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DOI:
[10.1039/C6SM01563H](https://doi.org/10.1039/C6SM01563H)

Document Version
Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Musa, M. S., Milani, A., Peter, S., Simpson, G., Lovell, P., Eaves, E., Hodson, N., & Saunders, B. (2016). Tuning the modulus of nanostructured ionomer films of core-shell nanoparticles based on poly(n-butyl acrylate). *Soft Matter*, 12(39), 8112-8123. <https://doi.org/10.1039/C6SM01563H>

Published in:
Soft Matter

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Tuning the modulus of nanostructured ionomer films of core-shell nanoparticles based on poly(*n*-butyl acrylate)

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ABSTRACT: In this study we investigate the structure-mechanical property relationships for nanostructured ionomer films containing ionically crosslinked core-shell polymer nanoparticles based on poly(*n*-butyl acrylate) (PBA). Whilst nanostructured ionomer films of core-shell nanoparticles have been previously shown to have good ductility [*Soft Matter*, 10, 4725, 2014], the modulus values were modest. Here, we used BA as the primary monomer to construct core-shell nanoparticles that provided **films containing** nanostructured **polymers** with much higher glass transition temperature (T_g) values. The core-shell nanoparticles were synthesised using BA, acrylonitrile (AN), methacrylic acid (MAA) and 1, 4-butanediol diacrylate (BDDA). Nanostructured ionomer films were prepared by casting aqueous core-shell nanoparticle dispersions in which the shell -COOH groups were neutralised with KOH and ZnO. The film mechanical properties were studied using dynamic mechanical analysis and tensile stress-strain measurements. The use of BA-based nanoparticles increased the T_g values to close to room temperature which caused a strong dependence of the film mechanical properties on the AN content and extent of neutralisation of the -COOH groups. The Young's modulus values for the films ranged from 1.0 to 86.0 MPa. The latter is the highest modulus reported for cast films of nanostructured ionomer films prepared from core-shell nanoparticles. The films had good ductility with strain-at-break values of at least 200%. The mechanical properties of the films were successfully modelled using the isostrain model. From comparison with an earlier butadiene-based system this study demonstrates that the

nature of the primary monomer used to construct the nanoparticles can profoundly change the film mechanical properties. The aqueous nanoparticle dispersion approach used here provides a simple and versatile method to prepare high modulus elastomer films with tuneable mechanical properties.

INTRODUCTION

Core-shell nanoparticles continue to attract considerable interest¹⁻³ because of the ability to tune their properties through independent control of the materials comprising the core and shell structures. Core-shell nanoparticles can also exhibit interesting stimuli-responsive physical and chemical properties³⁻⁵. Much of this research is driven by their property changes in response to external stimuli, such as temperature⁶, pH⁵ and ionic strength⁷. However, elastomeric films constructed using core-shell nanoparticles containing COOH groups have received less attention. Our previous work introduced ductile nanostructured elastomeric films prepared by casting films from aqueous dispersions of low glass transition temperature (T_g) core-shell nanoparticles in the presence of ZnO^{8,9}. The latter was used to neutralise the surface -COOH groups and introduced ionic inter-particle crosslinking. Those core-shell nanoparticles were prepared using 1,3-butadiene (Bd), acrylonitrile (AN) and methacrylic acid (MAA). The proportions of AN and MAA and extents of neutralisation were shown to affect the modulus values^{8,9}. Whilst those nanostructured ionomer films had good ductility, their modulus values were low. Also, the use of Bd, which has a boiling point of -5 °C, restricted the versatility for nanoparticle preparation because a high pressure reactor was required⁸. In this study, we sought to overcome *both* the versatility and modulus deficiencies by investigating core-shell nanoparticles prepared using *n*-butyl acrylate (BA) in place of Bd. BA has a much higher boiling point (145 °C) which enabled conventional (non-pressurised) emulsion polymerisation equipment to be used for nanoparticle preparation. Furthermore, poly(*n*-butylacrylate) (PBA) has a T_g of -49 °C¹⁰ which is about 20 °C higher than the T_g for PBd⁸. We hypothesised that increasing the T_g of the nanoparticle phases would provide higher modulus nanostructured films with built-in modulus tuneability afforded by the AN and MAA groups. Accordingly, an aim of the study was to investigate the role of T_g on the mechanical properties of nanostructured ionomer films.

Ionomers are polymers which contain a low concentration (less than ~ 15 mol. %) of ionic groups¹¹⁻¹³ e.g., carboxylates. These groups can strongly enhance the modulus due to the presence of physical crosslinks involving ionic aggregates. In a low dielectric constant

polymer matrix containing ionic groups multiplets and ionic clusters can form¹²⁻¹⁴. Multiplets contain a small number of closely spaced ion pairs; meanwhile, ionic clusters contain many multiplets¹². Whilst conventional ionomers are now well understood¹³, there have been relatively few studies involving core-shell nanoparticle ionomer films¹⁵, which are the subject of the present work. Kim et al.¹⁶ studied ionomer films prepared using poly(butyl methacrylate) dispersions and showed that neutralisation converted the acid-rich phase at the interparticle boundary into an ionomer phase. Gurney et al.¹⁷ recently studied the effect of pH on the mechanical properties of PBA-poly(acrylic acid) diblock copolymers. Bose et al. studied self-healing for PBA ionomers cast from solution and proposed that reversible ionic crosslinks were formed¹⁸. Ionomers prepared using polymer chains with precisely sequenced ionic groups have also been studied¹⁹. The overwhelming majority of ionomer films studied to date have been prepared by casting films of linear polymers from organic solvent-based solutions²⁰ or using compounding²¹ or compression molding^{15, 22}. However, there has been relatively little work reported for nanostructured ionomeric films prepared from aqueous dispersions^{8, 9}, which is an approach with obvious environmental benefits.

