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PAPER

Relative modulus–relative density relationships in low density polymer–clay nanocomposite foams

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Polymer–clay nanocomposite (PCN) foams represent an important class of new materials in structural engineering, biomedical fields and packaging. This paper reports the relative modulus–relative density relationship, a crucial correlation in cellular solids, for low-density PCN foams. Polyurethane (PU)–natural clay nanocomposite foams with a porosity of 97% were used for studies of such relationship. The foam structures were characterised by Scanning Electron Microscopy and X-ray Micro-Computed Tomography and the modulus was obtained from compressive testing. It was found the relative modulus–relative density relationship of low-density PCN foams with porosities higher than 95% closely followed the normalised Gibson–Ashby models for open cells and closed cells, and in the case of PU–clay nanocomposite foams the geometric constant of foam C_1 was determined to be approximately 0.45–0.88 in the well-established model for conventional open-cell foams, namely $E_f/E_s = C_1(\rho_f/\rho_s)^2$ where E and ρ refer to modulus and density and subscripts f and s stand for foam and solid. The effects of clay, clay content and mixing sequence on the cell structure, physical and mechanical properties of the polymer foam were also discussed.

1. Introduction

Since they were first reported in 1987,¹ polymer–clay nanocomposites (PCNs) have presented an unusual interest due to their unique properties.² These new materials are the result of dispersing inorganic clay fillers with dimensions in the nanometric range into a polymer matrix.³ PCNs often exhibit superior or distinct properties from the ones possessed by the pristine polymers or the conventional composites, which can be mainly attributed to the large interfacial surface area between the organic and inorganic phases and the intrinsic properties of clay platelets and tactoids.^{2,4,5} For best property enhancements, the content of clay fillers is typically kept under 10 wt%⁶ due to its high aspect ratio and small size⁷ in comparison with up to 50 wt% for a conventional reinforcing agent such as carbon black or calcium carbonate, in a thermosetting polymer matrix.¹

There are three common methods for preparing polymer–clay nanocomposites: *in situ* polymerization, solvent intercalation and melt processing which are known to lead to the formation of intercalated and exfoliated structures as well as mixtures of both.^{8,9} Depending on the degree of dispersion,¹⁰ these nanocomposites usually provide improvements in mechanical,^{11–14} thermal,^{15,16} and barrier properties.¹⁷ The extent of enhancement

is influenced by the type, surfactant and content of clay and the intrinsic properties of the polymer (*e.g.* molecular weight and polarity), as well as the processing conditions when preparing the nanocomposites.

The most used clay is montmorillonite which is a layer silicate composed of two silica tetrahedral sheets and a central alumina sheet that are held together by van der Waals and electrostatic forces.² Each layered silicate sheet is approximately 1 nm thick and possesses a lateral dimension that varies from 30 nm to several microns and therefore an aspect ratio of up to several thousand.¹⁸ The space between two neighbouring negatively charged silicate layers is defined as the gallery and characterized by the presence of cations (*e.g.* Na⁺ and Ca²⁺) and water molecules.¹⁹ Expansion of the basal space leads to the occurrence of intercalated structures and the loss of registration of the ordered silicate layers causes exfoliated structures, which are responsible for the improvements observed in the properties of polymer–clay nanocomposites.

Foams can be defined as the dispersion of a gas in a liquid which once solidified consists of individual cells (pores) and walls that form a skeletal structure.²⁰ They present an array of applications varying from weight-bearing structures to isolations and tissue engineering scaffolds for cell attachment and growth.²¹ The mechanical and thermal properties of foams depend mainly on the relative density (the density of the foam divided by the density of the solid), which also dictates the porosity of foams.²² In the case of polymer foams, the cell size is also found to play an important role in influencing the properties leading to the

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classification of the polymer foams into macrocellular (>100 μm), microcellular (1–100 μm), ultramicrocellular (0.1–1 μm) and nanocellular (0.1–100 nm).²¹ They can also be classified according to the nature of the cells into open and closed cell foams and according to the rigidity of the skeletal structure into rigid and flexible foams. A number of polymers, such as polyurethane (PU), polystyrene (PS), polycarbonate (PC) and polyethylene (PE), have been foamed using different chemical compositions and different processing conditions²⁰ in order to obtain foams for sound, vibration and heat insulation, impact resistance and light weight applications.^{23,24}

