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# Synthesis and characterisation of styrene butadiene styrene-g-*N*-isopropylacrylamide via UV polymerisation for potential use in biomedical applications

**James E. Kennedy · Clement L. Higginbotham**

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**Abstract** The work undertaken investigates the mechanical and thermal properties of a styrene butadiene styrene (SBS) grafted with *N*-isopropylacrylamide (NIPAAm) for potential use in the field of biomaterials. SBS-g-NIPAAm was synthesised using UV polymerisation and analytical techniques such as differential scanning calorimetry (DSC), attenuated total reflectance Fourier transform spectrometry (ATR-FTIR), dynamic mechanical thermal analysis (DMTA) and tensile tests were used to characterise the grafted copolymers. The ATR-FTIR spectrum for NIPAAm illustrates bands corresponding to C=O stretching and NH bending for secondary amides at 1655 and 1544 cm$^{-1}$, respectively. These bands are represented as shoulders in SBS-g-NIPAAm copolymers. In relation to the thermal analysis, the butadiene domain present in the SBS and the grafted SBS copolymers were analysed using DSC. It was evident that all of the grafted samples have a broad thermal transition when compared to the PB domain present in SBS, suggesting that grafting had occurred within each of the SBS-g-NIPAAm copolymers. This was confirmed by the use of DMTA, where the results showed an increase in $T_g$ values from −92 to −74 °C for SBS-g-NIPAAm copolymers.

## Introduction

For many years, during the early stages in the development of biomaterials science, it was considered that biocompatibility required a state of mutual co-existence between material and tissue such that neither affected the other. Biomaterials are any materials which are designed to restore, augment or replace the natural functions of the living tissue or organs of the body [1]. Biocompatibility can be characterised by a whole series of negatives, for example that the material was non-toxic, non-irritant, non-thrombogenic, non-carcinogenic and so on. Such a state of compatibility was most likely to be achieved by a material being inert and unrecognisable by the tissue.

Hydrogels have physical properties similar to those of human tissue and possess excellent tissue compatibility and thus have been used as biomedical materials. However, the main disadvantages of hydrogels are their poor mechanical properties after swelling. To overcome this problem, hydroxyethyl methacrylate (HEMA) was grafted onto styrene butadiene styrene (SBS) and the mechanical properties of SBS-g-HEMA were found to be superior to those of poly(HEMA) and were almost identical to those of SBS [2]. From measurements of the contact angle and blood clotting time, the wetting and non-thrombogenic properties of SBS-g-HEMA were better than those of SBS as found by Yang and Hsiue [2]. Furthering their work, Yang et al. [3] researched the graft copolymerisation of dimethyl amino ethyl methacrylate (DMAEMA) with SBS and found that the degree of grafting was related to the irradiation time, DMAEMA concentration and temperature. The adsorption of albumin and fibrinogen decreased with an increase in the amount of grafting. They continued their work by the substitution of amino groups on the SBS-g-DMAEMA graft copolymer membrane which was treated

J. E. Kennedy (✉) · C. L. Higginbotham
Materials Research Institute, Athlone Institute of Technology,
Dublin Rd., Athlone, Co. Westmeath, Ireland
e-mail: jkennedy@ait.ie

C. L. Higginbotham
e-mail: chigginbotham@ait.ie

with heparin to prepare the heparin containing SBS-g-DMAEMA (SBS-g-DMAEMA-HEP). It was found that with increased grafting and heparin content, the surface tension and the water content of the SBS-g-DMAEMA membrane increased, whereas the contact angle decreased [4].

Kennedy et al. [5] have successfully grafted SBS with acrylic acid via UV polymerisation techniques for use as a potential biomedical material and in doing so; they proved that the glass transition values for each of the grafted copolymers increased in the butadiene domain, thus proving that grafting had occurred.

Over the past few years, *N*-isopropylacrylamide (NIPAAm) has appeared in the literature with increasing frequency [6–13]. Lee and Chen [14] have grafted NIPAAm onto SBS via solution polymerisation using benzoyl peroxide as the initiator. This was carried out to improve the water absorption and thermo sensitivity of SBS. Thus, a biomedical material often needs to function dependably without significantly altering the physical or mechanical properties of the substrate. The purpose behind the current investigation is to develop a smart biomedical material which would maintain or surpass the mechanical properties necessary for the successful operation of a medical device. In this article, the mechanical and thermal properties of SBS grafted with NIPAAm via UV polymerisation using benzophenone (BP) as photoinitiator were explored. This was performed by differential scanning calorimetry (DSC), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), dynamic mechanical thermal analysis (DMTA), white light profilometry and tensile studies.