Previously, we explored the structure-property relationships for low modulus Bd-based core-shell nanostructured ionomer films and probed methods for controlling their mechanical properties^{9, 23, 24}. For those soft films it was shown that inclusion of AN was an effective method for tuning the modulus of the films⁸. AN is known to increase the surface hardness²⁵, modulus²⁶ and tensile strength²⁷ and thermal stability^{28, 29} of copolymers due to the strong polarity of nitrile groups²⁸ and strong molecular interactions³⁰. However, all of our previous nanostructured ionomer films used Bd as the main structural monomer^{9, 23, 24}. For the core-shell systems, Bd comprised more than ~ 70 wt.% of the nanoparticles and the Young's modulus values were less than 12 MPa^{8, 9, 24}. Here, we replaced Bd with BA in order to explore the role of the T_g of the main structural component in determining the mechanical properties of the nanoparticle films. PBA-based core-shell nanoparticles have been the subject of a number of studies^{15, 31-33}. However, they have not been studied as nanostructured ionomer films cast from aqueous dispersions to the best of our knowledge.

The approaches used to synthesise the core-shell nanoparticles and prepare the nanostructured ionomeric films studied in this work are depicted in Scheme 1a and b, respectively. The core-shell nanoparticles were prepared by seeded emulsion polymerisation. Two types of core-shell nanoparticle systems were synthesised: a *high* core volume fraction

system (lower branch of Scheme 1a) and a *low* core volume fraction system (upper branch of Scheme 1a). The starting point for both systems was the PBA *seed* (Cs100(0)) nanoparticles. (The code used for all the nanoparticles is shown in Scheme 1b.) The *seed* was grown further for the *high* core volume fraction systems (Stage 2) to produce larger PBA *core* (C100(0)) nanoparticles. Higher T_g copolymer shells of PBA-AN-MAA-BDDA (BDDA is 1,4-butanediol diacrylate) were then grown on the *core* C100(0) nanoparticles (Stage 3, lower branch of Scheme 1a). By contrast, the *low* core volume fraction system used copolymer shell growth directly from the *seed* Cs100(0) nanoparticles (upper branch of Scheme 1a). For both core-shell nanoparticle systems the nanostructured films were formed by casting pH-adjusted mixed aqueous dispersions containing the nanoparticles and ZnO (Scheme 1b) which resulted in the -COOH groups being neutralised by both K^+ and Zn^{2+} .

In this study, we investigated the effect of both PBA-based core-shell nanoparticle composition and neutralisation on the mechanical properties of new PBA-based nanostructured ionomer films. The characterisation data for the core-shell nanoparticles are first discussed and the effect of neutralisation on nanoparticles are then studied to establish conditions for film formation. We then investigated the effect of nanoparticle composition on the film mechanical properties. For these films the AN content was found to be crucial in positioning the film T_g either close to or above room temperature and this was shown to have a major effect on the mechanical properties as well as the ionomer contribution to the film modulus. We also show that the isostrain model can be used to describe the mechanical properties of the nanostructured films and compare the results for the BA-based systems with a Bd-based system from previous work. This study provides a simple route to high modulus nanostructured films with good ductility using procedures that are water-based and versatile.

EXPERIMENTAL

Materials

Unless otherwise stated all materials were purchased from Aldrich. Aerosol MA-80 (Cytec, $\geq 80\%$), potassium persulphate (KPS, $\geq 99\%$), BDDA ($\geq 99\%$) and *t*-dodecylmercaptan ($\geq 99\%$) were used as received. Inhibitor was removed from the BA (Merck, $\geq 99\%$) and AN ($\geq 99\%$) by washing with dilute aqueous NaOH solution and water. MAA (99%) was purified by passing the monomer through a column filled with aluminium oxide (alumina) gel. ZnO (55 wt.%) was obtained from Aquaspersions Ltd., UK and had an average particle size of ~ 600 nm. Ultrahigh purity deionised water was used in all experiments.

Synthesis of core-shell nanoparticle dispersions

The core-shell nanoparticle dispersions were synthesised using seed-feed or seed/core-feed emulsion polymerisation (See Scheme 1a). The code used for the nanoparticles is $Cv(w)-x(y)$; where v , w , x and y are the nominal total core vol.%, wt.% BDDA in the core, wt.% AN in the shell and wt.% BDDA in the shell, respectively. Accordingly, C55(0)-30(1) nanoparticles contained a (crosslinker-free) core volume fraction of 55 vol.% and the shell contained 30 wt.% AN and 1 wt.% of BDDA. PBA *seed* dispersions (Cs100(0), Stage 1) were synthesised by emulsion polymerisation. For most of the systems a second growth stage of PBA was used to produced larger *core* nanoparticles (C100(0), Stage 2) using the Cs100(0) nanoparticles as the seed.

