

How much do nanoparticle fillers improve the modulus and strength of polymer foams?

Juan Lobos and Sachin Velankar

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Abstract

Nanofiller reinforcing agents can significantly improve the strength and modulus of polymer foams. But these improvements are often accompanied by changes in foam density (or equivalently the expansion ratio or void volume). The efficacy of nanofillers as reinforcing agents can only be judged once the density differences are accounted for. We review the literature and show that representing the data on Ashby charts of modulus against foam density is an effective way of evaluating whether nanofillers have a significant reinforcing effect or not. The literature suggests that strength and improvements due to nanofiller – after accounting for foam density changes – are typically modest for thermoplastic foams. However, major improvements are possible for reactively generated foams, especially flexible polyurethane foams.

Keywords

Foam, filler, thermoplastic, porous, polyurethane

Introduction

Nanofillers such as carbon nanofibers (CNFs) or nanotubes, silica, or organoclays are often added to foamed polymers for a variety of reasons including increasing nucleation, reducing cell size, or improving barrier properties. In many such cases, the addition of nanofillers is also intended to improve the mechanical properties of the foams. Figure 1 illustrates an example of an especially dramatic improvement in the strength of polyurethane (PU) foams with addition of montmorillonite

Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, USA

Corresponding author:

Sachin Velankar, University of Pittsburgh, 1249 Benedum Hall, 3700 Ohara Street, Pittsburgh, PA 15261, USA.

Email: velankar@pitt.edu

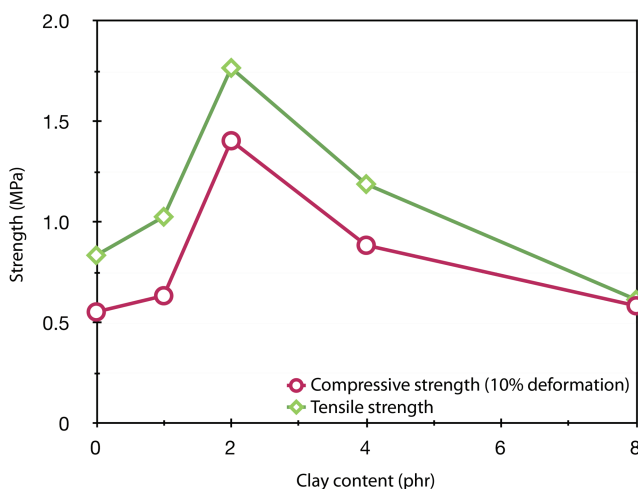


Figure 1. Compressive and tensile strength of PU foam/organoclay nanocomposites.¹

(MMT) clay: the addition of only a few weight percent clay improves the tensile strength and the compressive strength by 110% and 152%, respectively.¹ Many such examples of nanofiller-induced improvements in modulus or strength are cited in the literature²⁻⁶ and the supplementary information has compiled data from numerous articles showing similar results. A recent review article also commented on the efficacy of nanofillers at improving foam properties.⁷ In the light of these results, the question “Do nanofillers improve modulus and strength of foams?” seems to be answered with an unequivocal “Yes” in many cases. However, this conclusion cannot be sustained *solely* based on data such as Figure 1 because the nanofiller may simultaneously change the foam density which itself affects mechanical properties. For instance, if the filler increases the density of the foam, one would see an increase in strength for that reason alone – regardless of the reinforcing effect of the filler. Thus, for any practical application, the foam strength may be improved by simply reducing the expansion (i.e., foaming to a higher density) rather than by adding a nanofiller. Depending on the costs of the nanofiller, the polymer and the processing operation, increasing the density of the filler-free foam may be more economical than adding the filler to achieve the same final foam properties. Clearly then, addressing the question posed in the title of this paper requires accounting for changes in foam density with particle addition. The goal of this article is to examine – after accounting for the changes in foam density – the extent to which nanofillers affect foam mechanical properties.

Remarkably, a large number of articles on polymer foams, including Xu et al.¹ (Figure 1), do not quote the density of the foams at all. Thus, a quantitative “normalization” for the effect of foam density, or even a qualitative judgment of whether density changes may have affected the mechanical properties, is not

possible from the data. There are also numerous articles,^{2,8-11} especially in the microcellular foams literature, in which the foam density is not given explicitly but the mean cell size and the cell number density, N_f , are both quoted. At first glance, a combination of the two should give the foam density since

$$(\text{void volume fraction}) = \langle V_{cell} N_f \rangle = \left\langle \frac{1}{6} \pi D_{cell}^3 \right\rangle N_f = \left(1 - \frac{\rho_{foam}}{\rho_{solid}} \right) \quad (1)$$

where D_{cell} and V_{cell} are the cell diameter and cell volume, respectively, and the angular brackets denote an average. However, there are potential problems with this approach. Often the cell number density is calculated from electron microscope images of cross-sections of the foams using the equation^{2,12-14}

$$N_f = \left(\frac{n}{A} \right)^{\frac{3}{2}} \quad (2)$$

where n is the number of cells in an scanning electron microscope (SEM) cross-sectional image of area A . Equation (2) makes several assumptions including that the cells are isotropic, that the foam density is low, and that the cell size distribution is not too polydisperse. If these assumptions are not met, equation (1) may give wrong results. To further complicate matters, numerous articles do not specify clearly how the average cell size has been calculated. Equation (1) requires that the cell size be the volume-weighted average $\langle D_{cell}^3 \rangle^{1/3}$, whereas if the size-weighted average, $\langle D_{cell} \rangle$, has been quoted, it would not be appropriate to use equation (1). Moreover, if the cells are anisotropic, each cell size is itself an average of its dimensions along two orthogonal directions. In that case, calculating the average cell volume from this average size would give incorrect results even if the cell size polydispersity was low. Finally, to further complicate matters, some articles¹⁵⁻¹⁸ report the cell density, N_0 , calculated as

$$N_0 = \left(\frac{n}{A} \right)^{\frac{3}{2}} \frac{\rho_{solid}}{\rho_{foam}} \quad (3)$$

This N_0 is the number of cells per unit volume of the *unfoamed* polymer which cannot be used in equation (1). For all these reasons, applying equation (1) to estimate foam density may cause large errors. For instance, using equation (1) can sometimes¹⁹⁻²³ yield an unphysical result that the $\rho_{foam} < 0$. This must not be regarded an error in the values of cell density or of cell size quoted in the original articles since those values were not intended for back-calculating foam density. However, it does mean that data from those articles cannot be “normalized” to account for foam density variations.

Accordingly, this review is chiefly focused on articles in which the following three criteria were met (1) nanofiller-containing foams were compared against corresponding nanofiller-free foams, (2) mechanical properties were measured, and (3)

foam density was cited explicitly in the paper. Approximately 30 articles were found to satisfy all the three criteria. The bold texted rows in Table 1 summarize some of the key information in these papers: the polymer, the type and amount of filler, the foaming method, and which mechanical properties were measured. The Online Supplementary Information summarizes the mechanical property data in each paper. Based on all of these articles, we conclude that (1) the improvement in mechanical properties due to nanofiller addition is typically modest for thermoplastics, although occasional cases of much larger improvements have been documented,^{8,21,24} (2) dramatic improvements are possible when the matrix is rubbery,^{3,6,25} (3) filler surface modification and the foaming operation can have a significant effect on the efficacy of reinforcement.^{2,11,26}

In addition, there are numerous articles where the addition of nanofiller was shown to affect mechanical properties, but foam density was not stated. These articles are also included in Table 1, but datasheets for those papers are not presented in the Online Supplementary Information.

