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The synthesis and characterisation of grafted random styrene butadiene for biomedical applications

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Abstract The work undertaken investigates the spectral, thermal and surface characteristics of a random styrene butadiene rubber (SBR) with monomeric graft(s) of acrylic acid (AA), *N*-vinyl-2-pyrrolidinone (NVP) or *N*-isopropylacrylamide (NIPAAm) synthesised using UV polymerisation. The grafted materials were characterised by differential scanning calorimetry (DSC), modulated differential scanning calorimetry (MDSC), attenuated total reflectance infrared Fourier transform spectrometry (ATR-FTIR) and atomic force microscopy (AFM). Thermograph analysis has shown an endothermic transition occurring at ~75 °C for all random SB-g-NVP copolymers, whereas the T_g value for random SB copolymer was found at 60 °C, thus suggesting that a chemical reaction between styrene and NVP had occurred. Similar thermal profiles to that of random SB-g-NVP copolymers were evident when random SB was UV polymerised with AA. When NIPAAm was grafted onto random SB, a notable exothermic transition was evident in all samples tested using DSC. It was established using MDSC that this exothermic transition was caused by the breakdown of crosslinks as a result of UV polymerisation.

Introduction

The introduction of a hydrophilic material onto a hydrophobic thermoplastic elastomer has the potential to create a material with desirable mechanical and thermal properties for use in adhesive or biomedical applications. According to Rao and Rao [1], maleic anhydride (MAH) was grafted onto acrylonitrile butadiene styrene (ABS) by the addition to the double bond initiated by benzoyl peroxide (BPO). Sheng and co-workers [2] found that BPO initiated the removal of an allylic hydrogen atom while azobisisobutyronitrile (AIBN) acted upon the addition of the double bond of styrene butadiene rubber (SBR), which is in agreement with the findings of Huang and Sundberg [3–6]. Mrrov and Velichkova [7] described how MAH was grafted onto styrene isoprene styrene (SIS) only by the removal of an allylic hydrogen atom, whereas Aimin and Chao [8] have investigated the grafting mechanism of styrene butadiene styrene (SBS) with MAH using BPO and AIBN. They found that the variation of C=C content in SBS-g-MAH was used to verify the different graft mechanisms of BPO and AIBN. They concluded that the grafting reaction occurs by the addition onto C=C bond when AIBN was used, while the removal of an allylic hydrogen atom was evident when BPO was used to initiate the reaction. Lee and Chen [9] have grafted *N*-isopropylacrylamide (NIPAAm), a thermo-sensitive hydrogel, onto SBS using BPO as the initiator. This was carried out to improve the water absorption and thermo sensitivity of SBS. Hydrogels have physical properties similar to those of human tissue and

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possess excellent tissue compatibility and are used as biomedical materials. However, the main disadvantage of hydrogels is their poor mechanical properties after swelling which maybe overcome by the grafting of a thermoplastic elastomer. With this in mind, the intent of this work was to develop hydrophilic thermoplastic elastomers using acrylic acid (AA), *N*-vinyl pyrrolidinone (NVP) or NIPAAm hydrogels as the grafted entities.

Experimental

Materials

The samples were prepared by UV polymerisation. The base polymer, random SBR, was supplied by BASF under the trade name of Styroflex 2G66. The monomers used were acrylic acid (AA, supplied by Aldrich), *N*-vinyl-2-pyrrolidinone (NVP, supplied by Aldrich) and *N*-isopropylacrylamide (NIPAAm, supplied by TCI Europe) and were used as-received. Benzophenone (BP, supplied by Aldrich) was used as a UV-light sensitive initiator. Percentages by weight (0.1, 0.5, 0.75, 1, 2, 3%) of polyethylene glycol (600) di-methacrylate (PEG600DMA, supplied by Polyscience Inc.) were added to the required solutions to act as crosslinking agents.

Synthesis of grafted random styrene butadiene via UV polymerisation

Random styrene butadiene (2 g) was dissolved in chloroform (20 mL) at 40 °C. Known concentrations of monomer[1] (2 g), benzophenone (0.06 g) and where applicable a crosslinking agent (Xg)[2] were added at room temperature and stirring continued for 2 h. In order to prepare samples for UV polymerisation, moulds were prepared from silicon mould compound (W.P. Notcutt, Middlesex). The silicon moulds were prepared with rectangular shapes (5 × 2 × 0.5 cm) in order to produce the required sample shapes for testing. All solutions were cured in silicon moulds under two UVA 340 UV lamps (Q-panel lab products) for 2 h in an enclosed environment to ensure complete curing. The samples were placed in a fume cupboard for 24 h and then in an oven at 40 °C for 120 h.