The linear elastic properties²⁵ of foams can be described as a function of relative density by the general empirical formula (eqn (1)):²⁶

$$\frac{\text{Foam property}}{\text{Solid property}} = C \left(\frac{\rho_f}{\rho_s} \right)^n \quad (1)$$

where C is property of the polymer matrix which includes all the geometric constants of proportionality,²² n represents the deformation mode of the struts that make up the foam,²⁶ e.g. tensile or compressive,²⁵ and is characterized by values between 1 and 4²⁷ and ρ is the density, for which the subscripts s and f refer to the solid and the foam structures, respectively. C and n present a complex dependence on the microstructure of the foam including the cell type (e.g. open or closed), geometrical arrangement of cells,²⁶ cell size²⁸ and angle of intersection.²⁷ One of the most important properties of foams is Young's modulus for which an array of models considering different cell geometries,²⁹ cell regularities,³⁰ relative densities and material deformation mechanisms have been developed and selected models based on eqn (1) are presented in Table 1.^{22,27,31–41}

The deformation suffered by the pristine foam is strongly dependent on the cell type; in most of the cases, the values for n lie between 1 and 2 for closed cells,^{38–41} while for open cells the values lie between 1 and 4.^{22,27,31–37} The different values of n reflect the change in the dominant deformation mechanism.⁴² According to Gibson and Ashby,²² the variation of the relative Young's modulus with the relative density for open cells is best

described by a deformation value of 2, value which accounts for the bending and the stretching of the cells³⁰ and relates the relative density of the cells with the thickness and the length of the cells.²² Substituting the property and n in eqn (1) with Young's modulus and 2 leads to:

$$\frac{E_f}{E_s} = C_1 \left(\frac{\rho_f}{\rho_s} \right)^2 \quad (2)$$

where E_f and E_s are the Young's moduli of the foam and the fully dense solid that makes up the strut respectively, and C_1 is a function of strut porosity.²²

For closed-cell cellular solids the variation in the relative modulus with the relative density is the result of three contributions: cell-edge bending, compression of the cell fluid and membrane stretching,²² represented in eqn (3).

$$\frac{E_f}{E_s} = C_1 \phi_s^2 \left(\frac{\rho_f}{\rho_s} \right)^2 + C_2 (1 - \phi_s) \frac{\rho_f}{\rho_s} + \frac{p_0 (1 - 2\nu_f)}{E_s \left(1 - \frac{\rho_f}{\rho_s} \right)} \quad (3)$$

where p_0 is the atmospheric pressure, ν_f is Poisson's ratio, ϕ_s is the volume fraction of solid contained in the cell edges and C_1 and C_2 are geometric constants for the cell edges and the cell faces, respectively. Another contribution that may be added to eqn (3) is the bending of the cell faces; however, due to the small thickness presented by the membranes it may be ignored.²²

Following the success of reinforcement of non-cellular polymers with clays, a wide range of polymer–clay nanocomposite foams have been developed and investigated, including for example: polypropylene (PP)–clay,²⁴ PE–clay,⁴³ poly(methyl methacrylate)–clay,⁴⁴ PS–clay,⁴⁵ PC–clay,⁴⁶ PU–clay,^{11,15,16,23,47,48} poly(lactic acid)–clay⁴⁹ and poly(ϵ -caprolactone) (PCL)–clay⁵⁰ nanocomposite foams. Similarly, it has been shown that the addition of clay improves the specific compressive modulus (the ratio of modulus to density) of a polymer foam and in some cases the compressive modulus without considering the density.^{15,47} The presence of clay is often found to decrease the cell size and increase the cell density, acting as a nucleating agent during foaming and decreasing the density of the polymer foam.^{15,51} Saha *et al.*¹⁶ discovered that the cell diameter of a PU foam decreased by 20% with the addition of 1 wt% clay and the compressive modulus increased by 20%. Thirumal *et al.*⁴⁷ reported a 30% decrease in the density of a PU foam with the addition of 4.3 wt% organoclay. Liu *et al.*⁵⁰ showed that at low clay loads, clay may provide nucleation sites for PCL foams that lead to smaller cells and thinner cell walls; however, a clay content of over 10 wt% causes an increase in the cell thickness and cell size.⁵²

Despite the significant development in PCN foams, the structure–property correlations of this new class of foams are yet to be well understood and their relative modulus–relative density relationships were not adequately addressed in the literature. The main goal of this work was to determine the relationship between relative modulus and relative density for high-porosity polymer–clay nanocomposite foams by using the established theories for conventional cellular materials as reviewed above. PU was selected for this study because of its wide applications,^{11,15,21} easy processing^{15,53} and high polarity which allows it to form nanocomposites with natural clays^{54,55} and to provide idealised polymer–clay systems without involvement of an organic surfactant.