The outline of this article is as follows. The next section discusses, with one illustrative example, how differences in foam density may be accounted for when judging the reinforcement efficacy of nanofiller. Next, we will cite exemplary data supporting the conclusions listed in the previous paragraphs. Finally, we will discuss some potential mechanisms whereby the fillers can affect the mechanical properties of foams.

Accounting for differences in foam density

Figure 2 illustrates an example of the Young's modulus of foams reinforced by CNFs.⁸ Figure 2(a) compares the modulus of the foams obtained at two different nanofiber loadings against the modulus of the filler-free foams. Foams of various densities, which have been tagged in Figure 2 as "low," "medium," and "high" density, were obtained by varying the processing conditions. Three comments may be made (1) the modulus of the unfilled foam increases significantly with density which is well recognized in the foam literature,²⁷ (2) under a given set of processing conditions, the modulus increases with nanofiber addition analogous to Figure 1, and (3) the foam density also increases with nanofiber addition. As mentioned in the Introduction section, it is the last effect that must be "subtracted out" when judging the efficacy of the nanofiller in improving mechanical properties.

One immediate solution may be to normalize the mechanical property of each foam by the foam density, e.g., by comparing specific strength or specific modulus.^{3,6,11,28} This comparison is shown in Figure 2(b), and while the difference between samples appears somewhat smaller, nanofiber addition still appears to have a beneficial effect, i.e., it improves the specific modulus $\frac{E_{\text{foam}}}{\rho_{\text{foam}}}$. Nevertheless, simple normalization by the density may not entirely account for foam density variations because the mechanical properties of foams often vary non-linearly with density.²⁷ For instance, in the limit of low densities, a wide

variety of foams have been shown to approximately follow a quadratic relationship²⁷

$$\frac{E_{foam}}{E_{solid}} = K \left(\frac{\rho_{foam}}{\rho_{solid}} \right)^2 \quad (4)$$

where K is nearly 1.²⁷ Such a relationship suggests that the specific modulus $\frac{E_{foam}}{\rho_{foam}}$ is not independent of the foam density: if a nanofiller doubles the foam density, the specific modulus doubles even if the filler has no reinforcing effect at all. In such a situation, one may erroneously conclude that the nanofiller improves the mechanical properties, when in fact the nanofiller merely reduces foam expansion. As mentioned in the Introduction, in such a case, the same improvement in modulus could have been realized without nanofiller, simply by reducing the foam expansion. This same issue remains even if equation (4) is not exactly correct, or if properties other than modulus are under consideration: simply normalizing a property by density is justifiable only if that property is inherently proportional to density.

The best solution then is to compare samples with and without nanofillers at a constant foam density. This, however, is difficult since most foaming operations cannot control foam density accurately. More precisely, if the neat polymer and the filled polymer are foamed under identical conditions, they will typically not have the same density. In some cases, the changes in foam density due to nanofiller happen to be quite small,^{26,29} and later in this article, one such case will be discussed in greater detail. It is also possible to guarantee samples of exactly the same density by foaming in a closed mold, thus limiting the expansion to a pre-specified value.^{29–31} Even in such cases, however, a density gradient between the core and the walls^{32–36} may provide misleading results. In extreme cases, the formation of a skin at the surface may significantly affect mechanical measurements, especially if the foam density is very low. In summary, although foam properties ought to be compared at fixed foam density, such comparisons are often not possible.

The next best approach is to obtain the mechanical properties across a wide range of densities, e.g., finding the entire E_{foam} vs. ρ_{foam} curve, often known as an Ashby chart,^{37,38} and then finding how this curve is affected by the addition of nanofillers. Indeed, the article of Shen et al.⁸ (Figure 2) provides three densities at each nanofiber loading, allowing a rough modulus–density graph to be plotted (Figure 2(c)). The solid line corresponds to the quadratic dependence of equation (4) (with $K = 1$), which seems to capture the modulus–density relationship for the filler-free foams at least approximately. At the lowest densities, the nanofiller-containing foams appear to follow this same relationship almost quantitatively, suggesting that a comparable modulus improvement might have been obtained by reducing foam expansion rather than by adding nanofiller. At higher density, however, the modulus appears to increase more sharply than the solid line suggesting that nanofiller addition may have a reinforcing effect.

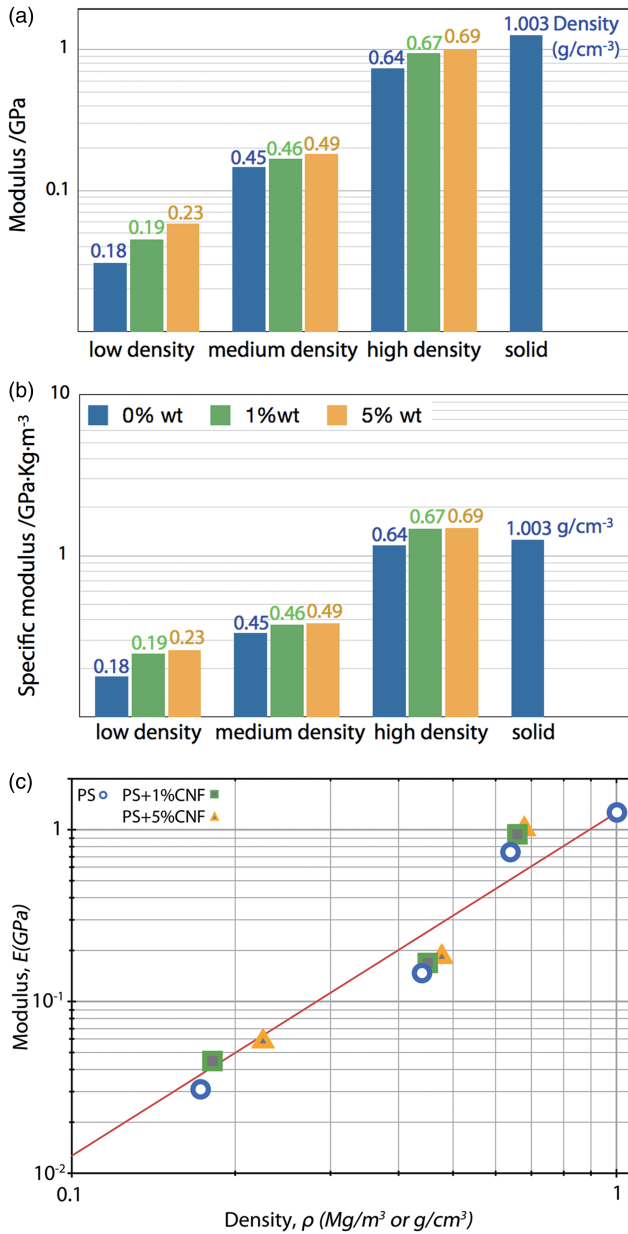


Figure 2. (a) Young's modulus of the PS-CNF foams.⁸ (b) Specific modulus of the PS-CNF foams (ratio of modulus to density). (c) Ashby chart of modulus vs. density. Note that the moduli of the low- and medium-density foams were measured in compression while the moduli of the high-density samples were measured in tension.