The following provides an example for the preparation of C55(0)-30(1). All polymerisations were carried out under an Ar atmosphere at 75 °C. Water (300 g) was added to a 2 L reaction vessel. Then, a surfactant solution of Aerosol MA-80 (14 g in 76 g of deionised water) was added. After 5 min of stirring, BA (54.0 g, 0.42 mol) was added which was then followed by KPS addition (1.37 g in 54 g of deionised water). After polymerisation for 60 min the *seed* (Cs100(0)) nanoparticles were obtained. To prepare the *core* (C100(0)) nanoparticles, a mixture of deionised water (171.5 g), Aerosol MA-80 (2.97 g), *t*-dodecylmercaptan (0.085 g) and BA (237.5 g, 2.13 mol) were slowly added at 5.5 g min⁻¹ and the particle growth continued. Then a mixture of Aerosol MA-80 (2.97 g), *t*-dodecylmercaptan (0.085 g) and shell co-monomer feed solution (237.5 g) was added to the C100(0) *core* dispersion at a feed rate of 3.2 g min⁻¹. The feed solution contained BA (64 wt.%), AN (30 wt.%), MAA (5 wt.%) and BDDA (1 wt.%). After 4 h, the latex was filtered through a sieve (28 µm). Samples were taken during the reaction and the % conversion determined gravimetrically and the z-average diameter (d_z) measured using DLS. Other systems were prepared using the same approach as described above by preserving the MAA content used for the shell and varying the AN content as required. In the case of C19(0)-55(1) the shell stage used the *seed* (Cs100(0)). Table 1 gives a summary of the system compositions prepared for this study.

To investigate nanoparticle growth during the emulsion polymerisation processes the number-density of nanoparticles (N_p) was calculated from the measured d_z values and the mass of monomer converted (m) per unit volume to polymer using:

$$N_p = \frac{6m}{\pi \rho d_z^3} \quad (1)$$

where ρ is the density of the copolymer (1.0 g/ml). Theoretical d_z values for the nanoparticles during growth were calculated using the values for m and the assumption that all of the core nanoparticles were converted to core-shell nanoparticles.

Nanostructured ionomeric film preparation

The method for pH adjustment, ZnO neutralisation and film preparation was similar to that described earlier³⁴. The nominal extent of neutralisation is the mol. % of total cation added (K^+ and Zn^{2+}) with respect to the nominal mol.% of MAA present within the nanoparticles. Three extents of neutralisation were investigated; 0, 50 and 100%, which are termed 0n, 50n and 100n, respectively. The films prepared without pH adjustment (0n) were cast in the as-made state. The initial pH of those dispersions was 3.0. The 50n nanoparticle films were cast from dispersions that were adjusted to pH 8.0 using KOH solution. The 100n nanoparticle films were cast at pH 8.0 in the presence of ZnO. The latter films were neutralised by K^+ (50%) and Zn^{2+} (50%).

The following is an example for the preparation of C55(0)-30(1) 100n films. An aqueous dispersion of C55(0)-30(1) (~ 30 wt.%) was stirred at 200 rpm for 15 min at room temperature and adjusted to pH 8.0 with aqueous KOH solution (0.9 M). Sufficient ZnO dispersion to achieve 100n was added and the dispersion was equilibrated overnight. A clean glass plate (100 mm width x 125 mm length x 5 mm depth) was used for dispersion casting. The nanoparticle dispersion (20 g) was poured onto the plate. The cast films were allowed to dry for three days in air circulating constant temperature oven at 25 °C in a humidity controlled environment (50% RH). The dried nanostructured films had a thickness of $450 \pm 50 \mu m$.

Characterisation techniques

Titration measurements were performed using a Mettler DL titrator in the presence of aqueous NaCl solution (0.1 M). The d_z values were measured by dynamic light scattering (DLS) using a Zetasizer NanoZS (Malvern Instruments Ltd., UK). TEM observations were conducted using a Philips CM 20 operated at an accelerating voltage of 200 kV. The nanoparticles were negatively stained using phosphotungstic acid solution (2 wt. %). At least 100 particles were counted to determine the number-average particle diameter (d_{TEM}). AFM measurements were conducted using an Asylum Research MFP-3D operated in tapping mode to map the surface topography of the film under ambient conditions. Imaging was performed at a scan speed of 1 Hz using Olympus high aspect ratio etched silicon probes (OTESPA) (Bruker AXS S.A.S, France) with a nominal spring constant of 42 N/m. A 1 cm x 1 cm

section of film was cut and mounted on glass slide and placed inside the instrument. Measurements were made on film surfaces using a tip oscillation frequency of 307 - 346 kHz; height and phase images were captured at a scan size of 2 x 2 μm (sampled at 512 x 512 pixels). Dynamic mechanical analysis (DMA) data were measured using a TA-Q800 instrument using the film tension mode geometry and a frequency of 1 Hz. Tensile tests were performed using a Hounsfield H10KS-0079 tensile testing instrument. Samples were prepared as dumbbell shapes. The lengths and widths were 75 mm 4.0 mm, respectively. The extension rate was 500 mm min⁻¹. The measurements were performed at 25 °C and 50% relative humidity.