Table 1 Summary of selected models from the literature for open and closed cells

Cell type	Geometrical constant (C)	Density exponent (n)	Reference
Open	1	2	Gibson and Ashby ²²
Open	0.376	1.29	Roberts and Garboczi ²⁷
Open	0.535	1.81	Roberts and Garboczi ²⁷
Open	4.2	3.15	Roberts and Garboczi ²⁷
Open	0.3	2	Hagiwara and Green ^{27,31}
Open	90	2	McCullough <i>et al.</i> ³²
Open	68	1	McCullough <i>et al.</i> ³²
Open	1.05	2.54	Liu <i>et al.</i> ³³
Open	0.167	1	Thomas and Gent ^{34,35}
Open	0.88	2	Choi and Lakes ³⁶
Open	0.7	2	Dement'ev and Tarakanov ^{36,37}
Closed	0.33	1	Renz and Ehrenstein ^{38,39}
Closed	0.0598	1.066	Mills and Zhu ⁴⁰
Closed	0.0807	1.155	Mills and Zhu ⁴⁰
Closed	0.977	1.627	Mills and Zhu ⁴⁰
Closed	0.64	1.4	Roberts and Garboczi ⁴¹
Closed	0.76	1.7	Roberts and Garboczi ⁴¹

A typical commercial formula for preparation of rigid PU foams, described as the mixing of a polyol with a diisocyanate, was adopted. PU–natural clay nanocomposite foams containing different clay amounts were prepared by varying the mixing sequence of the polyol, diisocyanate and natural clay. The structures of the foams were investigated by using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray Micro-Computed Tomography (Micro-CT) and the modulus was obtained from compression testing.

2. Experimental

2.1. Materials

A liquid polyol blend with a density of 1.09 g cm⁻³ and a viscosity of 735 mPa s (Bayer VP.PU 29HB74, denoted as polyol) and a liquid mixture of diphenylmethane-4,4'-diisocyanate with an N=C=O content of 30.5–32.5 wt%, a density of 1.23 g cm⁻³ and a viscosity of 160–240 mPa s (Desmodur 44V20L, denoted as MDI) were kindly supplied by Bayer Materials Science (Germany). Natural sodium montmorillonite clay (325 mesh) was generously supplied by Bentonite Performance Materials LLC (Wyoming Plant, South Dakota, USA). The inorganic content of the clay was determined as 88.6% by Loss on Ignition by heating the clay from room temperature to 600 °C at a rate of 10 °C min⁻¹ with a dwell of 600 s at 600 °C in a Eurotherm 2416CG furnace (Lenton Thermal Designs LTD). The chemical composition of the clay was analyzed to be SiO₂, 64.12 wt%; Al₂O₃, 18.92 wt%; Fe₂O₃, 3.78 wt%; MgO, 2.29 wt%; Na₂O, 1.88 wt%; CaO, 1.19 wt%; K₂O, 0.44 wt%; and TiO₂, 0.13 wt% by using a Panalytical Axios X-Ray Fluorescence Spectrometer according to BS EN ISO 12677 method at CERAM (Stoke-on-Trent, UK). All the materials were used as received.

2.2. Preparation of polyurethane–clay nanocomposite foams

PU–clay foams were prepared by *in situ* polymerization with reference to the method supplied by the manufacturer for preparing the pristine PU foam. The pristine PU foam was prepared by mixing 30 g of polyol with an equal amount of MDI in a rectangular container (20 cm × 11 cm × 3 cm) for 10 s at room temperature. PU–clay nanocomposite foams containing different clay contents were prepared using three mixing sequences. In the first sequence 30 g of polyol, 30 g of MDI and a pre-weighed amount of clay were mixed simultaneously for 10 s in the rectangular container, denoted as polyol/MDI/clay. In the second sequence 30 g of polyol were mixed with the clay for approximately 120 s and then 30 g of MDI were added and mixed for 10 s, denoted as polyol/clay + MDI. In the third sequence 30 g of MDI were mixed with the clay for approximately 120 s and then 30 g of polyol were added and mixed for a further 10 s, denoted as MDI/clay + polyol. Following mixing, each of the foams was kept in the container at room temperature for approximately 600 s to grow and stabilize before it was removed for preparation of test specimens. In all the three methods, two amounts of clay platelets, *i.e.* 4 wt% and 8 wt%, were used. The material compositions and mixing methods of the samples are summarised in Table 2.