Admittedly, Figure 2 shows only three points on the modulus–density curve; moreover, the moduli of different samples were measured differently (in tension for the high-density foam and in compression for the medium- and low-density foams). Therefore, the conclusion of the previous paragraph is only tentative. Nevertheless, if more data were collected, this approach offers the potential for drawing unambiguous conclusions about whether the nanofiller truly has a reinforcing effect. The advantage of this approach is that it is purely experimental and does not depend on specific models of foam mechanics: the sole criterion is whether the properties of foams with nanofiller systematically lie above or below the curve for foams without filler. For instance, Figure 7 illustrates such an example where the modulus–density curve for filled foams is consistently above that of the unfilled foams indicating a true reinforcing effect.²¹ In contrast, Zhang et al.³⁹ (see corresponding graph in the Supplementary Information) show an excellent example where nanofiller induces large change in the modulus, strength, and density, yet, foams with and without nanofiller fall on exactly the same curve. These results³⁹ suggest that the dominant role of the nanofiller in Zhang et al. is simply reducing foam expansion with little or no reinforcing effect.

The disadvantage of this approach is that it is experimentally tedious: it requires sufficient number of samples that a continuous curve of E_{foam} vs. ρ_{foam} can be drawn with confidence. In fact only a few articles^{4,8,21,40} have reported samples at sufficient number of densities that such a curve can be drawn at all. Nevertheless, this idea of comparing foams on an Ashby chart where a particular property is plotted against density is very useful: it can not only judge whether nanofiller addition has a beneficial effect but also identify which particle loadings, particle types, or foaming conditions offer the greatest improvements. Accordingly, all the data in this paper and in the Online Supplementary information are compiled in this form of Ashby charts. In the following section, we will present data from specific articles that have been selected to illustrate the key effects of nanofiller on foam mechanics.

Nanofiller effects in polymer foams

Figure 3 compares the Young's modulus data for a single material, polystyrene (PS), from four different papers,^{2,8,24,41} including the article of Figure 2. To our knowledge, these four are the only papers on PS foams which satisfy the three criteria listed at the end of the Introduction section, viz. using nanofillers, citing foam density, and measuring mechanical properties. The lines with slope 2 correspond to equation (4), where E_{solid} was assigned the modulus of the unfoamed filler-free PS quoted in each paper. In each case, the unfilled points correspond to the foams without filler, and in each, equation (4) is found to be in qualitative agreement with the results although deviations of as much as $1.5 \times$ (in either direction) are sometimes evident. Various nanofiller types, and at various filler loadings are included in Figure 3. The advantage of representing the data in this form is especially evident for the data of Han et al.² shown as purple diamonds; here the fillers

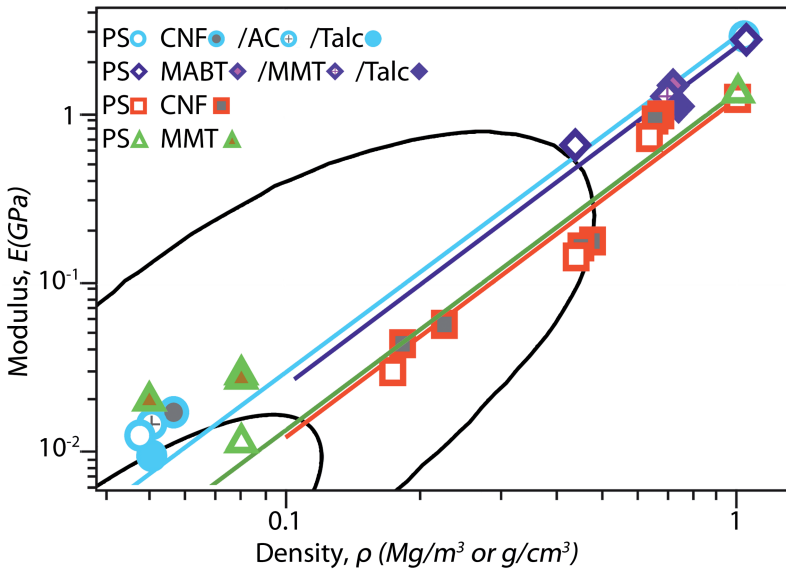


Figure 3. Modulus of the PS foams vs. density.^{2,8,24,48} The lines correspond to equation (4). The elliptical boundaries correspond to the envelope of properties expected from closed- and open-celled polymeric foams.^{72,73} See Table I for abbreviations.

increase both the foam density and modulus significantly, but these filler-containing foams do not deviate much from the quadratic line. This behavior is similar to that of Zhang et al.³⁹ mentioned above. Thus, if equation (4) is valid for these foams, then we would conclude that the improvements in foam properties are entirely attributable to nanofiller-induced changes in foam density rather than nanofiller-induced reinforcement. Examining Figure 3, the filler effects appear modest for most samples. In fact, the data on all the papers in the Online Supplementary Information suggest that this is true for a majority of thermoplastic foams: the improvements in modulus or strength are typically below 20%. Nevertheless, it must be emphasized that the y-axis in Figure 3 is a logarithmic scale spanning over three orders of magnitude; such a large-scale magnitude can mask some significant improvements. Most strikingly, in the case of the MMT-reinforced foams from Ogunsona et al.²⁴ (green triangles in Figure 3, which correspond to different MMT loadings), the filler simultaneously induces an almost two-fold decrease in foam density and a two-fold increase in modulus. There are a few other examples in the literature where similar large improvements of strength or modulus were realized.^{8,21,42} In summary, Figure 3 illustrates the value of uniting different data for a single thermoplastic onto a single graph: it has the potential to identify filler types or filler loadings that can give the greatest improvement in properties.

Not only the nature of the solid filler used but the processing conditions may also affect the improvement in mechanical properties. Figure 4 illustrates an example of LDPE foams prepared by two different methods:^{11,30} batch foaming (BF)