RESULTS AND DISCUSSION

Core-shell nanoparticle synthesis and characterisation

For this study six core-shell nanoparticle dispersions were prepared using emulsion polymerisation (Table 1). Two sizes of core nanoparticles were prepared (Scheme 1a). The *seed* (Cs100(0)) had a d_z of 45 nm and was used directly to prepare the C19(0)-30(1) nanoparticles. The latter had the *lowest* core volume fraction of all the core-shell systems studied and a d_z of 76 nm (Table 1). To prepare the nanoparticles with *higher* core volume fractions (C55(0)- x (1), $x = 20 - 30$), the *seed* was grown further to produce *core* C100(0) nanoparticles (Stage 2) which had a d_z of 79 nm.

Particle growth during nanoparticle synthesis was studied using DLS and data for C19(0)-30(1) and C55(0)-30(1) are shown in Fig. 1a and b, respectively. (Particle growth data for C55(0)- x (1) ($x = 20, 23$ and 28) are shown in Fig. S1a - c.) The transition from the initial *seed* Cs100(0) to the core-shell nanoparticles is indicated for C19(0)-30(1) in Fig. 1a using the numbers 1 and 3. For C55(0)-30(1) the Cs100(0) *core* was prepared during Stage 2. For all of the systems the values for N_p remained approximately constant during the various growth stages and there was reasonable agreement between the calculated and theoretical diameters (Fig. 1 and Fig. S1). These data indicate that secondary nucleation was *not* significant for the dispersions and support the view that core-shell nanoparticles were successfully prepared. The d_z values for the final core-shell nanoparticles were in the range of 76 to 97 nm (Table 1).

TEM images for C19(0)-30(1) and C55(0)-30(1) nanoparticles are shown in Fig. 1c and d, respectively. (TEM images for C55(0)- x (1) ($x = 20, 23$ and 28) are shown in Fig. S1d – f, respectively.) The C19(0)-30(1) nanoparticles (Fig. 1c) were smaller than the C55(0)-30(1) nanoparticles (Fig. 1d) due to the use of the smaller *seed* Cs100(0) nanoparticles used for the

former. (Fig. 1e and f show TEM images for *seed* Cs100(0) and *core* C100(0) nanoparticles). There was little, if any, evidence of secondary nucleation from the TEM images for the core-shell nanoparticles. The d_{TEM} values (Table 1) for the core-shell nanoparticles (63 - 93 nm) were reasonably close to the respective d_z values, which shows that the dispersions were colloidally stable. The shell thicknesses (δ) were calculated using the d_z values for the core-shell nanoparticles and those for the respective core nanoparticles (Cs100(0) or C(100(0))) and appear in Table 1. The δ values were largest for C19(0)-30(1) (15.5 nm) and were smallest for the C55(0)- x (1) systems (6.0 - 9.0 nm), as expected.

Potentiometric titration was used to determine the MAA contents and apparent pK_a values for the nanoparticles (Fig. S2). The MAA contents were in the range 2.1 – 3.8 wt.% and were close to the values expected from the nominal compositions (Table 1, last column). These results seem to show that all of the -COOH groups were accessible, and not buried within the interior of the nanoparticles. However, it is not possible to be completely certain that all of the -COOH groups were accessible. The pK_a values for the core-shell nanoparticles were in the range of 6.7 to 7.4. The latter values were much lower than the pK_a values reported earlier for related PBd-AN-MAA core-shell nanoparticles⁸, which had pK_a values ≥ 9.1 . These results show that the nature of the primary structural monomer has a major effect on the pK_a for this family of core-shell nanoparticles, which is a new observation.

The procedure used to prepare nanostructured films followed our earlier approach⁸ and required the pH of concentrated dispersions to be increased to 8.0 (See Experimental section). The dispersions contained added ZnO particles which provided a source of soluble Zn^{2+} . Films were subsequently cast onto flat glass molds (Scheme 1b). The use of pH 8.0 ensured a balance between the supply of soluble Zn^{2+} (which decreases with increasing pH³⁵) and dispersion stability⁸. Whilst this procedure worked very well for our previously reported Bd-based nanoparticle dispersions⁸ (which had pK_a values ≥ 9.1) our initial attempts using crosslinker-free BA-based nanoparticles (i.e., C55(0)-30(0)) resulted in poor quality cast films. Variable-pH DLS measurements showed that the d_z values for these nanoparticles increased with increasing pH (Fig. 2a). The nanoparticles swelled as the pH approached the pK_a , which was 7.0 (Table 1). A tube inversion study (Fig. 2b) showed that concentrated C55(0)-30(0) dispersions formed a physical gel at pH 8.0. The latter prevented smooth films being prepared using our dispersion casting method.

In an effort to restrict shell swelling we prepared nanoparticles containing 1.0 wt.% BDDA,

e.g., C55(0)-30(1). Not only did the (C55(0)-30(1) nanoparticles *not* show pH-triggered swelling as evidenced by variable pH DLS data (Fig. 2a), a tube inversion study for concentrated C55(0)-30(1) dispersions at pH 3.0 and 8.0 (Fig. 2b) showed that the C55(0)-30(1) dispersion remained fluid at pH 8.0 (Fig. 2b). We therefore extended this approach to prepare a range of core-shell nanoparticle dispersions (Table 1). It was found that inclusion of 1 wt. % BDDA within the nanoparticle shells prevented pH-triggered swelling (Fig. 2a) and enabled good quality films to be obtained by casting for all of the C55(0)- x (1) ($x = 20$ to 30) and C19(0)-30(1) dispersions.