## Experimental

### Materials

The base polymer, an SBS, was supplied by Shell Chemical Company (Eschborn, Germany) under the trade name of Kraton D1101 (see Table 1). The monomer used was NIPAAm which was supplied by TCI Europe (Antwerp, Belgium) and used as-received. BP (supplied by Sigma-Aldrich, Dublin, Ireland) was used as a UV-light sensitive initiator. In order to prepare samples for UV polymerisation, moulds were prepared from silicon mould compound (W.P. Notcutt, Middlesex, UK). The silicon moulds were prepared with rectangular shapes (5 cm × 2 cm × 0.5 cm) in order to produce the required sample shapes for testing. All solutions were cured in the silicon mould under two UVA 340 UV lamps (Q-panel lab products) for 2 h in an enclosed environment to ensure complete curing.

**Table 1** Structural properties of Kraton D1101

| | |
|---|---|
| Butadiene/styrene ratio (wt%) | 69/31 |
| Total molecular weight | 102,000 g/mol |
| Microstructure of PB | |
| 1,4-*trans* (%) | 42 |
| 1,4-*cis* (%) | 49 |
| 1,2 (%) | 9 |

### Synthesis of SBS-g-NIPAAm copolymers via UV polymerisation

SBS (2 g) was dissolved in chloroform (20 mL) at 40 °C. Known concentrations of NIPAAm (*X* g)* and BP (0.06 g) were added at room temperature and the mixture was stirred for 2 h. The solution was poured into silicone moulds which were placed in a UV chamber for 2 h. The samples were placed in a fume cupboard for 24 h and then an oven at 40 °C for 120 h.

$(X\ \mathrm{g})^{*} = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5$ and 4.0 g of NIPAAm.

### Synthesis and preparation of SBS-g-NIPAAm copolymers for soxhlet extraction

SBS (2 g) was dissolved in chloroform (20 mL) at 40 °C. Known concentrations of NIPAAm (2 g) and BP (0.06 g) were added at room temperature and the mixture was stirred for 2 h. The solution was poured into silicone moulds which were placed in a UV chamber for 2 h. The samples were placed in a fume cupboard for 24 h and an oven at 40 °C for 120 h. Samples of the grafted SBS copolymers were placed in soxhlet extractors using methanol at 60 °C for 1–8 days. The washed samples were placed in a fume cupboard for 24 h and then an oven at 40 °C for 120 h. Thermal–mechanical testing was carried out on each sample using DMTA.

### Preparation of SBS and grafted SBS copolymers for tensile testing

SBS (2 g) was dissolved in chloroform (20 mL) at 40 °C. Known concentrations of NIPAAm (2 g) and BP (0.06 g) were added at room temperature and the mixture was stirred for 2 h. The solution was poured into silicone moulds which were placed in a UV chamber for 2 h. The samples were placed in a fume cupboard for 24 h and an oven at 40 °C for 120 h. Samples of grafted SBS copolymer were placed in soxhlet extractors using methanol at 60 °C for 5 days. The washed samples were placed in a fume cupboard for 24 h and then an oven at 40 °C for 120 h. Mechanical analysis was then carried out on each sample using a tensile tester.

### Differential scanning calorimetry

UV-polymerised samples were tested using a TA 2010 differential scanning calorimeter with sample mass between 9.10 and 9.24 mg. The samples were placed in sealed pans, with a temperature range from −120 to 300 °C at a temperature heating rate of 10 °C/min. All DSC tests were carried out under a 20-mL/min flow of nitrogen to prevent oxidation. Calibration of the instrument was performed using indium as standard.

### Attenuated total reflectance Fourier transform infrared spectroscopy

FTIR was carried out using the attenuated total reflectance (ATR) mode on a Nicolet Avator 360 FTIR, with a 32-scan per sample cycle and a resolution of 8 $cm^{-1}$. The samples were scanned between the following wavelengths of 400 to 4000 $cm^{-1}$.

### Dynamic mechanical thermal analysis

DMTA scans were carried out using a Rheometric scientific mark 3 DMTA in tensile mode. The temperature profile ranged from −130 to 120 °C at a 2 °C/min heating rate with a frequency of 1 Hz. The specimens for DMTA testing (12 mm × 4 mm × 0.5 mm) were cut from the selected samples.