Differential scanning calorimetry (DSC)

Each sample was tested using a TA 2010 differential scanning calorimeter. The sample weights varied between 9.10 and 9.24 mg. The samples were sealed and tested within a temperature range of −120 to 300 °C. All DSC tests were carried out under a 20 mL per minute flow of nitrogen to prevent oxidation. Calibration of the instrument was performed using indium as standard.

Modulated differential scanning calorimetry (MDSC)

MDSC scans were carried out using a TA 2920 modulated differential scanning calorimeter. The samples were cooled to −60 °C and isothermally held for 5 min, after which the samples were modulated ±1 °C every 60 s with a ramp rate of 3 °C per minute up to 300 °C. The samples' sizes ranged from 9.10 to 9.24 mg. All MDSC tests were carried out under a 20 mL per minute flow of nitrogen to prevent oxidation. The instrument was calibrated using indium as standard.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

Fourier transform infrared spectroscopy 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. The samples were scanned between the wavelengths 400 and 4000 cm^{-1}.

Atomic force microscopy (AFM)

The samples were analysed using a Veeco Explorer scanning probe microscopy (SPM). Samples were mounted onto a metal stub using a double-sided adhesive tape such that the cross section of each sample was facing upwards. Topography and phase imaging were obtained on 50 × 50 μm sample regions in non-contact mode, using SPM tips. Three regions were analysed from each sample. Surface roughness calculations were obtained from all three regions.

Results and discussion

Thermal analysis of UV grafted random SB copolymers

N-vinyl-2-pyrrolidinone (NVP) was chosen as the initial grafting monomer for UV polymerisation as there has been substantial work carried out on this material in our research laboratory [10]. A DSC thermograph containing random SB-g-NVP copolymers with varying concentrations (0.1, 0.5, 0.75, 1, 2 and 3% w/v) of polyethylene glycol 600 dimethylacrylate (PEG600DMA) chain extender is illustrated in Fig. 1.

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[1] Monomer = AA, NVP or NIPAAm.

[2] Xg = 0.002, 0.01, 0.015, 0.02, 0.04 and 0.06 g of crosslinking agents.

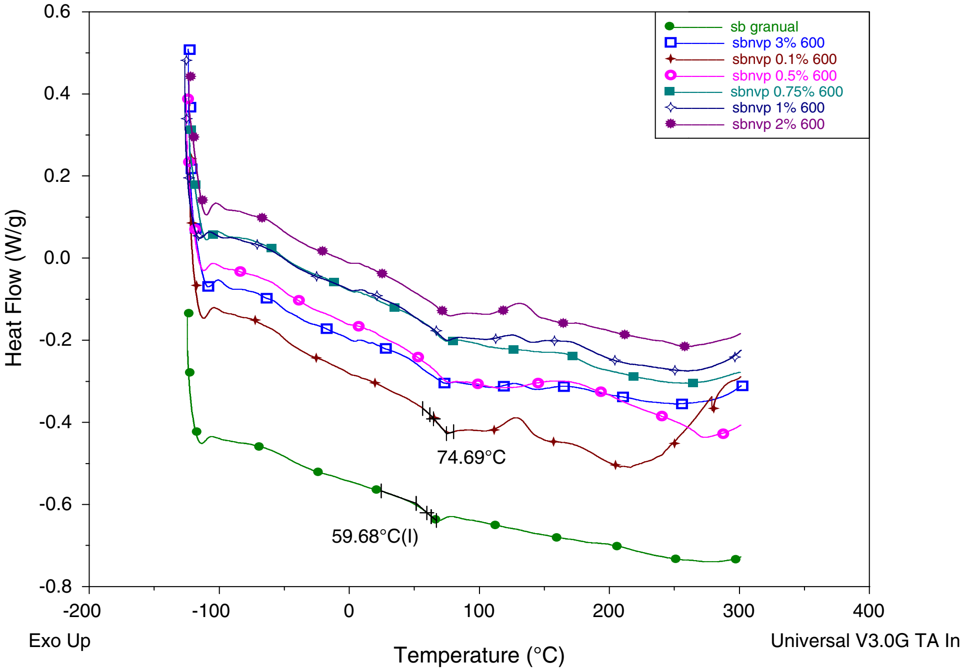


Fig. 1 A DSC thermograph representing random SB copolymer and UV-polymerised random SB-g-NVP copolymers using varying concentration (0.1, 0.5, 0.75, 1, 2 and 3% w/v) of PEG600DMA

Notable thermal transitions occur at around 75 °C for all SB-g-NVP copolymers, as presented in Fig. 1. However, the T_g value for random SB copolymer was 60 °C, suggesting that a chemical reaction between styrene and NVP had occurred. The T_g value for the butadiene domain was non-detectable due to possible grafting or its initial low content which may have been shielded by the hydrogel. When random SB was UV-polymerised with AA using different concentrations of PEG600DMA, similar thermal profiles to that shown in Fig. 1 were obtained. The glass transitions occurred at ~74 °C for random SB-g-AA copolymers and these thermal transitions are presented in Fig. 2. The same principles, regarding glass transition and the butadiene domain, for random SB-g-NVP copolymers apply for random SB-g-AA copolymers.