Nanostructured ionomer film morphology

The topography of the films was investigated using AFM. Phase images for C19(0)-30(1), C55(0)-30(1) and C55(0)-20(1) nanoparticle films in the non-neutralised (0n, top row) and neutralised (100n, bottom row) states are shown in Fig. 3. Whilst there was some distortion of the nanoparticles due to local strain, the C19(0)-30(1) (Fig. 3a and b) and C55(0)-30(1) (Fig. 3c and d) films showed nanostructured topographies that consisted of interconnected nanoparticles. Those nanoparticles appeared to be mostly spherical for the 100n films. Ionic crosslinking within the shells increased the ability of the nanoparticles to retain their spherical morphology. By contrast the C55-20(1) (Fig. 3e and f) film topographies were less well-defined (especially in the non-neutralised, 0n, state) and showed greater extents of coalescence of neighbouring nanoparticles. As will be shown below, the T_g of the nanoparticle shell phase was lowest for C55(0)-20(1) (See Fig. 4f). It appears from the images shown in Fig. 3 that the extents of inter-nanoparticle coalescence increased with decreasing nanoparticle T_g , which is expected because of increased polymer segment mobility. When combined with the core-shell morphology established above the data support the depiction of the nanostructured film morphology shown in Scheme 1b.

Nanostructured ionomer film mechanical properties

DMA has been shown to be a very useful technique for studying conventional¹³ and nanostructured⁹ ionomer mechanical properties. DMA data for the present films are shown in figures 4 and 5. The T_g values obtained from these data are shown in Table S1. Considering first the data for the C19(0)-30(1) and C55-30(1) films two main $\tan \delta$ maxima can be seen from figures 4a and c. (Note that $\tan \delta = E'' / E'$, where E'' and E' are the loss and storage modulus values, respectively.) The $\tan \delta$ maximum in the temperature range of -40 to -45 °C corresponds to the T_g value for PBA residing in the core of the nanoparticles, i.e., $T_{g(c)}$. This

range of temperatures is comparable to the reported T_g value of $-49\text{ }^{\circ}\text{C}$ for PBA¹⁰. The relative size of the $T_{g(c)}$ maxima was smallest for C19(0)-30(1) (Fig. 4a) which is expected because those nanoparticles contained the lowest core volume fraction (19 vol.%). The higher temperature maximum present at $33 - 46\text{ }^{\circ}\text{C}$ was dependent on the extent of neutralisation and corresponds to the T_g from PBA-AN-MAA within the shells ($T_{g(s)}$). This T_g value is much higher than that for PBA because of contributions from AN and MAA. The T_g s of PAN and PMAA are $105\text{ }^{\circ}\text{C}$ ³⁶ and $228\text{ }^{\circ}\text{C}$ ¹⁰, respectively. The variable temperature E' and E'' data (Figures 4b and d) indicate that the two $\tan \delta$ maxima discussed above originated from temperature-triggered decreases of E' and increases of E'' .

DMA data for C55(0)- x (1) ($x = 20, 23$ and 28) films are shown in Fig. 5. Similar low and high temperature $\tan \delta$ maxima were also present for the these films (Fig. 5a, c and e). The variable temperature E' and E'' data for these films (Figures 5b, d and f) showed similar trends to those apparent from Fig. 4b and d. Considering all of these variable-temperature E' and E'' data it can be seen that a consequence of ionic crosslinking (either 50% or 100 % neutralisation) was that the E' values increased relative to the non-neutralised films for temperatures greater than $\sim 50\text{ }^{\circ}\text{C}$. Moreover, a higher temperature $\tan \delta$ shoulder was also evident at $\sim 100 - 110\text{ }^{\circ}\text{C}$ for most of the neutralised films (e.g., Fig. 5e) and this T_g is ascribed to domains containing ionic crosslinks ($T_{g(i)}$) involving K^+ and / or Zn^{2+} with $-\text{COO}^-$. It is proposed that the temperature-triggered structural transition that occurred for the latter was disruption of ionic crosslinks. Attractive electrostatic interactions of ion pairs within polymers are known to become less effective at elevated temperatures³⁷. The $\tan \delta$ peaks due to $T_{g(c)}$, $T_{g(s)}$ and $T_{g(i)}$ discussed above are highlighted in Fig. 5e.

The variation of the $T_{g(s)}$ values with the AN content (x) for the C55(0)- x (1) films is shown in Fig. 6. (Data are also shown for the C19(0)-30(1) film.) Clearly, the $T_{g(s)}$ values increased with x . The $T_{g(s)}$ values also increased with neutralisation (see C19(0)-30(1) data); however, this trend was generally less pronounced. The increase of the $T_{g(s)}$ values with x is expected because AN segments are known to increase the T_g value for copolymers³⁸ and contribute strong nitrile dipolar interactions between polymer chains³⁹, which increase chain stiffness.