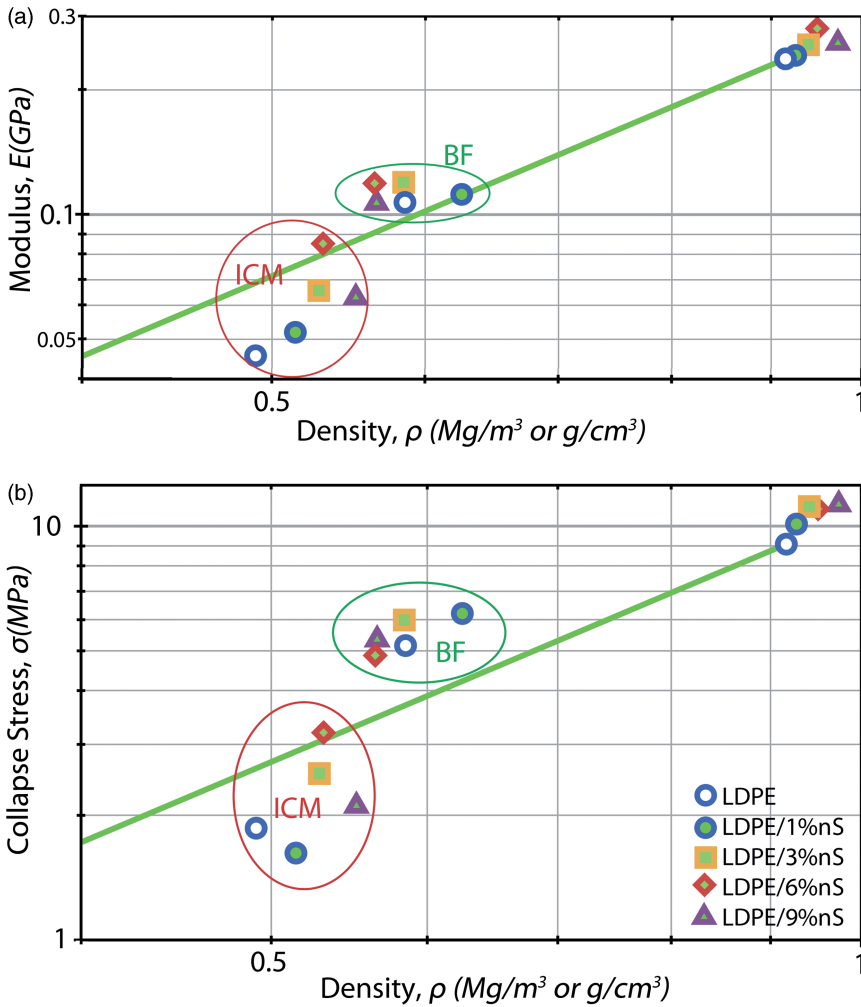


Figure 4. Effect of processing conditions on the mechanical properties of LDPE foams with nanosilica (nS).^{11,29} The quadratic lines correspond to equation (4) in the text and 5.18 b in Gibson and Ashby.⁶⁵

using carbon dioxide and improved compression molding (ICM) using a chemical blowing agent. In the BF method, samples were saturated with CO_2 at high pressure and temperature, and then the pressure was decreased rapidly with simultaneous cooling. In this case, the addition of nanosilica was seen to reduce the density with a slight improvement in modulus and collapse stress, at least at the 3% and 6% silica loading. In the ICM method, the polymers, blended with 5% of azodicarbonamide as a blowing agent, were introduced into a cylindrical mold in a hot plate press. The blowing agent was allowed to decompose by heating without

permitting foam expansion, followed by rapid foam expansion and simultaneous cooling. In this case, the filler was seen to increase the modulus significantly, at least up to 6% silica, along with a modest increase in foam density. Thus, the effect of filler loading is qualitatively consistent in the two experiments (best improvement appears at 3–6% loading in both cases), although the actual density values realized are somewhat different. It is noteworthy that regardless of foaming technique, the method used for dispersion of the nanofiller into the thermoplastic was identical; thus, the difference in foam properties is not likely due to the state of dispersion of the nanosilica, but instead due to differences in the foam structure (in particular, the open cell content) obtained from the two different processes.¹¹ Incidentally, in the case of BF, the modulus increased while density reduced – a combination that strongly suggests that the nanofiller does have a reinforcing effect. As with Ogunsona et al.²⁴ discussed in the previous paragraph, in such situations the filler reinforcement effect is clearly evident even though samples are not compared at fixed foam density.

The surface chemistry of the filler can also affect the foam properties. First, favorable interactions between the polymer and the filler can improve the dispersion of the filler. Second, the adhesion between the filler and the polymer, which is critical for stress transfer from the polymer to the filler, may also be improved with appropriate surface chemistry. Such chemical interactions can be improved by including functional groups into the polymer to act as compatibilizing agents. Indeed, Table 1 shows numerous cases in which maleated polymers are added as compatibilizers. It is also common in the nanoclay composite literature to use organic modification of the clay to improve compatibility with the polymer.^{43–46} Such compatibilization can have a significant effect on mechanical properties as exemplified in Figure 5. This figure shows the tensile strength and ultimate elongation of ethyl vinyl acetate foams with MMT clay nanofiller²⁶ at a single filler loading of 3 wt%. In addition to the native unmodified MMT clay, three organoclays were used. As clear from Figure 5,

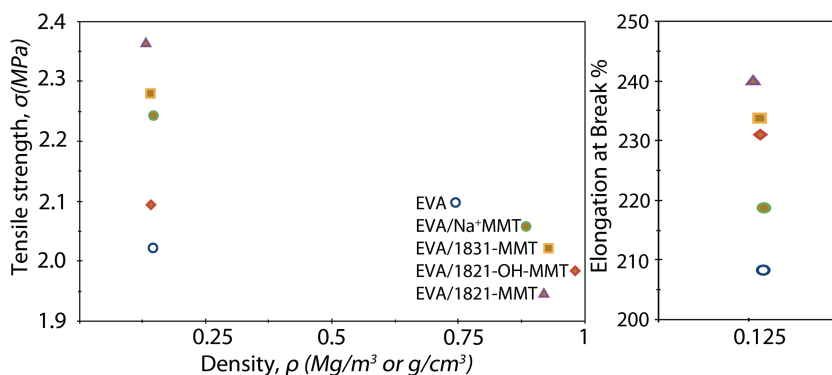


Figure 5. Effect of different clay types (all at 3 wt% loading) on the mechanical properties of ethyl vinyl acetate foams.²⁶

although clays improved the strength and ultimate elongation in all cases, there was a significant effect of the type of clay used, with the best improvement coming from a clay dubbed D1821-MMT which was MMT modified with a surfactant having highly hydrophobic tail. These differences in mechanical properties with clay functionalization were shown to be directly related to the quality of dispersion of clay as judged by SAXS: the native Na-functional MMT and the hydroxyl-functional MMT had the worst dispersion and the least improvement in strength, whereas the organoclays D1821-MMT and 1831-MMT had the best dispersion and greatest improvement in strength. More details of the chemical nature of the organic modification are available in Table 1 and in the supplementary datasheet.

The data of this figure are unusual in that because the foaming was conducted by compression molding in a closed mold, all the foams have nearly the same density. Thus, this is a rare example of where the reinforcing effect of nanofiller can be made *quantitative* without normalizing for foam density. Incidentally, it is noteworthy that in organoclays, the organic surfactant comprises a significant fraction of the mass and volume of the clay. Thus, even though all the foams contained 3% by weight of the organoclay, the fraction of the aluminosilicate platelets, which are the actual reinforcing agent, was not constant. In the case of Na-functional MMT, all of the mass of the clay was capable of being a reinforcing agent, whereas in the other extreme of D1821-MMT, only 65% of the clay mass could act as a reinforcing agent (the remaining 35% being surfactant). Thus, it is noteworthy that the D1821 clay increased the strength of the foams to a greater extent even though the loading of the actual reinforcing agent was lower. This testifies to importance of the better dispersion and adhesion realized due to the organic modifier.