Table 2 Material compositions and mixing sequences of PU and PU–clay nanocomposite foams

Sample ID	Mixing sequence	Content of clay platelets (wt%)
PU	Polyol/MDI	—
M14	Polyol/MDI/clay	4
M18		8
M24	Polyol/clay + MDI	4
M28		8
M34	MDI/clay + polyol	4
M38		8

2.3. Structural characterization and mechanical testing

XRD was carried out on a Phillips PW1720 X-Ray Diffractometer with a CuK α_1 (λ = 0.15406 nm) anode tube at the standard conditions of 40 kV and 20 mA. The samples were tested from 2° to 10°, 2 θ angle, at a step size of 0.02° and duration of 2.5 seconds per step. Powder samples grounded from the foams were used.

SEM was performed on a Tescan Mira Variable Pressure Field Emission Scanning Electron Microscope and a Zeiss Ultra Scanning Electron Microscope. The images were taken at voltages of 5.0 kV (Tescan) and 6.0 kV (Zeiss) and analyzed with the ImageJ software to characterize the cell diameter. The cell size was measured for an array of cells, considering only the cells that appear to be fully and well defined inside the SEM image. The average value for 20 cells with a confidence level of 95% was reported. Prior to being analyzed the samples were mounted on stubs and their surface was gold (Tescan) or platinum (Zeiss) coated.

Micro-CT was run on a Scanco Micro-CT 40 (Scanco Medical AG, Switzerland) at the standard resolution (acquisition: 250 projections per 180° with 1024 samples each, an energy of 55 kVp and a current of 145 μ A). The micrographs were realized using a predefined threshold that was found to give the most accurate interpretation of the image throughout the whole scan in order to assess the structure and porosity of the foams. The densities of the foams were determined by measuring the weights and volumes of five prismatic specimens for each type of foam, using a balance and a calliper.

Compressive tests were carried out on an Instron 1011 universal testing machine with a load cell of 500 N and at a rate of 10 mm min⁻¹. Testing was arbitrarily terminated at the deformation of 50% according to ASTM C365-05. Four surface grounded prismatic specimens (25.4 mm × 25.4 mm × 12.7 mm) were tested for each type of foam. The mean and standard deviation values reported represent a confidence level of 95%. Statistical significance was assessed by a Two-tailed, Type II 't' test with a criterion that the probability of a difference in means due to chance should be less than 0.05.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of natural clay and polyurethane–clay nanocomposite foams obtained from different mixing sequences and at different clay loadings. Natural montmorillonite presents a peak at 2 θ $\approx$ 7.1° corresponding to

a $d_{(001)}$ of 1.24 nm. By mixing the clay, polyol and MDI simultaneously (mixing sequence 1), $d_{(001)}$ increases to 1.85 nm regardless of the clay content which is similar to the values obtained for the natural clay intercalated with poly(ethylene glycol)s and glycerol.^{56–58} The increase in $d_{(001)}$, as also found by Cao *et al.*¹⁵ and Harikrishnan *et al.*,¹¹ suggests the presence of an intercalated structure in the nanocomposite. Natural montmorillonite is a hydrophilic clay that presents approximately 6 wt% water molecules between the layers.⁵⁹ Intercalation of the polyol into clay galleries is mainly driven by the entropic change associated with the loss of these water molecules from the galleries.⁶⁰ Similar d -spacings and peak shapes are obtained for mixing sequence 2 (*i.e.* polyol/clay + MDI), suggesting that the nanostructures formed are similar for these two mixing sequences. Change of the clay content from 4 wt% to 8 wt% increases the peak intensity indicating the presence of more intercalated clay tactoids in the latter.