The present nanostructured films can be divided into two groups according to their $T_{g(s)}$ values compared to room temperature (horizontal line in Fig. 6). Accordingly, the C55(0)-20(1) and C55(0)-23(1) films had relatively low $T_{g(s)}$ values. By contrast, the C55(0)-28(1), C55(0)-30(1) and C19(0)-30(1) films had relatively high $T_{g(s)}$ values. For comparison, the $T_{g(s)}$

values for the previously studied nanostructured films prepared using Bd-nanoparticles⁸ were *less* than 0 °C irrespective of the AN contents. Consequently, the present BA-based films enabled $T_{g(s)}$ values, which were close to room temperature, to be switched from being more glass-like to more rubber-like (and closer to Bd-based films) by judicious selection of x .

Next we investigated the effects of film composition on the tensile properties. Tensile stress-strain data for the nanostructured films are shown in Fig. 7. (The tensile parameter values appear in Table S1.) There were pronounced differences for the curves as either x or the extent of neutralisation was varied. Considering first C19(0)-30(1) and C55(0)-30(1) (Fig. 7a and b) the data show a steep linear increase of stress with increasing strain (pure elastic behaviour) followed by an inelastic deformation region and, finally, strain hardening prior to failure. These features were also present for the other films (Fig. 7c – e)); however, their extents differed. An increase of the shell volume fraction (ϕ_s) from 0.45 (for C55(0)-30(1)) to 0.81 (for C19(0)-30(1)) increased the extent of the initial linear region and the final shear-at-break (σ_b). Interestingly, comparison of the data shown in Fig. 7a and b (and Table S1) reveals that an increase of the ϕ_s value by a factor of ~ 2 increased the E values by a factor of ~ 2 with only a small decrease of the strain-at-break (ϵ_b), and hence ductility. This result is consistent with a property tuning advantage reported earlier for lower modulus nanostructured ionomer films constructed from Bd-based core-shell nanoparticles where stiffness and ductility could be independently tuned²⁴.

Turning next to the effect of AN content (x) it can be clearly seen from comparison of the data in Fig. 7a - e that the films with the highest x values had the highest E and σ_b values (Table S1). The maximum E value for this work was 85.5 MPa which was measured for the fully neutralised C19(0)-30(1) film. The latter value is the highest modulus that has been reported for nanostructured ionomer films prepared by casting aqueous dispersions of core-shell nanoparticles. All of the films had ϵ_b values of at least 200%, which compares well with other ionomers⁴⁰. The non-neutralised C55(0)-20(1) film had the highest ϵ_b value of 445%.

Fig. 7f shows the variation of E as a function of x for the C55(0)- x (1) films. Data are also shown for the C19(0)-30(1) film. A major E increase occurred when x reached 28%. The latter film (C55(0)-28(1)) had a $T_{g(s)}$ value of ~ 40 °C (Table S1), which was well above the tensile stress-strain measurement temperature (25 °C) and those films were relatively glass-like. The high AN contents within the shells provided associative crosslinking which

restricted the mobility of the copolymer chains. By contrast, the C55(0)-20(1) and C55(0)-23(1)) films (which had the lowest x and $T_{g(s)}$ values) had the lowest E values (Fig. 7f). These data show that the x value had a major effect on the E values for these films due to its control of the $T_{g(s)}$ values in a temperature region that was reasonably close to room temperature. Considering the E value spread shown for each x value in Fig. 7f it can be seen that the effect of neutralisation on E was most pronounced for the films with the highest x values, which in turn gave the highest $T_{g(s)}$ values (Fig. 6). Thus, the ionomer contribution to the film stiffness was enhanced when $T_{g(s)}$ was shifted to above room temperature. This is a new finding for this class of ionomer films.

A simple model describing the stiffness and ductility of the nanostructured ionomer films

The isostrain model was originally developed by Morris⁴¹ for biphasic gels and is tested here for the present BA-based nanostructured films. For this mechanical model we consider the nanostructured films to consist of two phases (See Scheme 1b). The continuous phase consists of interlinked, relatively hard, PBA-AN-MAA-BDDA shell copolymer. The dispersed phase consists of relatively soft PBA core polymer. According to the isostrain model the modulus should be the volume fraction-weighted average for each phase and both phases should experience the same strain. Accordingly,

$$E = \phi_c E_c + \phi_s E_s \quad (2)$$

$$\varepsilon_b = \varepsilon_{b(c)} = \varepsilon_{b(s)} \quad (3)$$

where E_c and E_s are the Young's modulus values for the core and shell phases, respectively. The parameters $\varepsilon_{b(c)}$ and $\varepsilon_{b(s)}$ are the strain-at-break values for the core and the shell phases, respectively. The E values for the films were all greater than 1 MPa in this work. Furthermore, PBA films are known to be very soft⁴² and the E value measured here for C100(0) was only 0.19 MPa (Table S1). Consequently, we assume that $\phi_c E_c \ll \phi_s E_s$ for all of the systems studied here which allows equation 2 to be rearranged to the following.

$$E_s \sim \frac{E}{1 - \phi_c} \quad (4)$$

Values for E_s were calculated using equation (4) are shown as a function of neutralisation in Fig. 8a and b. The E_s values for the high $T_{g(s)}$ films (C19(0)-30(1), C55(0)-30(1) and C55(0)-28(1)) are shown in Fig. 8a; whereas, data for the low $T_{g(s)}$ films (C55(0)-23(1) and C55(0)-20(1)) are shown in Fig. 8b. The E_s values for the C19(0)-30(1) and C55(0)-30(1) values

were not significantly different. This result was expected because the shells had the same composition (30% AN) and supports the use of the isostrain model.