### Tensile testing

Tensile tests were performed on a Lloyd LRX tensile tester using a 2.5-kN load cell, with a test speed of 50 mm/min. The samples were cut into the required dumbbell shape, in accordance with ASTM D 882, and the thickness of each sample was recorded. There were five specimens of each batch and were mechanically tested for statistical purposes.

### White light profilometry

A New View 100 white light profilometer was employed to analyse the surface characteristics of selected materials.

## Results and discussion

### Synthesis of grafted copolymers of SBS via UV polymerisation

UV polymerisation has become a well-established technology which has found a large number of industrial applications due to the relative ease in which the reaction occurs. In general, a liquid resin containing a photoinitiator, BP, is transformed into a solid polymer simply by exposure to UV light [15–18].

In the context of this study, it was postulated that an allylic hydrogen atom was abstracted from the butadiene backbone by the BP which then reacted with NIPAAm, thus forming the reaction sequence illustrated in Fig. 1.

### ATR-FTIR analysis of SBS-g-NIPAAm copolymers

ATR-FTIR spectroscopy was carried out on SBS, NIPAAm and SBS-g-NIPAAm copolymers as shown in Fig. 2. The main bands for characterising the butadiene segment within SBS (Fig. 2a) are $CH_2$ scissoring at 1449 $cm^{-1}$, *trans*-1,4 C=C out of phase deformation at 964 $cm^{-1}$, =CH stretching at 3005 $cm^{-1}$ and C–H stretching at 2916 and 2844 $cm^{-1}$. Regarding the PS segments, styrene absorption occurs at 697 $cm^{-1}$, C–H out of plane deformation occurs at 3060 $cm^{-1}$ and aromatic C–C stretching occurs at 1601 $cm^{-1}$ [1, 19, 20]. The ATR-FTIR spectrum for NIPAAm shown in Fig. 2b illustrates bands corresponding to C=O stretching and NH bending for secondary amides at 1655 and 1544 $cm^{-1}$. These bands are present as small shoulders in SBS-g-NIPAAm copolymer shown in Fig. 2c. The peak at 1545 $cm^{-1}$ for NIPAAm and SBS-g-NIPAAm copolymer was assigned as a symmetric deformation of $NH_3^+$. These results correspond to the finding of Erbil et al. [21] and Ju et al. [22]. However, the peaks present at 1617 $cm^{-1}$ (C=C) and 1407 $cm^{-1}$ ($CH_2$=) in the NIPAAm spectrum disappeared for SBS-g-NIPAAm copolymer as illustrated in Fig. 2b. This suggests that NIPAAm had grafted to SBS resulting in the loss of the double bond associated with the monomer.

### Thermal analysis of SBS-g-NVP copolymers

Various DSC thermographs representing several concentrations of SBS-g-NIPAAm copolymers are illustrated in Fig. 3. As depicted in the DSC thermographs, exothermic variability existed in the temperature region between 50 and 200 °C for each of the grafted copolymers. This variability was the result of the breakdown of crosslink's which were formed within the SBS copolymer during UV polymerisation.

When analysing the butadiene domain, shown in Fig. 4, all of the grafted samples have a broad thermal transition when compared to the PB domain of SBS, suggesting that grafting had occurred within each of the SBS-g-NIPAAm copolymers.