Compared to the cases in the first two mixing sequences, the (001) peak of the clay shifts to a higher 2θ value and becomes broader for mixing sequence 3, implying the $d_{(001)}$ is reduced and the clay layers become less ordered in the nanocomposite.^{61,62} It is known that the reaction between an isocyanate and water produces an amine and carbon dioxide (Scheme 1). By reacting the water present inside the clay galleries⁵⁹ with the MDI an amine is formed, minimizing the degree of intercalation of the polyol in the later stage,^{2,63} but at the same time CO_2 is also produced presumably causing some clay layers to lose their ordered structures and perhaps to expand their layer spacing slightly further. Regardless of the clay content, a value of 1.61 nm is obtained. This value is close to the ones reported for the amine-intercalated natural clay, being 1.4–1.5 nm,⁶⁴ confirming the formation and the presence of the amine in clay galleries. Such amine may adopt a monolayer conformation in the galleries⁶⁴ in contrast to the bilayer conformation adopted by the polyol,² leading to a smaller d -spacing in M34 and M38 (curves 6 and 7) compared to that from the first two mixing sequences (curves 2–5). The fact that the first two mixing sequences lead to similar nanostructures in the nanocomposites which are, however, different from the one produced from the third mixing sequence, implies the natural clay prefers to intercalate the polyol as opposed to the MDI under a competitive absorption process.

Fig. 1 XRD profiles of natural clay and polyurethane-clay nanocomposite foams.

Scheme 1 Reaction between an isocyanate and water.

From the representative SEM images given in Fig. 2 it can be observed that the PU foam mostly presents a structure of closed cells with a cell diameter of approximately 760 μm . Additions of clay substantially reduce the cell size and increase the number of cells observed in the same image size, which is in accordance with the previous findings^{15,16,47,65} on the ability of clay platelets to act as nucleating agents during a foaming process. The results from quantitative analysis of 20 cells with a confidence level of 95% using the ImageJ software show that in the presence of clay the cell diameter of the PU foam decreases by 41–67% for 4 wt% clay content (column 2, Table 3). The cell diameter is found to increase with the augmentation of the clay content for the first two mixing sequences; however, it remains 32–49% lower compared to the value for the pristine PU foam. These comparisons are statistically significant as determined by a Two-tailed Type II 't' test with $p < 0.05$.

Changes of the cell diameter of the polymer foam arise from two competing effects of the clay: the nucleation effect^{15,16} which decreases the cell diameter and the blowing effect⁶⁶ which increases the cell diameter. The former depends on the interfacial surface area between the polymer and the clay and hence the degree of clay dispersion in the polymer. The latter is due to the presence of water in clay galleries. Both are related to the clay content. Reductions of the cell diameter by the clay (Fig. 2 and Table 3) suggest the nucleation effect is dominant in all cases. An increase in the clay content leads to a growing amount of water available in the clay galleries which either directly acts as the blowing agent for foaming in the first two mixing sequences or reacts with the intercalating MDI to produce CO_2 in the third mixing sequence. The increase in the cell diameter with increasing clay content implies that the blowing effect has a greater impact compared to the nucleation effect in these cases.

The effects of clay addition, clay content and mixing sequence on the cell size are confirmed by Micro-CT images, presented in Fig. 3. Reconstruction of 3D images shows the foams have uniform cell size throughout the sample (*e.g.* Fig. 3A2 and E2). Since clay decreases the cell diameter, the uniform reduced cell size indicates clay is well dispersed in PU, agreeing with the XRD results which suggest intercalation of PU into clay. However, the cells, which were found to be mostly closed in the SEM micrographs (Fig. 2), appear to be opened in the Micro-CT scans. This is because most of the solid material is drawn by the surface tension towards the cell edges during the foaming process⁶⁷ so the cell faces are too thin for the Micro-CT to detect at the pre-set threshold.

The densities of the PU and PU-clay nanocomposite foams and solids as well as the porosities of the foams are given in Table 3, columns 3–6. The density of the PU-clay nanocomposite foams decreases compared to the density of the pristine foam, with statistical significance for the higher amount of clay present in mixing sequences 1 and 2 and for 4 wt% clay content present in

Fig. 2 Representative SEM images of (A) PU foam (scale bar: 500 μm) and PU-clay nanocomposite foams (scale bar: 200 μm): (B) M14; (C) M18; (D) M24; (E) M28; (F) M34; and (G) M38.