The DSC thermographs shown in Fig. 3 illustrate the T_g values at ~65 °C and exothermic peaks between 150 and 170 °C for UV-polymerised random SB-g-NIPAAm

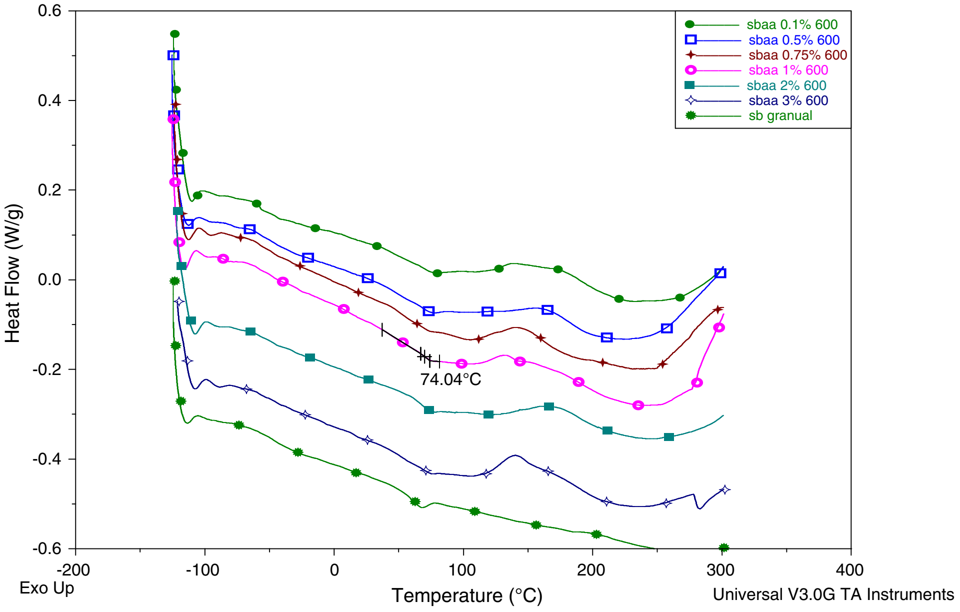
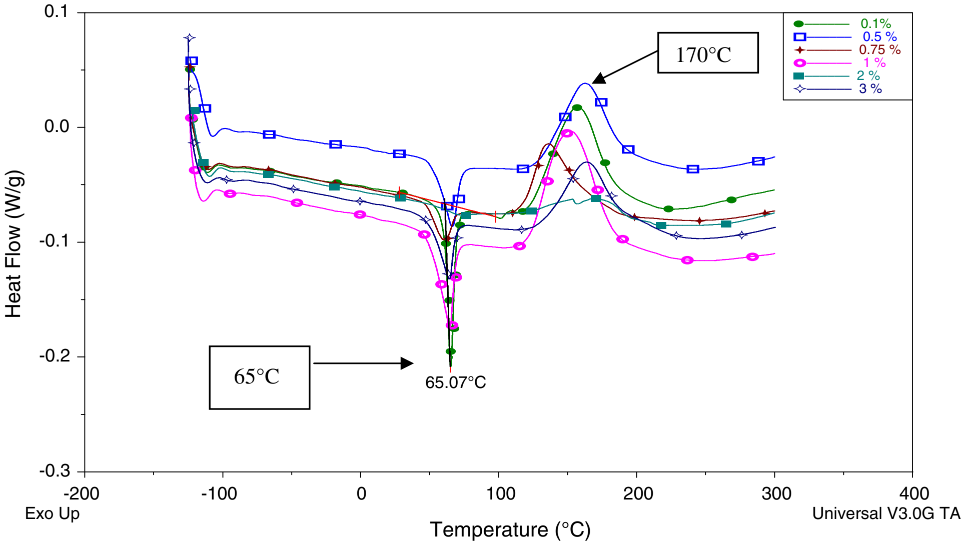


Fig. 2 A DSC thermograph representing random SB copolymer and UV-polymerised random SB-g-AA copolymers using varying concentrations (0.1, 0.5, 0.75, 1, 2 and 3% w/v) of PEG600DMA

Fig. 3 DSC thermographs representing UV-polymerised SB-g-NIPAAm copolymers using varying concentration (0.1, 0.5, 0.75, 1, 2 and 3% w/v) of PEG600DMA



