EFFECT OF THE FILLER SHAPE ON THE PROPERTIES OF RIGID POLYURETHANE FOAM

V. Yakushin, L. Belkova, I. Sevastyanova

Latvian State Institute of Wood Chemistry, Dzerbenes 27, LV-1006, Riga
yakushin@edi.lv

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Abstract
The effect of filler shape and volume content on the properties of low-density rigid polyurethane foams was investigated. Mechanical properties of foams filled with milled carbon fibers of average length 100 and 60 µm and glass microspheres with average diameter 65 µm were compared. An increase of characteristics in compression in the foam rise direction with increasing of filler content was noticed. Critical content of fillers above which the appropriate mechanical properties of filled foams began to decrease, was found. The order of distribution of different type of filler in the elements of polyurethane foam cellular structure was studied.

1 Introduction
Various types of fillers are commonly used to improve properties of foamed polymers. Among them nanoparticles, attract particular interest [1, 2]. Despite traditional fibrous and disperse fillers [3] nowadays seems fell by the wayside, they still remain in use and are attractive for researchers. New modifications of already known fillers, as well as materials, never used before as filler, come into use. In particular, now rigid polyurethane foams often fill with natural fibrous materials with different grinding degree [4, 5]. Despite of wide variety of new types of fillers, general questions of theory and practice of filled foams remain the same: when use of filler of certain dimension and shape gives expected effect and when not.

The reinforcing mechanism of the filled polymeric foams depends, first, on the filler dimensions. Most commonly, dimensions of the filler (e.g. chopped fibers) significantly exceed cell dimensions. In such cases the fibers, coated with polymer in effect set up additional composite strands, running through the cellular structure of foam. At that adjacent cells grow in direct contact with such strands. Thus, the dimensions of cells adjacent to the fibers can vary locally depending on amount of heat absorbed by the filler.

Structural models, proposed for such type of filled polymeric foams and numerous experimental works [6–8], evidenced that successful result can be achieved with fiber length exceeding certain critical value. The critical length of the fibers in its turn is function of the foam density. Besides, successful results can be achieved only if the fiber content does not exceed maximal allowable amount, which is a function of fiber length [3].

The other way of polymeric foams reinforcement consists in use of very short (milled) fibers or dispersed particles, which directly strengthen elements of cellular structure, being entirely
distributed in cells’ struts, nodes or walls. However, few experimental works consider such kind of fillers. Particularly, it was shown in work [9], that loading milled glass fibers of various lengths in rigid polyurethane foam cause significant increase of their strength and modulus of elasticity. At that, the shorter are fibers the bigger is strengthening effect. Yet, if the polymeric foam density is less than 80-100 kg/m³ the effect of such filler loading can be also negative.

Use of such particular dispersed filler as hollow microspheres, is also effective in polymeric foams of medium and high density. Strengthening effect of microspheres increases with polymeric foam density [10–12]. However, as with other type of fillers, use of microspheres in low-density rigid polyurethane foams by no means always give successful results.

It is known, that cellular structure of low-density rigid polyurethane foams composed of struts (ribs), nodes and walls of cells shaped as polyhedrons. Dimensions of listed structural elements are quite small. Filler can cause various structural defects of foamed polymer cellular structure and corresponding decrease of mechanical properties, if dimensions of filler particles are bigger then dimensions of cells’ struts and nodes.

The other important influence is quality of filler dispersion in the foamed polymer. Critical content of filler, above which used technology cannot completely disperse all filler in polymer matrix as separated particles, is typical for all types of filled materials. Upon that, remaining or newly formed particle aggregates cause, as a rule, decrease of mechanical properties of polymeric foams.

The influence of shape and content of filler (milled fibers and glass microspheres), which dimensions comparable with that of cellular structure elements, on mechanical properties of low-density rigid polyurethane foam was examined in the present work. The influence of mentioned factors on cellular structure and filler distribution in structural elements of rigid polyurethane foams was also evaluated for various foam densities.

2 Materials and testing methods

Milled carbon fibers Tenax®-A HT M100 with average length 100 (50–150) and 60 (40–70) µm and hollow glass microspheres of 3M Scotchlite™ with average diameter 65 (15–125) µm was used as fillers. Microspheres true density was 125 kg/m³ (type K1). Carbon fibers diameter was 7 µm and density 1780 kg/m³.

Rigid polyurethane [13], obtained from mixture of polyether and polyester of Elastogran Group with total OH value 597 mg KOH/g and polyisocyanate Voratec SD 100 with NCO content 31.5% and functionality 2.7 of Dow Chemical was used as base matrix material to prepare filled polymeric foams. Filled polyurethane foams samples were prepared by hand mixing method. Initially the selected filler was loaded into a polyols mixture containing also catalysts and a surfactant. Then after careful stirring, the filler suspension in polyol was deaerated to remove all air bubbles. Further the suspension with partly settled fibers (floated microspheres) was repeatedly stirred and then foamed, adding calculated amount of a foaming agent [Solkane 365/227 (87:13)] and polyisocyanate. Quantity of foaming agent varied to get filled and neat polyurethane foams with various densities. The polyurethane composition was stirred in IKA RW20.n laboratory mixer at stirrer rotational speed 2000 rpm. Finally mixed polyurethane composition was poured into open 250×250 mm forms.