mixing method 3, and with statistical insignificance for the remaining foams. The reduction in the density of nanocomposite foams confirms the nucleation effect of the clay as discussed above. The densities of non-cellular PU-clay nanocomposites, ρ_s (column 4, Table 3), were calculated according to eqn (4), taking into account that both the clay and the polymer change their volumes during nanocomposite formation due to intercalation of some polymer molecules into clay galleries.⁶⁸

$$\rho_s = \frac{\mu_{cp} - \mu_c + \mu_c \mu_{cp}}{\frac{\mu_c d_2}{\rho_c d_1} + \frac{\mu_{cp} - \mu_c - s \mu_c}{\rho_p}} \quad (4)$$

where ρ_p is the density of the polymer, *i.e.* PU in this case which is 1200 kg m⁻³,²² and ρ_c is the density of natural clay platelets, *i.e.* 3100 kg m⁻³.⁶⁸ d_1 and d_2 are the basal plane spacing of natural clay and the clay intercalated with the polymer, s is the saturated ratio of the intercalating polymer to the clay (0.23 g polymer per g of clay)⁶⁸ and μ_{cp} is the mass fraction of the inorganic content in natural clay determined from the Loss on Ignition analysis, *i.e.* 0.886, while μ_c is the mass fraction of clay platelets in the composite, *i.e.* 0.04 or 0.08 in this work. Additions of clay slightly increase the density of the PU solid.

Table 3 Cell diameters, densities and porosities of PU and PU-clay nanocomposite foams

Sample	Cell diameter/mm	Foam density/kg m ⁻³	Solid density/kg m ⁻³	Porosity ^a (%)	Porosity ^b (%)
PU	0.76 ± 0.10	48 ± 9	1200 ^c	96	97
M14	0.25 ± 0.02	41 ± 4	1230	97	98
M18	0.52 ± 0.12	37 ± 5	1262	97	98
M24	0.33 ± 0.03	38 ± 4	1230	97	98
M28	0.39 ± 0.05	36 ± 4	1261	97	98
M34	0.45 ± 0.11	38 ± 3	1234	97	97
M38	0.48 ± 0.03	39 ± 5	1271	97	98

^a Calculated from the densities of the foams and solids presented in columns 3 and 4. ^b Calculated from Micro-CT results. ^c From literature.²²

The porosities given in the fifth column of Table 3 were calculated from the densities of the foam and its corresponding solid, *i.e.* $1 - \rho_f/\rho_s$. The as-prepared PU foam is highly porous with a porosity of 96%, and the presence of clay only provides marginal increases in the porosity because of the high starting value. These porosities are in excellent agreement with those obtained from Micro-CT by reconstructing the three-dimensional images of the foam samples (column 6). The negligible difference of approximately 1% is attributed to the thin cell faces and probably some cell edges that are undetectable with the preset threshold. Since $\rho_f/\rho_s < 0.05$, the PU-clay nanocomposite foams can be classified as ‘low-density foams’.⁶⁹

The compressive moduli for the PU and PU-clay nanocomposite foams determined from the compressive testing data are given in Fig. 4. Compared to pristine PU foam, the compressive modulus for simultaneous mixing of the three components (M14 and M18) is found to increase with the clay addition by close to 30%, while the mixing of 4 wt% clay with the MDI or polyol followed by the addition of the other component is found to decrease with the clay addition. The variations observed in these materials are without statistical significance compared to the pristine PU foam. The mixing of 8 wt% clay with polyol followed by the addition of MDI (M28) leads to a statistically significant increase of modulus by 35% as opposed to the pristine PU foam and by 69% compared to M38 where a different mixing sequence is adopted and a larger cell size is found. These results are different from the ones reported for PU/vermiculite foams containing between 1.2 wt% and 3.7 wt% clay in which the compressive moduli were found to be greater in mixing sequence 3 than in mixing sequence 2.⁷⁰ Besides cell size, the densities of the foam and its corresponding solid, the modulus of the corresponding solid, the geometric information of the cells in the foam and the deformation mechanism of the foam also affect the compressive modulus of the foam.

To eliminate the effect of foam density, specific compressive modulus of the foams was calculated and the results are also presented in Fig. 4. For mixing sequences 1 and 2, the augmentation of the clay content was found to increase the specific modulus by up to 81% for M28. However, when the clay was first mixed with the MDI the specific compressive modulus was found

Fig. 3 Micro-CT scans of (A1) PU foam and PU–clay nanocomposite foams: (B) M14; (C) M18; (D) M24; (E1) M28; (F) M34; and (G) M38 and 3D reconstructions of (A2) PU and (E2) M28 foams (scale bar: 500 μm).

to be similar to the one of pristine PU, regardless of the clay content. This confirms that the variation of the compressive modulus depends on the clay content and mixing sequence.