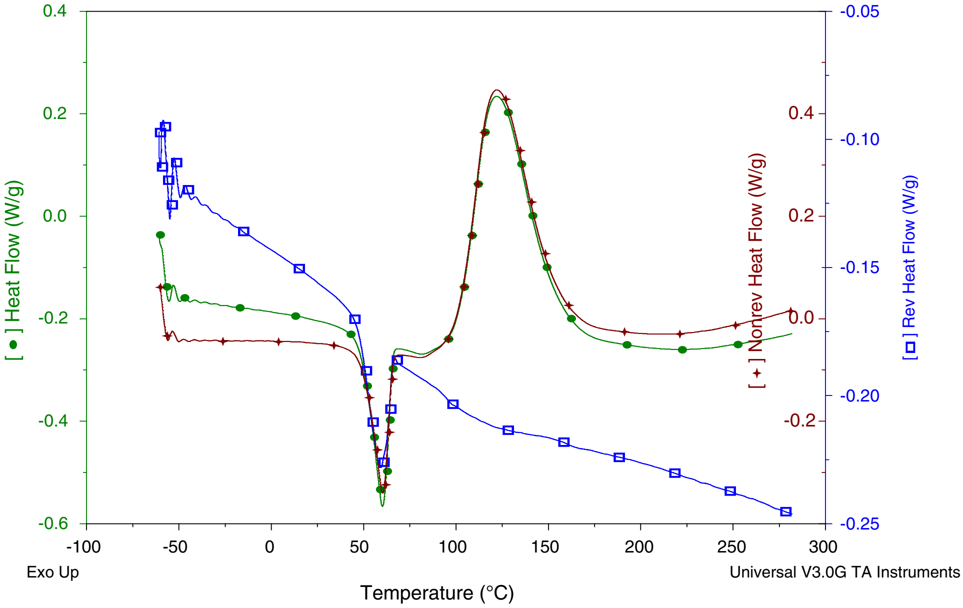
copolymers with varying concentrations (0.1, 0.5, 0.75, 1, 2 and 3% w/v) of PEG600DMA. The glass transitions were a lot more defined than previous UV-polymerised samples and this would suggest that this transition is in fact a melting transition. However, as shown in the DSC thermograph illustrated in Fig. 1, random SB copolymer has a T_g of 60 °C, which is within close proximity to the transition that occurred for random SB-g-NIPAAm copolymers.

MDSC is a much more sensitive technique than traditional DSC as it can break down thermal components into reversible and non-reversible transitions. A sample containing random SB-g-NIPAAm with a 1% w/v concentration of PEG600DMA was analysed. As illustrated in Fig. 4, a sinusoidal effect occurred between −50 and −25 °C. This sinusoidal effect was the result of *cis* and *trans* butadiene segments being shifted in and out of phase. There was also a sharp endothermic peak in the baseline at 65 °C which corresponds to the DSC thermograph illustrated in Fig. 3. However, the exothermic peak located at 150 °C was not present as a reversible transition, thus indicating that the exothermic process involved in the thermal transition is not reversible, which suggests that this transition is the result of the breakdown of crosslinks within the material.

ATR-FTIR of UV grafted random SB copolymers

The UV-polymerised samples were tested by ATR-FTIR spectroscopy. Spectra of random SB and random SB-g-NVP with 3% w/v PEG600DMA are outlined in Figs. 5 and 6, respectively. The characteristic carbonyl peak for

Fig. 4 A MDSC thermograph illustrating the reverse and non-reverse transitions for random SBS-g-NIPAAm with 1% w/v PEG600DMA