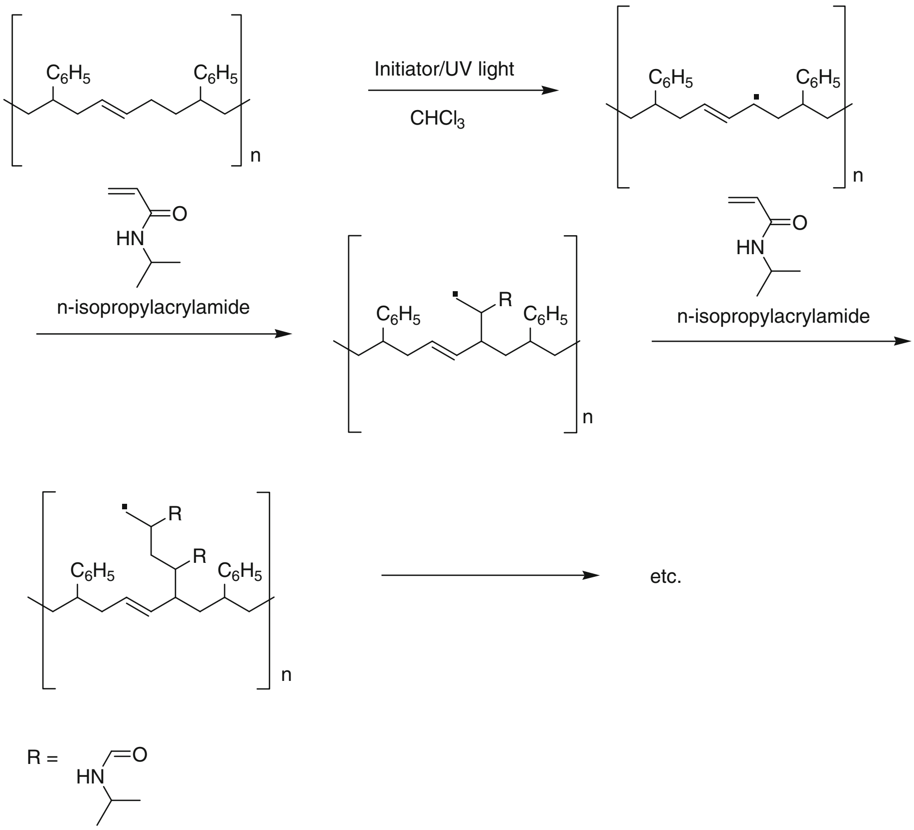


**Fig. 1** A scheme showing the reaction of SBS and NIPAAm to yield SBS-g-NIPAAm copolymers

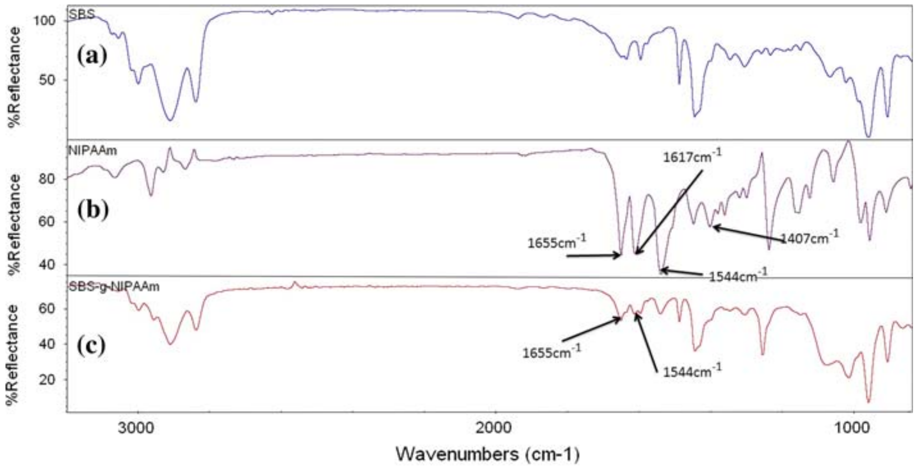


**Fig. 2** Comparisons between the different ATR-FTIR spectrums: **a** SBS, **b** NIPAAm and **c** SBS-g-NIPAAm

## DMTA analysis of SBS and the grafted SBS copolymers

From the DSC analysis as shown in Figs. 3 and 4, it was speculated that grafting had taken place for each of the samples tested. However, to further establish that grafting had occurred, DMTA studies were performed. In each of the loss tangent thermograms, illustrated in Fig. 5, the peak height of the tan $\delta$ value corresponds to the $T_g$ of the samples being tested. As illustrated in the thermograms, there are two notable transitions, the first and most obvious transition corresponds to the $T_g$ of the PB domain within the matrix at low temperatures ($\sim -90$ °C) and the second which is difficult to define is due to the grafted material becoming viscous as the temperature is increased, corresponding to the $T_g$ of the stiff PS domain. Thus, the thermograms reflect the microphase separation which exists within the SBS copolymer or grafted SBS copolymer systems.