Implicit within the use of equation 4 is the assumption that E_s should increase with neutralisation because of the formation of ionic crosslinks. The data in Fig. 8a also show that the E_s values for the films with the higher $T_{g(s)}$ values increased approximately linearly with neutralisation, which is expected based on rubber elasticity theory⁴³. Comparison with the data shown in Fig. 8b shows that the magnitude of the E_s increase was least for the low $T_{g(s)}$ films. Nevertheless, the increase of E_s with neutralisation for the latter films was stronger than that for the Bd-containing system (C50Bd) which has been included in this analysis from earlier work⁸. This low T_g system had $\phi_s = 0.5$ and similar MAA contents to the BA-containing films studied here and the data confirm the importance of T_g for the ionomer-induced modulus enhancement for this class nanostructured films.

It is commonly observed for conventional elastomers that the ductility decreases with increasing stiffness. This trend has also been observed for Bd-based nanostructured ionomer films²⁴ and has its origin in the inverse relationship between the number-density of elastically effective chains and the mean molecular weight between crosslinks. According to equation 3 the ε_b values for the films should be controlled by the ductility of the nanoparticle shells because that phase was the most brittle. The variation of ε_b with neutralisation is shown in Fig. 6c. Comparison with the data shown in Fig. 8a and b shows that the films which had highest ε_b values (C55(0)-20(1), C55(0)-23(1) and C50Bd) had the lowest E_s values. By contrast, the films which had the lowest lowest ε_b values (C19(0)-30(1), C55(0)-30(1) and C55(0)-28(1)) had the highest E_s values. Consequently, film ductility increased when the stiffness decreased for these systems and was controlled by the ionic crosslinks formed in the shells. Based on the above, we conclude that the isostrain model was able to successfully describe the mechanical properties of the nanostructured ionomer films.

The above discussion (and equations (2) and (3)) assumed that the soft PBA-phase was dispersed within interlinked, relatively hard, PBA-AN-MAA-BDDA shell copolymer. The inverse morphology should also be considered whereby the relatively hard shell copolymer is dispersed with a relatively soft continuous PBA phase. This situation corresponds to the *isostress* model of Morris⁴¹ and the following equation would apply.

$$\frac{1}{E} = \frac{\phi_c}{E_c} + \frac{\phi_s}{E_s} \quad (5)$$

As stated above it is reasonable to assume that $E_c \ll E_s$. Furthermore, a minimum E_s value can be estimated from the E value for C19(0)-30(1) because these core-shell particles contained ~ 81 vol.% shell copolymer. The latter value for the non-neutralised system was of 23.1 MPa (Table S1, †). That value was much greater than the E_c value which was estimated as ~ 0.19 MPa (above). Considering the ϕ_c and ϕ_s values for the systems studied here (0.19 to 0.55 and 0.81 to 0.44, respectively), then it follows that $\phi_c/E_c \gg \phi_s/E_s$. Hence, equation (5) becomes $E_c \simeq \phi_c E$. From the latter and the E data (Table S1, †) it follows that E_c would increase with increasing ϕ_c , neutralisation and x . Each of these relationships is physically implausible. Consequently, it can be concluded that the isostress model, equation (5) and the inverse morphology do not apply to the films considered above.

CONCLUSIONS

This study has investigated the structure and mechanical properties of nanostructured ionomer films comprised of BA-based core-shell nanoparticles. By replacing Bd with BA pronounced differences in the nanoparticle properties and film mechanical properties were demonstrated. A key difference was that inclusion of shell crosslinker (BDDA) was required to suppress pH-triggered shell swelling of the nanoparticles and enable ionomer film formation to occur. By varying the AN content within the shells it was possible to transform the stress-strain behaviour from that which was comparable to the earlier Bd-based films⁸ to a much higher modulus version. The DMA data showed that these changes were due primarily to the increase of the shell T_g . The maximum modulus value of 85.5 MPa reported here was a factor of at least seven higher than those reported earlier for Bd-based nanostructured ionomer films^{8, 9, 24}. The mechanical properties (i.e., E and ε_B) of the BA-based films were controllable via three composition-based variables: % neutralisation, AN content (x) and ϕ_s . More generally, we have also shown that the nature of the primary monomer used to construct nanostructured ionomer films based on core-shell nanoparticles provides a new parameter for tuning the mechanical properties. The mechanical properties of the films were successfully described using the isostrain model. The methods for synthesising the core-shell nanoparticles and casting the films used commonly available equipment (with no need for pressurised reactors⁸), were water-based and are versatile. Consequently, there should be scope for preparing nanostructured films with enhanced performance that are able to be cast from aqueous dispersions using new acrylate-based core-shell nanoparticles in future.

Acknowledgements

BRS is grateful to Synthomer Ltd and The Malaysian Government Agency (MARA) for funding this work.