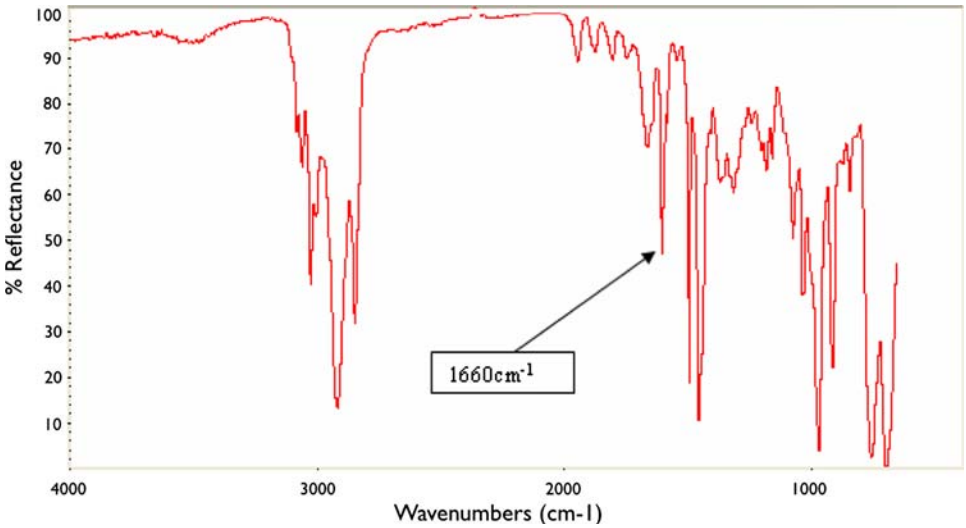


Fig. 5 ATR-FTIR spectrum of random SB copolymer

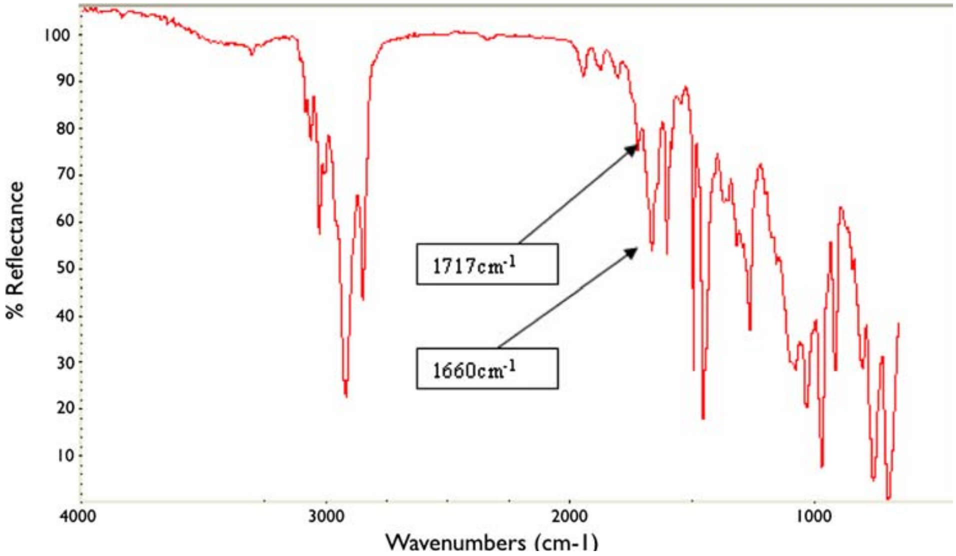


Fig. 6 ATR-FTIR spectrum representing a random SB-g-NVP copolymer with 3% w/v PEG600DMA

NVP and AA is a peak located between 1656 and 1663 cm^{-1}. However, this peak was also present in random SB copolymer. Therefore, it was speculated that processing aids were used in the production of random SB copolymer and these processing aids contain C=O bonds. Thus, it was difficult to determine the actual peaks involved in grafting. With the exception of the peak at 1717 cm^{-1}, these two spectra are almost identical as shown in Fig. 6. It has been suggested by Can [11] that this peak is associated with a new carbonyl of NVP resulting from UV radiation. However, according to Allen et al. [12, 13], this peak is due to the formation of end chain carboxylic acids resulting from chain degradation, chain scission and oxidation. Romero-Sanchez et al. [14] found that UV radiation produces oxidation of SBS and when analysed by FTIR spectroscopy, C=O stretching occurred at 1717 cm^{-1} when the samples were UV-radiated for more than 10 min. Since the samples are UV-polymerised for 2 h, Romero-Sanchez et al. [14] observations would coincide with the findings of the authors.

AFM of UV-polymerised random SB copolymers

AFM was used to determine the surface topography of each of the selected samples. AFM was carried out using an Explorer SPM LIMS 1132A and images were obtained from different areas (50 μm^2) for each sample. As illustrated in Figs. 7 and 8, the AFM scans illustrate the difference between phase and surface topography of random SB copolymers solvent cast onto glass and silicone. The random SB copolymer solvent cast onto glass showed a smoother surface with a height of 486 nm compared to a height of 7.25 μm when silicone was used.