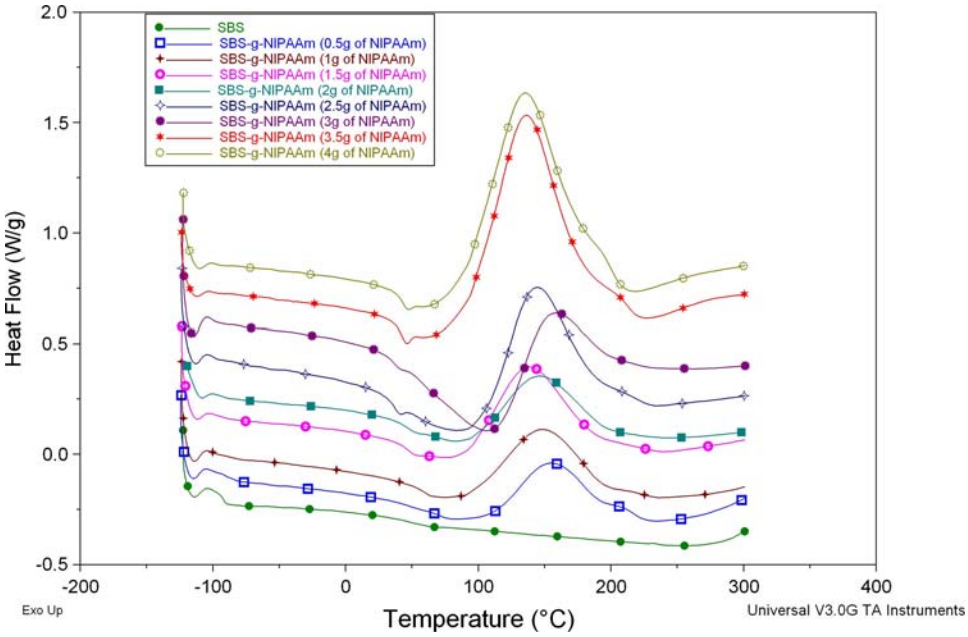


**Fig. 3** DSC thermographs of SBS-g-NIPAAm resulting from the reaction of SBS and various concentrations (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 g) of NIPAAm

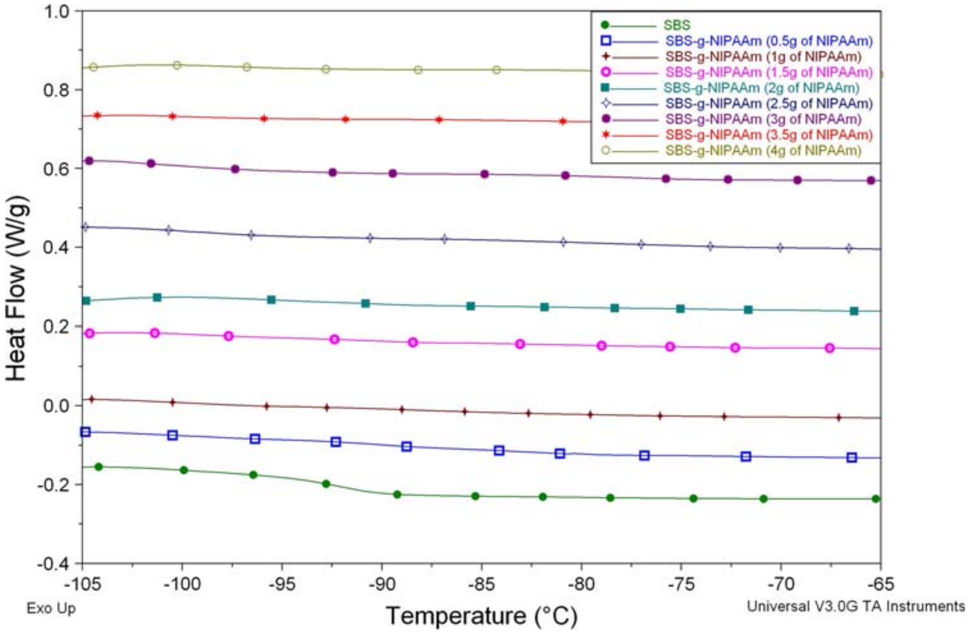


**Fig. 4** DSC thermographs showing the butadiene domain for SBS-g-NIPAAm resulting from the reaction of SBS and various concentrations (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 g) of NIPAAm

As illustrated in thermogram shown in Fig. 5, a glass transition value for SBS can be detected at −92 °C corresponding to the PB segment. However, there was an increase in $T_g$ from −92 to −79 °C for non-washed SBS-g-NIPAAm copolymer, indicating that a higher level of grafting had occurred. This is reflected in washed SBS-g-NIPAAm copolymer where the $T_g$ value shifted to −74 °C.

