thermogram for gumstock samples HTPE 5GE27 (A) and (B) HTPB 3G.

When a plasticizer was added to the formulations the behaviour changed, particularly for HTPE samples. In sample 5GE27 (Figure 15A), the onset of the thermal decomposition was greatly affected by the presence of the energetic plasticizer. In the HTPE gumstock the onset of the exothermic reaction occurred at around 139°C, whereas in the binder network sample, no thermal events occur before the endothermic peak at around 202°C; the first exothermic reaction onset is at around 352°C. A second exothermic peak is apparent at 276.9°C in the HTPE gumstock thermogram. In HTPE binder network samples, exothermic reactions were not observed around 276°C, so it is possible that the decomposition products of the energetic plasticizer- which will probably include nitrogen oxides- may be reacting with the urea or biuret groups present in the hard segment. However, in the case of HTPB gumstock, a lower intensity exothermic peak, compared with HTPE gumstock, can be seen at around 200°C, as presented in Figure 15B. This suggest that the plasticizer is delaying the onset of the exothermic reaction.

5. CONCLUSIONS

Several samples of hydroxy terminated co-polyether were synthesised by the cationic polymerisation of THF and EO. A comparison between HTPE samples of different THF/EO ratios suggests that there are slight differences in the thermal decomposition behaviour but major differences in the thermal properties. A comparison between the synthesised HTPE copolymer and HTPB R45M pre-polymer suggests that there are differences in the thermal decomposition behaviour and thermal properties.

HTPE gumstock and binder network behave in a similar way during thermal decomposition, becoming soft and even liquid, but the presence of *n*-BuNENA in the formulation lowers the temperature at which degradation occurs. In contrast, HTPB binder network and gumstock samples become harder and more brittle during heating. IR studies showed that the urethane groups were still present in the HTPE samples heated up to 240°C and therefore the change of the binder network physical characteristics was attributed to scission reactions of the biuret and urea groups present in the hard segment. No evidence was found from FTIR and DSC analysis to support the occurrence of scission of the polymer chain at these temperatures.

The similarity in the decomposition onset temperature between the HTPE and HTPB gumstock samples and the data from the HTPE and HTPB cook-off ignition suggests that plasticizers are driving the ignition process, especially in HTPE samples.

A liquid phase migration process was observed during the slow heating test for HTPE and HTPB samples. The change in R_a suggests that the migration process is promoted by the plasticizer. The migration process appears to be higher in HTPB than in HTPE gumstock and it is suggested that, non cured polymer and plasticizer or a combination of both plus fragmented polymer, are migrating to the surface. If that is happening, possibly some nano or micro cavities in the sample bulk may be produced during the migration process.

6. ACKNOWLEDGEMENTS

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