On investigating the topographies of random SB-g-AA copolymers containing 0.1% w/v EGDMA and 3% w/v PEG600DMA as shown in Figs. 9 and 10, average heights

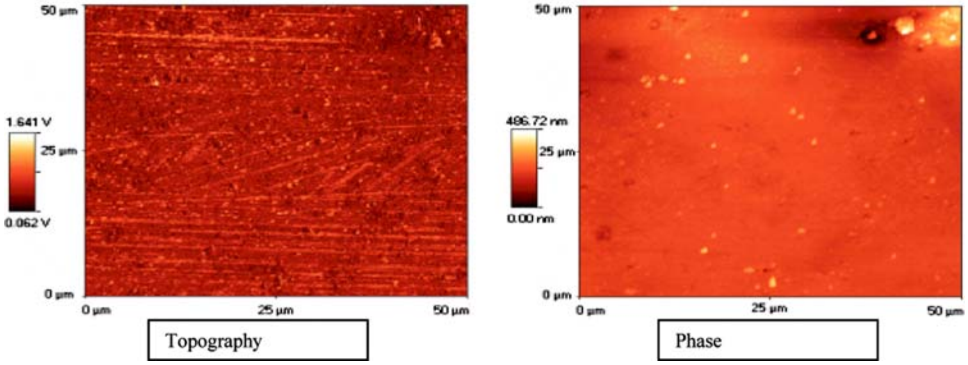


Fig. 7 Atomic force microscopy illustrating the phase and surface topography of random SB copolymer cast onto glass

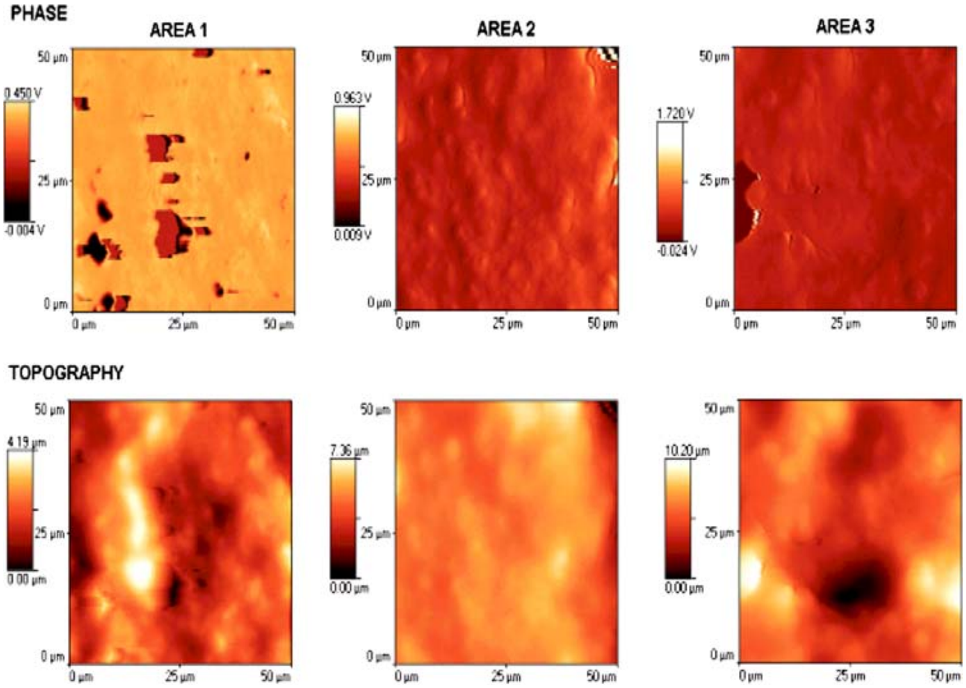


Fig. 8 Atomic force microscopy showing the phase and surface topography at three different areas of random SB copolymer solvent cast onto silicone

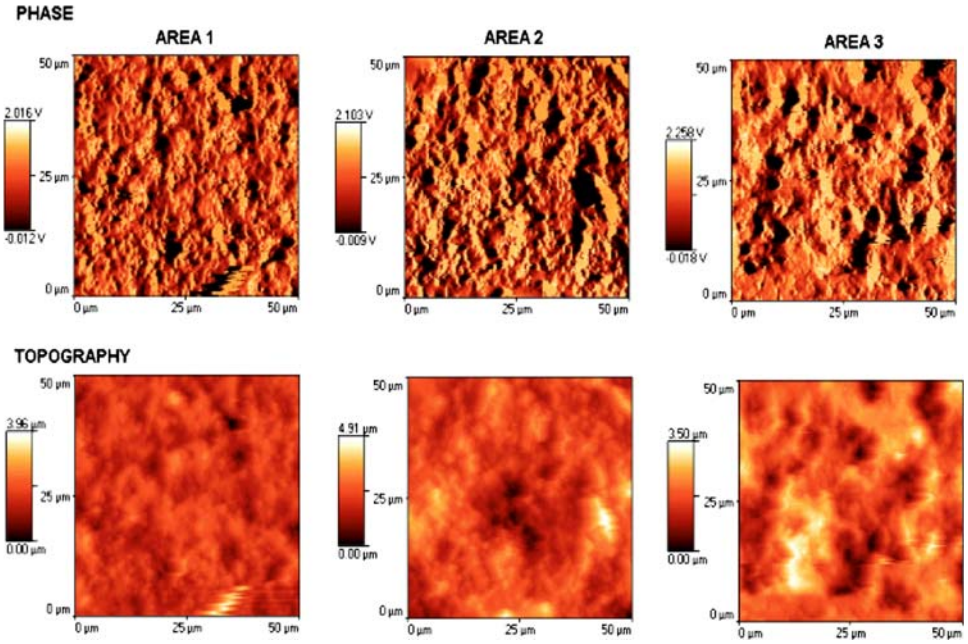


Fig. 9 Atomic force microscopy showing the phase and surface topography at three different areas of random SB-g-AA copolymer with 0.1% w/v EGDMA which was UV-cured onto silicone