From the DMTA results, it is evident that the glass transition values for each of the samples tested increased, establishing that grafting had occurred onto various butadiene segments along the SBS backbone. Therefore, it is suggested that grafting will increase the $T_g$ of the PB phase by increasing the thermal energy required to free polymer molecules from additional constraints.

## Tensile analysis of the grafted SBS copolymers

The grafted samples were solvent cast onto silicone. These samples were split equally into two batches, where one batch was soxhlet extracted (washed) for 5 days using

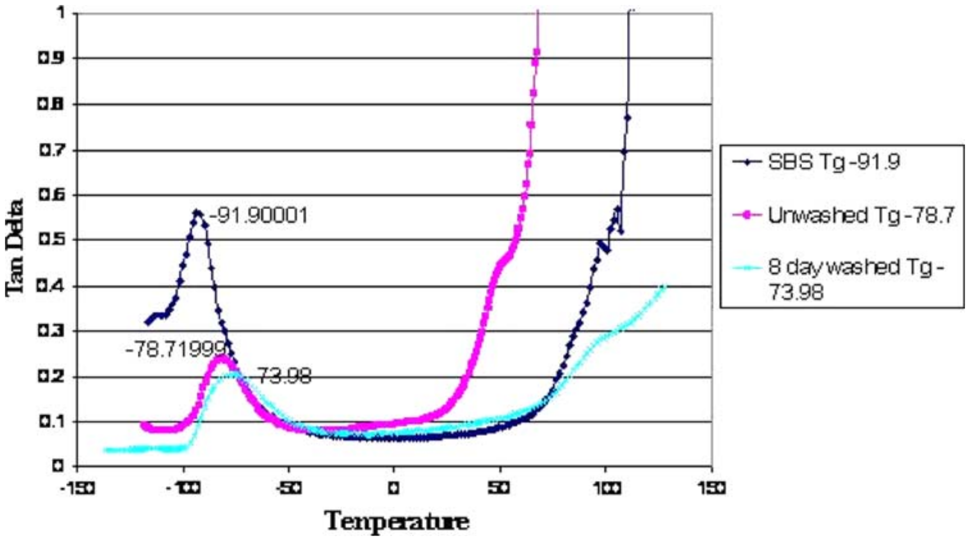


**Fig. 5** DMTA spectra representing SBS, non-washed SBS-g-NIPAAm and washed SBS-g-NIPAAm samples after 8 days

**Table 2** The tensile results for washed and non-washed SBS-g-NIPAAm copolymers

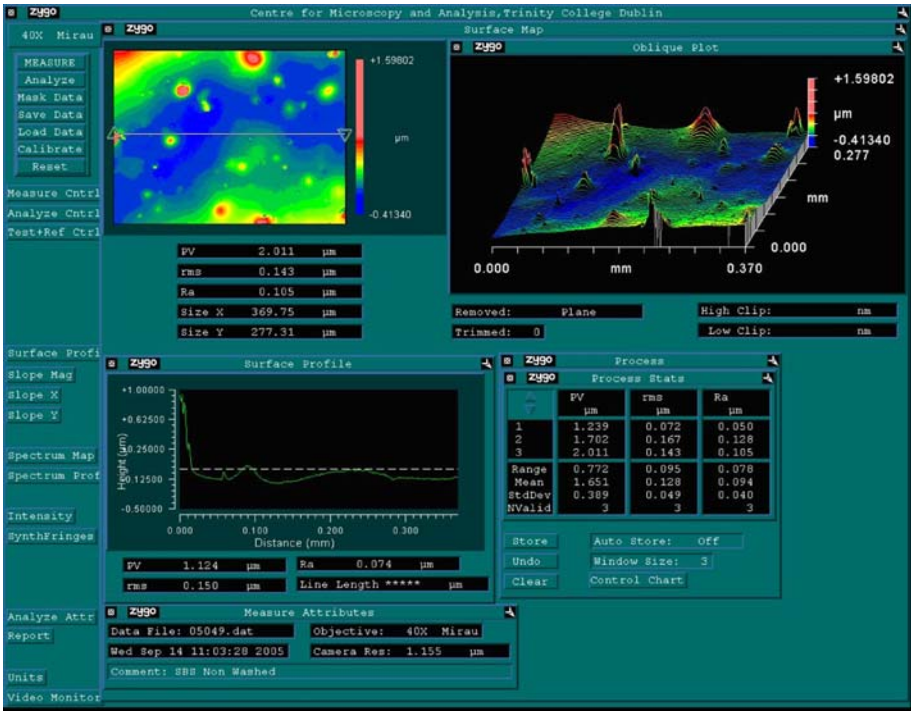
| | Max | Min | Mean | Median | SD |
|---|---|---|---|---|---|
| SBS-g-NIPAAm (washed) | | | | | |
| Young’s modulus (MPa) | 111.44 | 33.513 | 74.592 | 69.968 | 30.327 |
| Load at break (N) | 4.7835 | 2.464 | 3.910 | 3.886 | 0.828 |
| Deflection at break (mm) | 7.700 | 3.948 | 5.878 | 5.354 | 1.499 |
| Stress at break (MPa) | 7.972 | 3.851 | 5.61 | 5.528 | 1.363 |
| Strain at break (%) | 38.503 | 19.741 | 29.392 | 26.771 | 7.499 |
| SBS-g-NIPAAm (non-washed) | | | | | |
| Young’s modulus (MPa) | 156.03 | 30.741 | 93.678 | 101.24 | 55.098 |
| Load at break (N) | 9.8726 | 5.492 | 8.169 | 8.4935 | 1.342 |
| Deflection at break (mm) | 48.576 | 20.971 | 42.106 | 44.597 | 8.900 |
| Stress at break (MPa) | 6.6135 | 2.0849 | 4.1283 | 4.7364 | 1.7045 |
| Strain at break (%) | 242.88 | 104.85 | 210.53 | 222.98 | 44.503 |