To study the effects of densities of foam and solid, the modulus of solid on the modulus of foam, the geometric information of cells and the deformation mechanism of foams, the relationships between relative modulus and relative density of foams should be established. All the theoretical models for the relative modulus–relative density relationships of foams presented in eqn (2) and Table 1 were tested to investigate if they work for these nanocomposite foams. The moduli of the foams and the densities for the foams and solids were taken from Table 3 and Fig. 4. The moduli for nanocomposite solids were calculated by employing the Halpin–Tsai model (eqn (5) and (6)) with the van Es correction⁷¹ and considering the modulus of the unfilled rigid PU solid of 1600 MPa²² and clay platelets of 230 GPa.⁷²

$$\frac{E}{E_p} = \frac{1 + \zeta \eta \phi_c}{1 - \eta \phi_c} \quad (5)$$

where E is the modulus of the nanocomposite and subscripts c and p refer to the clay and the polymer matrix respectively. ϕ_c is the effective volume fraction of clay reinforcement, and ζ is the shape factor and is $2w/3t$ according to van Es⁷¹ where w/t represents the aspect ratio of the reinforcement filler^{71,73} (*i.e.* $w/t = 10$)⁷¹ and η is calculated using eqn (6).

$$\eta = \frac{(E_c/E_p) - 1}{(E_c/E_p) + \zeta} \quad (6)$$

Because the nanocomposites are the PU matrix reinforced by intercalated clay tactoids, clay reinforcement refers to

Fig. 4 Compressive modulus and specific compressive modulus of PU and PU–clay nanocomposite foams (error bars represent the standard deviation for compressive modulus).

intercalated clay tactoids. Thus, ϕ_c was calculated using eqn (7), which is substantially greater than the nominal volume fraction of the clay particles.⁶⁸

$$\frac{1}{\phi_c} = 1 + \frac{1 - \mu_c(1 + s)}{\rho_p \mu_c d_2 A} \quad (7)$$

where A is the specific gallery area of clay ($310 \text{ m}^2 \text{ g}^{-1}$).⁶⁸

Among all the models presented in Table 1, the ones developed by Dement'ev and Tarakanov ($C_1 = 0.7$ in eqn (2))^{36,37} and Choi and Lakes ($C_1 = 0.88$ in eqn (2))³⁶ best fit the experimental data despite that they are open-cell models, while the rest do not give reasonable predictions. The correlation between the experimental data for the PU–clay nanocomposite foams and the theoretical values predicted using these two models is given in Fig. 5 which shows reasonably good agreement. It is noted that both models were developed based on conventional polyester-based PU foams with 97% porosity, same as the value for the nanocomposite foams studied in this work. The good correlation indicates the relative modulus–relative density relationship for polymer foams is applicable to nanocomposite foams provided the porosities are similar.

As previously discussed, the PU and PU–clay nanocomposite foams are low density closed-cell materials with most of the material located within the cell walls. The fact that the above two models best fit the experimental data also suggests that the low density closed-cell foams can be considered as open cells, agreeing with the previous findings for general cellular solids that most of the load is carried out by the cell edges in this type of foams⁶⁹ and the low density closed cells tend to behave as open cells.⁶⁷

Among the remaining models presented in Table 1, the original Gibson–Ashby model for open cells, where $C_1 = 1$ and $n = 2$ for eqn (2), assumes a two dimensional continuous structure in which the cell edges meet at a 90° angle, have square cross-sections and the vertices link three edges.^{22,38} However, as it can be observed from the SEM and Micro-CT images, the cells present hexagonal cross-sections, a different angle at which the edges meet and a higher nodal connectivity, which may explain the fact that this model is inadequate to predict the values for the

pristine PU foam and PU–clay nanocomposite foams. In contrast, the tetrakaidecahedron cell shape observed for these foams is the same as the shape found in the foams studied for both the Dement'ev–Tarakanov³⁷ and the Choi–Lakes^{36,74} models, noting that such tetrakaidecahedron shape is commonly found for polymer foams for example other PU–clay foams,^{47,70} PCL–clay foams⁵⁰ and PP–clay foams.⁵²