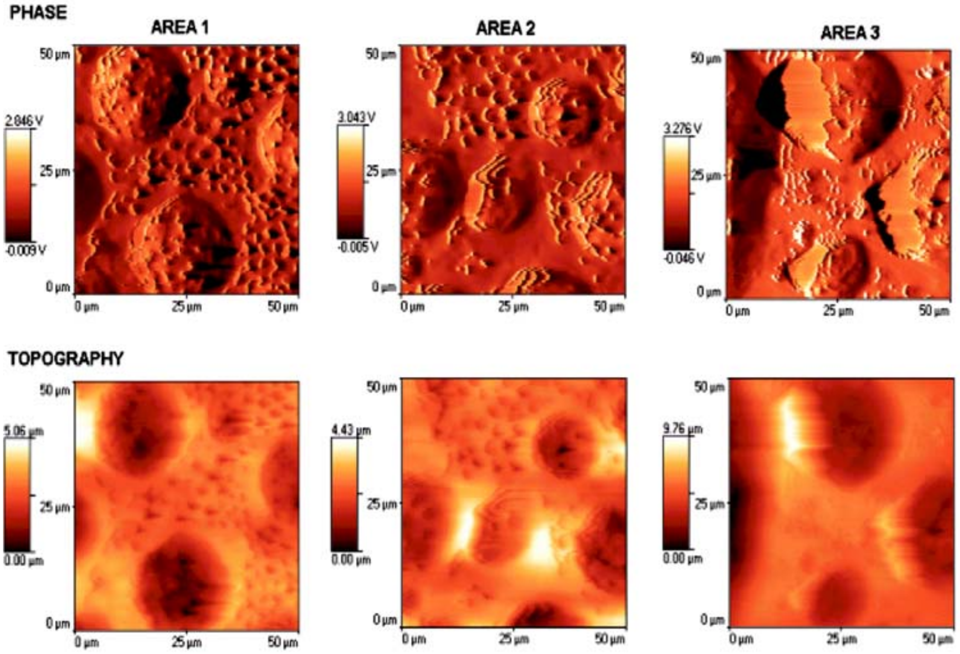


Fig. 10 Atomic force microscopy showing the phase and surface topography at three different areas of random SB-g-AA with 3% w/v PEG600DMA

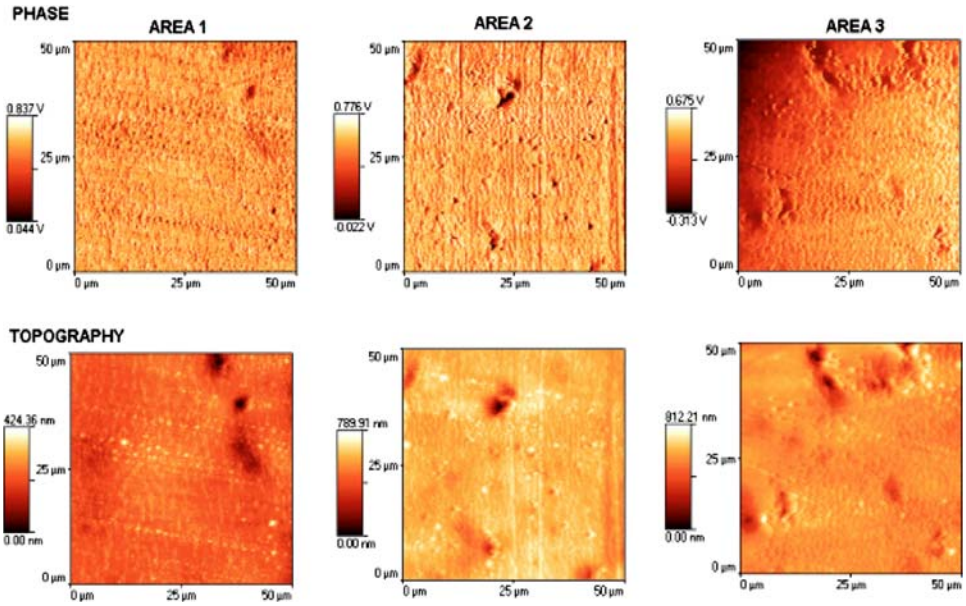


Fig. 11 Atomic force microscopy showing the phase and surface topography at three different areas of random SB-g-NVP with 0.1% w/v of EGDMA which was UV-cured onto silicone