methanol to remove the non-grafted homopolymer. Due to variations in each of the batches tested, the median tensile values were used herein for all tensile-related results. The information obtained from the tensile study (including standard deviations) is presented in Table 2.

From the tensile data results, as presented in Table 2, SBS-g-NIPAAm copolymers show a reduction in tensile values as a result of the washing procedure. To determine why there was a reduction in deflection at break and stress at break for washed SBS-g-NIPAAm samples, the size of non-grafted homopolymer comes under consideration. The non-grafted PNIPAAm is entangled within the grafted SBS copolymer resulting in the homopolymer acting as a plasticiser. With the removal of the homopolymer, the grafted SBS copolymer is much stiffer due to the grafting of NIPAAm on to the once flexible butadiene segments resulting in the deflection at break and stress at break values decreasing.

## White light profilometry of SBS and SBS-g-NIPAAm

As illustrated in Fig. 6, the root mean square (RMS), as well as peak-to-valley (PV) values (0.128 and 1.651 µm, respectively) for SBS, indicated that the material had a smooth surface. However, when these values were compared to an SBS-g-NIPAAm copolymer as shown in Fig. 7, the RMS parameter (1.125 µm) and the PV value (13.878 µm) were greater than that of SBS. Thus, it was found that the PV of each of the grafted copolymers tested was influenced by monomeric concentrations and the amount of chloroform still present in the sample after curing. The chloroform which occupies free volume space between chains migrates to the surface of the material by the process of evaporation, thus changing the morphology by creating crevices within the grafted samples, which affects the RMS values. This is an important property characteristic which directly affects the non-thrombogenic