In the normalised Gibson–Ashby model³⁸ for open cells, C_1 is the coefficient used for normalisation of the Young's modulus of the foam, namely $C_1 = (E_f^p/E_s^p)(\rho_s^p/\rho_f^p)^2$ where the superscript p refers to the pristine polymer. Inserting the normalisation coefficient into eqn (2) results in eqn (8), in which the coefficient is equal to 0.45 in this work. The theoretical values predicted using this normalised model are also presented in Fig. 5, showing good agreement with the experimental data in general and confirming that an open-cell model may be used for studying low-density nanocomposite foams.

$$\frac{E_f}{E_s} = \frac{E_f^p}{E_s^p} \left(\frac{\rho_s^p}{\rho_f^p} \right)^2 \left(\frac{\rho_f}{\rho_s} \right)^2 \quad (8)$$

The Gibson–Ashby model for closed-cell foams given in eqn (3) was also considered for prediction of the relative modulus of nanocomposite foams. Because the contribution of the cell fluid is minimal,²² eqn (3) can be reduced to eqn (9).

$$\frac{E_f}{E_s} = C_1 \phi_s^2 \left(\frac{\rho_f}{\rho_s} \right)^2 + C_2 (1 - \phi_s) \frac{\rho_f}{\rho_s} \quad (9)$$

In order to determine the volume fraction of solid (ϕ_s) contained in the edges of the cells, a relative volume of the cell faces to the cell edges of 0.1⁶⁹ (characteristic for rigid polyurethane foams) was used, which led to a ϕ_s value of 0.94.^{22,69} As previously introduced, C_1 is the geometric constant for the cell struts so it is the same as the constant for the open cells, *i.e.* 0.45. Inserting these two values and the moduli and densities for the pristine PU foam and solid into eqn (9), C_2 was determined as 0.03. Like the previous three models, the theoretical values predicted using eqn (9) are given in Fig. 5. It is seen that this additional curve almost overlaps with the curve for the normalised open-cell model, further confirming that the open-cell model is a simplified version of the closed-cell model and low density closed-cell foams can indeed be considered as open-cell foams.

As shown in Fig. 5, the theoretical relative moduli predicted using all the above-discussed four models appear to be reasonably close to the experimental data. In contrast, other models presented in Table 1 give values markedly deviated from the experimental results. These imply the normalised Gibson–Ashby models for open cells and closed cells work reasonably well for low-density nanocomposite foams ($\rho_f/\rho_s < 0.05$). In the case of high-porosity PU–clay nanocomposite foams, the C_1 in $E_f/E_s = C_1(\rho_f/\rho_s)^2$ is approximately 0.45–0.88. These results further suggest that the established models for conventional cellular solids can be applied to polymer nanocomposite foams provided that all the parameters in the models are correctly calculated.

4. Conclusions

PU–natural clay nanocomposites containing different clay contents were prepared with different mixing sequences and used

Fig. 5 Theoretical and experimental data of relative Young's modulus versus relative density for PU–clay nanocomposite foams showing they are in good agreement.

for the studies of relative modulus–relative density relationships in a relatively new class of foam materials, *i.e.* polymer–clay nanocomposite foams. It is found that the addition of clay decreases the cell size and density of the polymer foam, acting as a nucleation agent as previously reported by others, and the increase of clay content leads to a greater cell size which is the result of the blowing effect from the growing amount of water present in the clay galleries. The uniform cell structures with varying cell sizes in the PU–clay foams observed using SEM and Micro-CT, together with the shifts of the (001) peak for the clay detected by XRD, confirm the formation of nanocomposites between the polymer and the clay. The nanocomposite foam prepared by mixing the polyol blend with 8 wt% natural clay followed by the addition of diisocyanate provides an increase in the specific compressive modulus of the PU foam by 81%. This enhancement is attributable to the strong interactions between the polymer and the clay due to formation of hydrogen bonds and nanostructures, the large specific surface area and high stiffness of clay, and the small cell size that occurs due to the nucleation effect of clay.

Modelling the relative modulus *versus* relative density for the low density nanocomposite foams (with a porosity higher than 95%) finds that their relationship can be reasonably predicted by the classical Gibson–Ashby models for open-cell and closed-cell foams provided the modulus of the starting polymer foam is normalised to obtain the correct geometric constants and the modulus and density of the nanocomposite solids contained in the cells are properly calculated. In the case of high-porosity PU–clay nanocomposite foams, the geometric constant of foam C_1 in $E_f/E_s = C_1(\rho_f/\rho_s)^2$ was determined to be approximately 0.45–0.88.

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