We now turn from thermoplastic foams to reactive foams in which a low-molecular weight fluid is converted, in a single step, into polymer foam. These are typically PU foams made by reaction between polyol and isocyanate, with several other ingredients included in the reacting mixture. The foam expansion occurs either due to the boiling of a physical blowing agent such as a fluorocarbon mixed into the reacting mixture, or due to the reaction of one component of the reacting mixture with water. In such systems, foaming, polymerization, and often crosslinking or vitrification of the polymer, all happen simultaneously. Even in the absence of nanofiller, the situation is complicated because changes in foam density may go hand-in-hand with changes in the composition or glass transition temperature or crosslink density of the solid phase. Moreover, properties of the unfoamed solid phase, e.g., E_{solid} , are difficult to measure since it can be difficult to reproduce the exact same material in unfoamed form. Accordingly Figure 6, which summarizes modulus of some reactive foams, does not show any data for the unfoamed polymer. What is most noteworthy is that unlike thermoplastic foams, significant improvements due to nanofiller addition – either a decrease in foam density without loss of modulus, or an increase in modulus at fixed density, or both – are seen in many cases. However, these improvements can depend severely on the materials used. An excellent illustration of this is provided in Cao et al.³ where two PU foams were examined, with the only difference being the molecular weight of the polyester

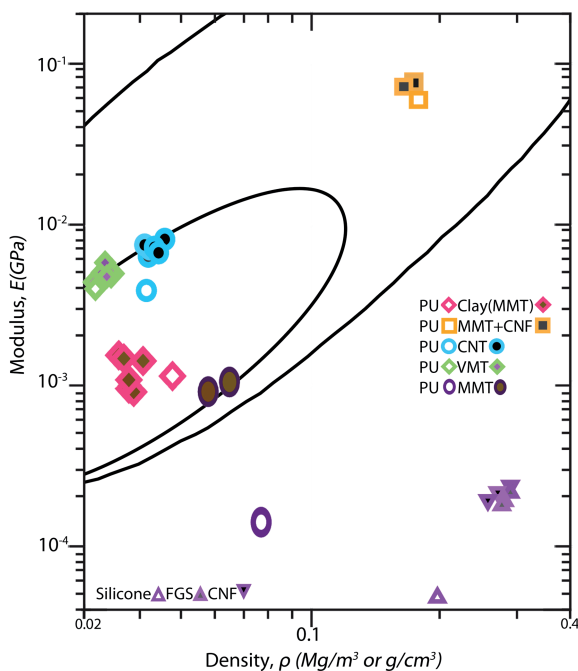


Figure 6. Modulus of reactively generated foams with various nanofillers.^{3,10,52–54} All examples are polyurethanes except the pink triangles which are silicone.^{6,25} The solid lines correspond to envelopes of closed and open-celled foams from Gibson and Ashby.⁶⁵

polyol used to prepare the foam. Using a polyol with a number-average MW of 540 g/mol gave a relatively soft PU (modulus 1.4×10^{-4} GPa), and addition of MMT clay raised this modulus significantly. These results are shown by the purple oval symbols in Figure 6. The polyol with a number-average MW of 300 g/mol gave a relatively rigid PU foam (modulus 0.19 GPa) and addition of clay was found to *reduce* the modulus of the foam. This latter series of PU foams are not included in Figure 6 because their densities were not cited in that paper.³ This example highlights the complexity of reactive foams: a modest difference in polyol MW – with no other changes in materials or processing – caused the nanofiller to increase modulus in one case and decrease it in the other.

Finally, Cao et al.³ (published in 2005) state that “the experimental results suggest that it is difficult to increase strength and modulus in rigid PU foams by adding nanoclay.” The later literature since 2005 broadly supports this statement: nanofillers can improve the strength and modulus of flexible foams much more than of rigid foams. One simple explanation for this may be rooted in the basic theory of reinforced composites which suggests the modulus of a matrix is increased much more if the ratio $\frac{E_{filler}}{E_{matrix}}$ is large. Thus, if a given filler is added to a soft elastomeric matrix, a very large improvement in modulus can be realized, whereas if the same filler is added to a rigid glassy matrix, a relatively smaller

improvement can be realized. Since the material comprising the cell walls of the foam is a nanofiller-reinforced composite, this suggests that nanofillers are likely to be more effective at modifying the properties of foams made from low-modulus polymers. Indeed, this is borne out by Figure 6: the greatest improvement in modulus appears for the flexible PU foam from Cao et al.³ and the silicone foams of Verdejo et al.^{6,25} – materials in which the nanofiller is added to a soft polymer.

Finally, we turn to discussing the potential mechanisms whereby nanofillers may improve the mechanical properties. Perhaps the simplest is equation (4) which suggests that the modulus of a foam is proportional to the modulus of the solid component of the foam. Even if the dependence on foam density is different,²¹ from what is predicted by equation (4), the basic idea is still valid: since nanofillers often improve the modulus of *unfoamed* polymers, a proportionate improvement in the foam modulus may be expected. Similar correlations have been developed for other mechanical properties,²⁷ and in most cases, any given foam property is proportional to the corresponding property of the solid material comprising the cell walls. Thus, it is of interest to compare the degree to which nanoparticles improve the mechanical properties of the foams versus those of the unfoamed polymer. Such comparisons can be done only infrequently using the published literature since many articles do not document the effect of nanofiller on the unfoamed polymer. A nice example which *does* provide data on both the foamed as well as unfoamed nanocomposites is Chen et al.²¹ The results from this paper are illustrated in Figure 7, which compares the modulus of foamed and unfoamed poly(methyl methacrylate) (PMMA) containing two different CNFs.²¹ For the foams without added nanofibers, the dependence on modulus on density does not follow equation (4); instead the modulus appears to decrease less sharply with density. Regardless, with the addition of F100 nanofibers,

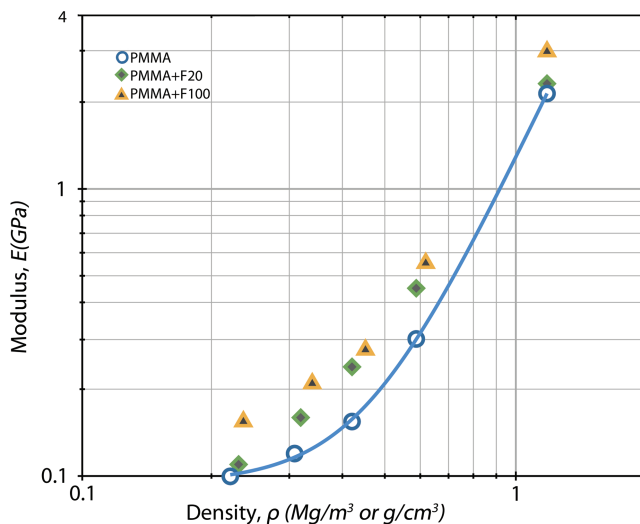


Figure 7. Modulus of PMMA foams containing two different carbon nanofibers.²¹

the general shape of the modulus–density curve is seen to remain the same but the curves move upwards by a factor that is roughly the same as the modulus increase for the unfoamed polymer. These results argue in favor of a very simple picture that the nanofiller affects E_{foam} and E_{solid} in exactly the same way: the foam is stiffer simply because the F100 nanofibers make the material of the cell walls stiffer.