PV 2.011 µm
rms 0.143 µm
Ra 0.105 µm
Size X 369.75 µm
Size Y 277.31 µm

Removed: Plane
Trimmed: 0
High Clip: nm
Low Clip: nm

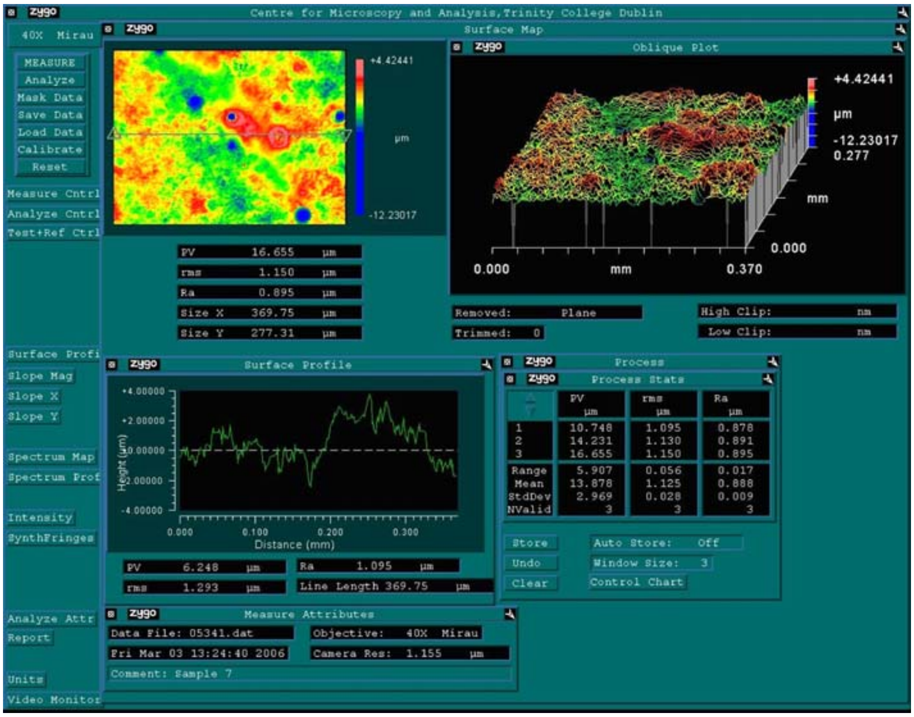
PV 1.124 µm
rms 0.150 µm
Ra 0.074 µm
Line Length ***** µm

| | PV µm | rms µm | Ra µm |
|---|---|---|---|
| 1 | 1.239 | 0.072 | 0.050 |
| 2 | 1.702 | 0.167 | 0.128 |
| 3 | 2.011 | 0.143 | 0.105 |
| Range | 0.772 | 0.095 | 0.078 |
| Mean | 1.651 | 0.128 | 0.094 |
| StdDev | 0.389 | 0.049 | 0.040 |
| NValid | 3 | 3 | 3 |

Auto Store: Off
Window Size: 3

Data File: 05049.dat
Wed Sep 14 11:03:28 2005
Objective: 40X Mirau
Camera Res: 1.155 µm
Comment: SBS Non Washed

**Fig. 6** A white light profilometry scan for a SBS copolymer illustrating 2D and 3D surface profiles as well as the PV value, 1.651 µm and the RMS parameter, 0.128 µm



PV 16.655 µm
rms 1.150 µm
Ra 0.895 µm
Size X 369.75 µm
Size Y 277.31 µm

Removed: Plane
Trimmed: 0
High Clip: nm
Low Clip: nm

PV 6.248 µm
rms 1.293 µm
Ra 1.095 µm
Line Length 369.75 µm

| | PV µm | rms µm | Ra µm |
|---|---|---|---|
| 1 | 10.748 | 1.095 | 0.878 |
| 2 | 14.231 | 1.130 | 0.891 |
| 3 | 16.655 | 1.150 | 0.895 |
| Range | 5.907 | 0.056 | 0.017 |
| Mean | 13.878 | 1.125 | 0.888 |
| StdDev | 2.969 | 0.028 | 0.009 |
| NValid | 3 | 3 | 3 |

Auto Store: Off
Window Size: 3

Data File: 05341.dat
Fri Mar 03 13:24:40 2006
Objective: 40X Mirau
Camera Res: 1.155 µm
Comment: Sample 7

**Fig. 7** A white light profilometry scan for a SBS-g-NIPAAm copolymer illustrating 2D and 3D surface profiles as well as the PV value, 13.878 µm and the RMS parameter, 1.125 µm

properties of the material within a specific biological environment, i.e. the smoother the surface, the less likely that thrombosis will occur. However, this roughness may aid in the muco-adhesion properties of the material, which is advantageous in biological environments such as arteries.

## Conclusion

In this study, we have evaluated the potential use of UV-polymerised SBS-g-NIPAAm copolymers for biomedical applications by evaluating the spectral, thermal and mechanical data. It was evident from the spectral analysis that representative bands for the PNIPAAm were present as shoulders on the grafted copolymer, thus indicating grafting. This was confirmed by the increase in glass transition values which were found using DSC and DMTA. Topography analysis indicated that the grafted material has a rougher surface when compared to the SBS copolymer which is desirable for muco-adhesion. Therefore, in conclusion a hydrophilic monomer was successfully grafted onto a hydrophobic polymer via UV polymerisation.

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