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Figures and Tables

Scheme 1 (a) Depicts core-shell nanoparticle synthesis by seeded emulsion polymerisation. The method diverged after Stage 1. In the lower branch the PBA *seed* (Cs100(0)) was grown (Stage 2) to give larger PBA *core* (C100(0)) nanoparticles which were then used to prepare *high* core volume fraction C55(0)-x(y) nanoparticles. In the upper branch the Cs100(0) seed was used directly to prepare *low* core volume fraction C19(0)-30(1) nanoparticles. (b) Depicts the formation of nanostructured ionomer films after dispersion pH adjustment and addition of ZnO followed by casting. The code used for the nanoparticles and films is shown in (b).

Fig. 1. (a) and (b) show measured particle diameters (red squares) during growth for C19(0)-30(1) and C55(0)-30(1), respectively. The theoretical diameter values (black squares) and the number-density of nanoparticles (blue squares) are also shown. The numbers at the top of the graphs show the different stages of growth (Scheme 1a). TEM images are shown for (c) C19(0)-30(1) and (d) C55(0)-30(1) which were prepared using (e) *seed* Cs100(0) and (f) *core* Cs100(0) nanoparticles, respectively.

Fig. 2. (a) Variable pH DLS data for various nanoparticle dispersions. (b) Photographs of dispersions of C55(0)-30(0) ((i) and (ii)) and C55(0)-30(1) ((iii) and (iv)). The pH of samples (i) and (iii) was 3.0. The pH of samples (ii) and (iv) was 8.0. The concentration was 30 wt. %

Fig. 3. AFM phase images for selected non-neutralised (0n, top row) and neutralised (100n, bottom row) nanostructured films. The films were C19(0)-30(1) (a and b), C55(0)-30(1) (c and d) and C55(0)-20(1) (e and f). The films were measured at 25 °C.

Fig. 4. Variation of $\tan \delta$ ($= E''/E'$, where E'' and E' are the loss and storage modulus, respectively) as well as E' and E'' with temperature for C19(0)-30(1) ((a) and (b)) and C55(0)-30(1) ((c) and (d)) films.

Fig. 5. Variation of $\tan \delta$, E' and E'' with temperature for C55(0)-28(1) ((a) and (b)), C55(0)-23(1) ((c) and (d)) and C55(0)-20(1) ((e) and (f)) ionomer films. The $\tan \delta$ maxima corresponding to $T_{g(c)}$, $T_{g(s)}$ and $T_{g(i)}$ are shown in (e). The small, sharp signal at ~ 60 °C in (c) for the 50n film is an artefact.

Fig. 6. Variation of $T_{g(s)}$ with x for the C55(0)- x (1) films. Data for C19(0)-30(1) are also shown. x is the nominal AN content in the shells of the core-shell nanoparticles.

Fig. 7. Tensile stress vs. strain data for (a) C19(0)-30(1), (b) C55(0)-30(1), (c) C55(0)-28(1) (d) C55(0)-23(1) and (e) C55(0)-20(1) films. (f) shows the variation of E with x for the C55(0)- x (1) films. Data for C19(0)-30(1) are also shown.

Fig. 8. (a) and (b) show the variations of the calculated shell modulus values from equation 4 with % neutralisation for the films with high shell $T_{g(s)}$ values (C19(0)-30(1), C55(0)-30(1), and C55(0)-28(1)) and low $T_{g(s)}$ values (C55(0)-23(1), C55(0)-20(1), and C50Bd), respectively. (c) shows the variation of the strain-at-break for all of the films with % neutralisation. The data for the Bd-based film (C50Bd) shown in (b) and (c) were taken from an earlier study (Ref. 8).

Table 1 Compositions and properties of the nanoparticles prepared for this study.

Code	$\phi_{c(nom)}^a$	$AN^b/wt\%$	d_{TEM}^c/nm	d_z^d/nm	δ_{DLS}^e/nm	pK_a^f	$MAA^g/wt\%$
Cs100(0)	1.00	-	43 (15)	45	-	-	-
C100(0)	1.00	-	80 (28)	79	-	-	-
C19(0)-30(1)	0.19	30	63 (16)	76	15.5	7.4	3.8 (4.0)
C55(0)-30(0)	0.55	30	93 (20)	97	9.0	7.0	2.9 (2.3)
C55(0)-30(1)	0.55	30	91 (15)	95	8.0	6.8	2.1 (2.3)
C55(0)-28(1)	0.55	28	84 (14)	96	8.5	6.7	2.6 (2.3)
C55(0)-23(1)	0.55	23	81 (24)	93	7.0	6.9	2.3 (2.3)
C55(0)-20(1)	0.55	20	83 (20)	90	6.0	7.0	2.5 (2.3)

^a Nominal volume fractions of core present based on 100% conversion. ^b Nominal AN concentration in shell assuming 100% conversion. ^c Number-average diameter measured by TEM (The numbers in brackets are the coefficient of variation). ^d Values determined from DLS. ^e Shell thicknesses calculated from DLS data using $\delta = (d_{z(cs)} - d_{z(c)})/2$ where the d_z values are for the core-shell and core nanoparticles, respectively. ^f Apparent pK_a values determined from titration data. ^g Overall concentration of MAA measured by titration. The numbers in brackets are the nominal values.