We speculate that $E_{foam} \propto E_{solid}$ is not necessarily true, and more complex behavior may be possible. Indeed, for the sample containing F20 nanofibers in Figure 7, nanofiber addition seems to increase E_{foam} more than E_{solid} . If the filler is highly anisotropic, one possible reason for this may be filler orientation. The filler in the unfoamed polymer is typically unaligned, whereas upon foaming, the filler can orient parallel to the cell walls.^{8,42,47} In reinforced composites, filler alignment generally improves the modulus and strength along the alignment direction. Thus, high-aspect ratio nanoparticles might improve the modulus to a greater extent in a foam (due to well-oriented filler in the cell walls) than in the unfoamed polymer (in which the filler is isotropically oriented).

On the other hand, it is also possible for the filler particles to serve as cell-opening agents. While we have not found any example of this being true in thermoplastic foams, this has been documented in PU foams,^{48,49} and indeed nanofillers may be added to PU foams specifically for this purpose. Models of foam mechanics suggest that decreasing the open cell content reduces the modulus²⁷; thus, even particles that are good reinforcing agents in an *unfoamed* polymer may end up *reducing* the modulus once the polymer is foamed. In such cases, not just modulus changes, but many other large changes in mechanical behavior may be expected.

Cell size may also play a role. Frequently, the addition of nanoparticles increases the nucleation⁵⁰; thus, if samples are compared at the same foam density, a higher nucleation density also implies a significantly smaller cell size. While the models of Gibson and Ashby²⁷ predict that most mechanical properties are independent of cell size, in reality, some cell size dependence may be present. The available data do not allow a definitive conclusion on whether nanofillers affect the mechanical properties via their effect on the cell size.

Conclusion

In summary, the efficacy of nanofiller at improving the strength and modulus of polymer foams can only be judged after the effects of nanofiller on foam density are controlled for. However, preparing foams with and without filler at exactly the same density is difficult. We show that comparisons of filled and unfilled foams across a range of densities are a powerful method of judging whether nanofillers have reinforcing effects. The same comparisons can identify which nanofillers are most efficacious and at what loadings. Furthermore, nanofiller can affect foam mechanical properties in many ways, e.g., mechanical reinforcement of the matrix, alignment of filler in the foam walls, changes in the open cell content, etc. Identifying which of these mechanisms is active becomes possible once the effects of foam density are accounted for.

The chief conclusions of this review are that improvements in modulus or strength exceeding few 10% (holding foam density fixed) are uncommon for thermoplastic

foams, but more common for soft elastomeric foams often made by reactive foaming. Moreover, the efficacy of nanofillers depends on processing conditions and on the surface chemistry of filler. Finally, we note that several articles^{1,20,23,31,51} on the mechanical properties of nanofiller-containing foams were excluded from this review because density was not cited explicitly. However, density is perhaps the most important attribute of foams and ought to be quoted in most research on foamed plastics.

This review focuses only on the narrow issue of how nanofiller affects mechanical properties. Nanofiller can have numerous other beneficial effects: nucleating foam bubbles,^{47,51,52} decreasing the cell size,^{53–55} acting as diffusion barriers,^{56–58} increasing electrical conductivity,^{59,60} stabilizing the foams through interfacial adsorption,⁶¹ stabilizing foam through reduced crystallinity,^{62,63} improving fire retardance,⁶⁴ reducing thermal conductivity,^{65,66} and increasing open cell content.⁴⁸ For some of these properties, the questions central to this review may be posed, e.g., how much does thermal conductivity reduce once samples are compared at the same foam density? Which nanofillers reduce thermal conductivity to the greatest extent once foam density variations are accounted for? What nanofiller loadings are optimal? Addressing these questions will promote the optimal use of nanofillers in polymer foams.

Conflict of interest

None declared.

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Table 1. Summary of literature on foams of filled polymers.

Acronyms used in the table		Fillers
Polymers		
ABS	Acrylonitrile butadiene styrene	AC
EVA	Ethylene vinyl acetate	af
HDPE	High-density polyethylene	cf
LDPE	Low-density polyethylene	ChNw
PBS	Polybutylene succinate	ChP
PBT	Polybutylene terephthalate	CNF
PC	Polycarbonate	CNT
PEEK	Poly(ether ether ketone)	EG
PEI	Polyetherimide	FGS
PEN	Poly(ethylene 2,6-naphthalate)	gf
PET	Poly(ethylene terephthalate)	Gn
PF	phenolic foam	GNS
PG	Polyglycerol	hf
PLA	Poly(lactic acid)	MFC
PMMA	Poly(methyl methacrylate)	MMT
PP	Polypropylene	mS
PS	Polystyrene	MWNT
PU	polyurethane	nClay
PVOH	polyvinyl alcohol	nS
TS	Tapioca starch	SWNT
		activated carbon
		Aramid fibers
		Cellulose fibers
		Chitin nanowhiskers
		Chitin powder
		carbon nanofibers
		carbon nanotubes
		expanded graphite
		functionalized graphene sheet
		glass fibers
		graphene nanoplatelets
		graphene nanosheet
		Hemp fibers
		microfibrillated cellulose
		montmorillonite
		Microsilica
		multi-walled carbon nanotubes
		Nanoclay
		Nanosilica
		single-walled carbon nanotubes

(continued)

Table 1. Continued

Acronyms used in the table	
Polymers	Fillers
	T Talc
	VMT Vermiculite
Blending process	Foaming process
insP	BC batch foaming process
InMx	CM compression molding
d-a	Ex extrusion foaming
MS	ICM Improved compression molding
TSX	IMf injection-molding foaming
PwC	Ly lyophilization process
SvPr	Mf Molding foaming
UsD	Rf Reactive foaming
WmCm	SsEx single-screw extrusion foaming
Mechanical test	
3PB	
C	Three-point bending
DMA	Compressive
T	Dynamic mechanical analysis
	Tensile

(continued)

Table 1. Continued.

Polymer	Filler	Filler wt.%	Surface modification	Blending	Foaming	Mech. test	Notes	Ref.
EVA								
EVA	MMT	0 and 2.7	Several. See notes.	InMx	BC	T	The EVA used contains 18% vinyl acetate. Four MMT surface modifications were used: Na-MMT; octadecyl trimethyl ammonium chloride (DI831-MMT); dimethyl octadecyl hydroxy ethyl ammonium nitrate (1821-OH-MMT); and dioctadecyl dimethyl ammonium chloride (1821-MMT).	²⁶
Epoxy								
Epoxy	MMT	0, 0.5, 1, 1.5, 2, 2.5, 3 and 5	Dimethyl benzyl-hydrogenated tallow ammonium	PwC	Mf	C	The relative density of the foams was between 0.27 and 0.37. The compressive toughness of the foams increased with the amount of MMT in the polymer matrix.	²⁴
HDPE								
HDPE + HDPE-g-MA	MMT	0, 0.5, 1, 2	Dimethyl dehydrogenated tallow alkyl ammonium	TSX	BC	T	Foams had fairly high density (relative density 0.9–0.99). HDPE-MA at 15 wt% of total.	²⁸
LDPE								
LDPE + PE-g-MA	nS	0, 1, 3, 6, 9	Dimethyldichlorosiane	TSX	ICM, BC	C	Saiz-Arroyo et al. ²⁹ evaluate the change of the mechanical properties of the foam with the addition of nanosilica. Saiz-Arroyo et al. ¹¹ use the same samples but a different foaming process. PE-g-MA used at 13 wt% of the silica content.	^{11,29}