of 4.12 and 6.41 µm were obtained, respectively. Horak et al. [15] found that with the addition of EGDMA to NVP a broad size distribution was produced with a rough surface. However, when the topography of random SB-g-NVP was investigated, as illustrated in Figs. 11 and 12, a smoother surface was apparent. The average height for random SB-g-NVP copolymer with 0.1% w/v EGDMA sample was 675 nm compared to 782.5 nm for random SB-g-NVP copolymer with 3% w/v PEG600DMA. These low heights correspond to random SB copolymer which was solvent cast onto glass.

Conclusions

Although SBR has been used in some non-invasive medical applications such as surgical gloves, it has not been used to date as a material in long-term invasive medical devices.

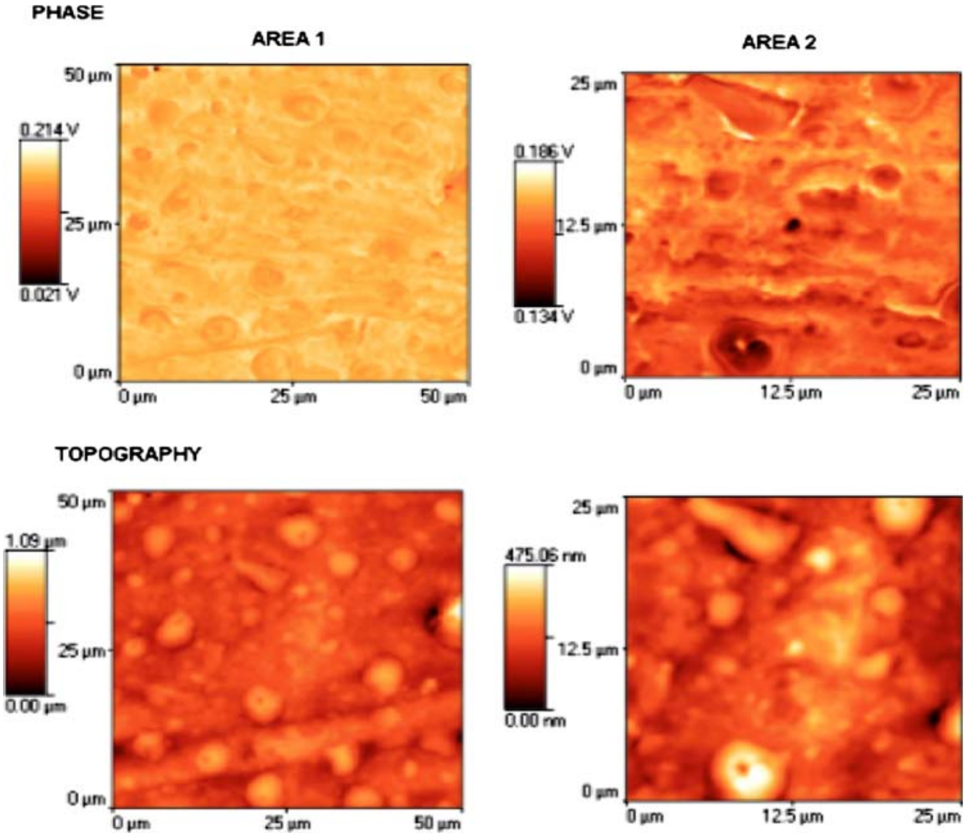


Fig. 12 Atomic force microscopy showing the phase and surface topography at two different areas of random SB-g-NVP with 3% PEG600DMA

SBR is a hydrophobic thermoplastic elastomer which can be converted into a hydrophilic polymer by grafting certain monomers onto its backbone structure. NVP and random SB copolymer were reacted via UV polymerisation and notable thermal transitions were seen to occur at around 75 °C for all random SB-g-NVP copolymers. Considering that the T_g value for random SB copolymer was 60 °C, a chemical reaction between the double bonds of butadiene and NVP was deemed to have occurred, resulting in the increased glass transition of the grafted copolymer. Accordingly, AA and NIPAAm were also reacted with random SB copolymer. The random SB-g-AA behaved in a similar fashion to the random SB-g-NVP. Regarding the SB-g-NIPAAm copolymers, the exothermic peak as shown by DSC was not present in the reversible transition as found by MDSC. This indicates that the exothermic process involved in the thermal transition is not reversible, which suggests the exothermic peak is the result of the breakdown of crosslinks within the material.

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