(continued)

Table 1. Continued

Polymer	Filler	Filler wt.%	Surface modification	Blending	Foaming	Mech. test	Notes	Ref.
LDPE + LDPE-g-MA	MMT	0, 1, 2, 3, 4, 5	Octadecyl ammonium	TSX	IMf	T	Influence of the compatibilizer (PE-g-MA) loading was examined, either at 1% MMT or at 2:1 PE-g-MA:MMT ratio. Mechanical properties of the foamed and unfoamed polymer blends were reported. Density of the foams was not included.	23
PBT								
PBT	MMT	0, 0.5, 1, 2, 3	Stearylbenzyl-dimethyl ammonium chloride	TSX	IMf	T	The cell size and cell density are only shown for one MMT type. Mechanical properties of foamed and unfoamed polymer are given. Density of the foams was not included. Also included is a study of wear resistance, melting temperature, and decomposition temperature.	20
PC/ABS								
PC/ABS	gs	0, 5, 10, 20	-	InMx	IMf	T, 3PB	Samples had a thick skin layer without cells, and core with a cellular structure with cells of few microns size. The mechanical properties are related to the thickness of the skin layer.	30
PEEK								
PEEK	CNF	0, 5, 10, 15	-	TSX	IMf	3PB, C, DMA	Foams had fairly high density (relative density ranging from 0.8 to 1). Two blowing agents used in Verdejo et al., ³¹ and thermal properties, melting temperature, crystallization temperature, and crystallinity are presented.	31,32

(continued)

Table 1. Continued

Polymer	Filler	Filler wt.%	Surface modification	Blending	Foaming	Mech. test	Notes	Ref.
PEI	MWNT	0, 0.5, 1, 1.5, 2, 2.5, 3	Carboxyl group (-COOH)	SvPr	BC	DMA	Focus is on the electrical properties of the PEI/MWNT nanocomposite foams. DMA of the foamed and unfoamed nanocomposites is given. Density of the individual foams was not included but there are references of the average value for all the composite foams for the two foaming processes used.	34.
PEN	EG	0, 0.1, 0.5, 1, 2.5	-	TSX	BC	3PB, C	The mechanical properties of the unfoamed material were evaluated by three-point bending, whereas the foams were evaluated in compression. The crystallinity of the polymer was reduced in the foams, and also reduced with the increasing graphite content.	34.
PET	MMT	0, 1, 3	Dimethyl benzyl-hydrogenated tallow ammonium.	TSX	BC	DMA	Pyromellitic dianhydride (PMDA 0, 0.25, 0.35% loading) was used as a chain extender to increase the molecular weight of the PET/organoclay nanocomposites. The mechanical properties were evaluated only for the unfoamed samples.	35.

(continued)

Table 1. Continued

Polymer	Filler	Filler wt.%	Surface modification	Blending	Foaming	Mech. test	Notes	Ref.
phenolic foam	af, gf	0, 1, 2, 3, 5	-	d-a	Mf	C	Desai et al. ³⁴ , include glass fibers only. Desai et al. ³² combine glass and aramid fibers simultaneously within the same samples. Mechanical properties compared against models.	^{34,32}
PLA	MFC	0, 1, 5	-	WmCm, TSX	BC	C	Foams with the same composition were produced with different densities. The addition of water during processing hydrolyzed part of the polymer.	³⁹
PLA + PLA-g-MA	ChP, ChNw	0, 1, 2, 5	-	TSX	BC	T	PLA-g-MA used at 2 wt%. The filler and polymer are both biodegradable. The mechanical properties were only evaluated in the unfoamed samples.	³⁹
PLA/PBS	MMT	0, 3	Methyl, bis hydroxyethyl, octadecyl ammonium	TSX	SsEx	T	Only evaluated the mechanical and rheological properties of the blends in the unfoamed samples.	⁴⁹
PLA/TS	MMT	0, 1, 3, 5, 7	Dimethyl benzyl-hydrogenated tallow ammonium.	TSX	Ex	C	The content of PLA is only 10%, the main component of the foams is Tapioca starch.	⁴⁴
PMMA	MWNT	0, 1	HNO ₃	SvPr	BC	C	Foams with the same composition were produced with different densities.	²¹
PMMA	MMT	0, 0.5, 1, 2	Dimethyl dehydrogenated tallow alkyl ammonium	SvPr, TSX	BC	T	Foams with the same composition were produced with different densities.	⁴

(continued)

Table 1. Continued

Polymer	Filler	Filler wt.%	Surface modification	Blending	Foaming	Mech. test	Notes	Ref.
PMMA	MWNT	0, 0.5, 1	HNO ₃	SvPr	BC	T	The blends produced by twin-screw extrusion (TSX) gave poorer mechanical properties than solvent co-precipitation (SvPr). Mechanical properties of foamed and unfoamed materials are given. This paper compares the mechanical behavior of foams with functionalized vs. non-functionalized nanotubes. Foam densities are not cited.	43
PP	cf, MMT, CNF	cf (20), PATF (10, 20, 25), MMT(5), CNF(5,10,20)	cf(-), PATF(cf + sodium hydroxide), MMT(methyl, Bis hydroxyethyl, octadecyl ammonium), CNF(-)	TSX	CM (MMT, CNF), BC (MMT, UTF, PATF, CNF)	CM (MMT, DMA)	Three cellulose fiber nanocomposites were compared with MMT or CNF nanocomposites.	43
PP + PP-g-MA	hf	10, 20, 30	-	InMx	CM	3PB	PP-g-MA at 2 wt% loading. The cellular structure of the core and the thickness of the skin were examined.	44
PP	Gn, CNF	0, 2.5, 5	-	InMx	CM, BC	DMA	Two processes, compression molding, and batch foaming were compared.	22
PP	MMT	5	-	TSX	CM	C	Mechanical properties of the foams without filler were not reported. Chief focus was on study of the cellular structure by X-ray microtomography.	45

(continued)

Table 1. Continued

Polymer	Filler	Filler wt.%	Surface modification	Blending	Foaming	Mech. test	Notes	Ref.
PP + PP-g-MA	MMT	0, 2, 4, 7.5	Stearyl ammonium chloride	TSX	BC	C	0.2% PP-g-MA used. Clay platelets shown to be aligned within cell walls.	⁴⁶
PP	CNF	0, 5, 10, 20	-	InMx	CM	DMA	The amount of filler was large (20 wt%). Cell size reduced with increase in filler content. Thermal and electrical properties were also reported.	⁴⁷
PS	CNF	0, 1, 5	-	TSX, SvPr	Ex, BC	T, C	Tensile for extruded foams and compressive for the foams produced by batch process with CO ₂ . The foams produced by extrusion had better mechanical properties, comparable to the unfoamed PS.	⁸
PS	CNF, AC, T	0, 1	-	TSX	Ex	C	Complete study of foam thermal conductivity was included.	⁴⁸
PS	MMT, T	0, 0.5, 2.5, 5, 7.5, 10	Dimethyl dehydrogenated tallow alkyl ammonium (Cloisite 20 A). And 2-methacryloyloxyethyl hexadecyl-dimethyl ammonium bromide	TSX, insP	Ex	T	Mechanical properties reported only at 5% filler loading for two surface modifications. Rheology and combustion tests were reported.	²
PS	MMT	0, 0.25, 0.5, 1, 2, 3	Stearylbenzyl-dimethyl ammonium chloride	TSX	IMf	T	The paper compares tensile strength, impact strength, and wear resistance. The relative density of the samples was around 0.9.	¹⁹

(continued)

Table I. Continued

Polymer	Filler	Filler wt.%	Surface modification	Blending	Foaming	Mech. test	Notes	Ref.
PS	MMT	0, 1, 3, 5	Bis(hydrogenated tallow alkyl)dimethylammonium bentonite	insP	BC	DMA, C	DMA is reported only for the unfoamed samples.	²⁴
PU	MWNT, MMT	MWNT (0, 0.05, 0.10, 0.15); MMT (0, 0.5, 1.5).	Bis(hydrogenated tallow alkyl)dimethylammonium bentonite	UsD	Rf	T		⁴⁹
PU	mS, nS, MMT	mS (0-30%), nS (0-20%), MMT(0-30%)	Some MMT formulations are Cloisite 10 A	UsD in polyol	Rf	3PB, C	High filler loadings (up to 30%) examined. Smaller particle sizes show greater increase in strength.	⁵⁴
PU	MWNT, FGS	0, 0.3	MWNT acid treated; graphene oxidized	UsD in polyol	Rf	DMA, C	Foam density was 53 kg/m ³ (no filler) and up to 90 kg/m ³ with filler. Over 10-fold increase in specific modulus was reported, with FGS giving greatest increase.	⁵⁴
PU	MMT	4, 8	-	UsD	Rf	C		⁵⁴
PU	MMT + CNTs	0, 0.25, 0.5, 1	-	MS	Rf	C	New kind of nanofiller was produced, a conjunction of MMT with carbon nanotubes.	¹⁰
PU	MMT	0, 5	(MMT-OH) methyl tallow bis-2-hydroxyethyl ammonium. (MMT-Tin) Dibutylidimethoxytin	MS	Rf	C	Two polyols were used. The MMT increased modulus in one case, but reduced in another case (see text).	³
PU	VMT	0, 2.2, 3.7, 5.7	-	UsD	Rf	C	The filler is introduced in the polyol or Isocyanate; the latter improved modulus and strength to a somewhat greater extent.	⁵⁴
PU	SWNT, MWNT, CNF	0, 0.5, 1	(-), HNO ₃	UsD	Rf	C	Nitric acid treatment improved modulus somewhat more than unmodified filler.	⁵⁴

(continued)

Table 1. Continued

Polymer	Filler	Filler wt.%	Surface modification	Blending	Foaming	Mech. test	Notes	Ref.
PU	MWNT	0, 0.2, 0.5, 1	66.6% HNO ₃ ; 33.3% H ₂ SO ₄	MS	Rf	C	Increasing mixing time increased modulus, strength, and density. However, the modulus-density curve and agreed well with a Gibson and Ashby type model regardless of mixing time.	54
PU	CNTs, GNS	0, 0.1, 0.2, 0.3	Silicone glycol copolymer Nlax L-580	UsD	Rf	C	Densities of individual samples were not listed, but all foams were reported to be around 200 kg/m ³	54
PU	MMT	0, 1, 2, 4, 8	Silicone glycol copolymer Nlax L-580	UsD	Rf	C, T	The maximum increase in the strength was obtained with 2% of MMT, the 4% and 8% show a lower increase in strength. The PU foams without MMT use 1% of water as blowing agent that is not used in the samples with MMT. Foam densities were not reported.	1
PU	cf/MMT	0-15 (MMT), 0-65(Esparto)	Dimethyl-distearyl ammonium chloride (MMT)	UsD	Rf	C;	Cellulose fibers (Esparto wool) were used as reinforcement fibers for PU foams, at the same time MMT nanoclays were used with the objective of developing new multi-scale rigid foams. The addition of MMT favored foaming and the formation of finer and homogeneous cellular structure.	54
PU	MMT	0-2.5	-,ditallow dimethylammonium salts, hydrogenated tallow alkylmethyl-(2-ethylhexyl)ammonium salts, dimethyl dehydrogenated tallow quaternary ammonium salts, methyl dehydrogenated tallow alkylammonium salts	UsD	Rf	C;	The effect of MMT and its surface modification on the open cells content is examined. The mechanical properties and density were measured for only a few samples.	54

(continued)

Table 1. Continued

Polymer	Filler	Filler wt.%	Surface modification	Blending	Foaming	Mech. test	Notes	Ref.
PU	Cf, MMT	0, 1	- , methyl dehydrogenated tallow quaternary ammonium salt, methyl tallow bis-2-hydroxyethyl, quaternary ammonium salt	UsD	Rf	C		⁶³
PU	MMT	0, 2		UsD	Rf	DMA	Only a few samples out of many were characterized mechanically.	⁶⁴
PU	MWNT	0, 0.1	Different surface modification, see on notes	UsD	Rf	C	The CNTs were introduced in a mixture of 25% HNO ₃ ; 75% H ₂ SO ₄ to introduce carboxyl groups on the surface; part of those nanotubes was mixed with ethylenediamine to change the carboxylic groups in to amide functionality. Also part of the nanotubes was introduced in a solution of Fe ₂ SO ₄ and H ₂ O ₂ to obtain a hydroxyl functionality. The density of the PU foams was 28 kg/m ³ and the density of the nanocomposite foams was between 29 kg/m ³ and 32 kg/m ³ , but the density of the foams was not reported by every type. Foams were not made using unmodified CNTs.	⁶⁴
PU	MMT	0, 3, 6, 9	Methyl-tallow-bis-2-hydroxyethyl ammonium(Cloisite 30B), -(Bentonite), -(Laponite RD)	UsD	Rf	C	The Cloisite 30B, the only MMT with surface modification, has the highest mechanical increase of all MMT used.	⁶⁴
PU/PG	MMT	0, 6	Methyl-tallow-bis-2-hydroxyethyl ammonium(Cloisite 30B), -(Bentonite), -(Laponite RD)	UsD	Rf	C	The soft segment was a mixture of a polyether glycol and a polyglycerol in various ratios (0, 35%, and 70% polyglycerol).	⁶⁴

(continued)

Table 1. Continued

Polymer	Filler	Filler wt.%	Surface modification	Blending	Foaming	Mech. test	Notes	Ref.
PVOH								
PVOH	MFC	0, 1, 3, 5	-	insP	Ly	C		41
Silicone								
Silicone	FGS, CNTs	CNTs:0, 0.1, 0.5,1 FGS: 0, 0.1, 0.2, 0.25	(FGS) nitric acid; potas- sium chlorate. (CNTs)-	UsD	Rf	C	Modulus increased by few hun- dred percent with the addition of 1% CNT or 0.25% graphene with less than 40% increase in foam density. Sound absorption of the foams was also evaluated.	6,25

Items in bold indicate that the results are summarized in individual datasheets in the Online Supplementary Information.