Loading of filler substantially increase viscosity of polyol mixture. Thus, the maximal viscosity of polyol, at which qualitative mixing of polyurethane composition still was possible, determined maximal amount of filler to be loaded. Maximal volume content for milled fibers was 8.4% of total amount of polyurethane components, without foaming agent.
Maximal volume content for glass microspheres was 34%. Hereinafter content of filler if not otherwise specified always valued in volume percents.

The quantity of used catalyst was minimized for maximal prolongation of stirring time (up to 10–12 s) and delay of cream time. Time of stirring is very important factor determining quality of filler dispersing in the composition. Delay of cream time specifies time, when air bubbles, captured during mixing could float on the mixture surface, thus not converting into structural defects of foamed polymer.

It is known, that with increase of filler content the quantity of urethane reaction heat, absorbed by the filler also rises [3], thus causing the increase of polyurethane foam density. To compensate such influence some additional quantity of foaming agent was loaded in compositions with high filler content. Besides that, correction of weighted portion of components allowed obtaining blocks of polyurethane foam of different densities with equal height, thus reducing eventual influence of cell oblongness in blocks of various thicknesses. Providing all mentioned actions ended in preparing of polyurethane foam blocks with slightly varying thicknesses (50 to 60 mm), at that the foam densities in each set of samples slightly deviated of desired values (54, 65, 80 and 90 kg/m$^3$).

Polyurethane foam testing on tension and compression was performed according to the basic requirements of ISO standards 1926:2009 and 844:2007. Testing samples were made following known procedure [13]. Strain rate in all tests was equal 10% min$^{-1}$. Compression tests were carried out in parallel ($z$) and perpendicular ($x$) to the foam rise direction, but tensile tests – only in perpendicular direction. All mechanical tests were performed on universal testing machine Zwick/Roell (500 N). Each experimental point is based on 6 tested samples. Sampling for the same type of testing was made from similar zones of the foam blocks core.

Closed cells volume content (ASTM D6226–10) was measured using gas pycnometer AccuPyc 1340 (Micrometrics Instrument Corporation). Cellular structure and filler distribution in the cellular structure elements were examined with optical microscope Leica 5500B and scanning electronic microscope Vega Tescan 5136MM.

3 Materials and testing methods

3.1 Properties of filled polyurethane foams

The technology used for filled polyurethane foams preparation allowed obtaining foam blocks with homogeneous structure and uniform distribution of filler in the foam volume. In particular, coefficient of variation for most of determined properties was in the limits of 5–10%.

Certain defects were found in cross-sections of the polyurethane foam blocks with high filler content. It was small air bubbles, caught during polyurethane component stirring and not floated on the surface of very viscose polyurethane composition before foam rising process starts.

Densities of polyurethane foams in various lots of blocks slightly differed despite of provided technological corrections. For this reason, approximating relations between polyurethane foam properties and density were obtained for each filler contents. Similar relations were also obtained for neat polyurethane foam [13].

Properties of filled foams were compared with properties of neat foams of the same density. In cases, where the real foam density slightly differed of desired value, characteristics to be compared were corrected using respective approximating curves. It should be noted, that characteristics of studied polyurethane foams at compression in examined range of densities quite precisely approximated with linear functions. Tensile properties of polyurethane foams...
approximated with sufficient precision by second order polynomial. In most cases, the coefficient of determination $R^2$ was within the limits of 0.95–0.98.

The results of comparison presented in relative units as the ratio between characteristics of filled and neat foams. Analysis of the obtained experimental results revealed the following tendencies.

As would be expected, 100 µm long milled fibers proved to be the most effective filler for rigid polyurethane foam properties at compression in the foam rise direction. Loading of 3% of 100 µm long fibers (CF 100) in 90 kg/m$^3$ foam caused increase of modulus of elasticity at compression ($E_z$) by 30% (Fig. 1). At that, $E_z$ of foam filled with 60 µm long fibers (CF 60) increased only by 20%. While filling of the polyurethane foam with 9% of glass microspheres (GM K1) caused increase of $E_z$ merely by 12%.

![Figure 1. Modulus $E_z$ and $E_x$ (on the right) at compression of 90 kg/m$^3$ foam vs. filler content.](image)

Maximal increase of compressive strength by 20% in the foam rise direction ($\sigma_z$) was also found in the foams, filled with 100 µm long fibers (Fig. 2). In case of two other fillers, increase of $\sigma_z$ was much the same: by 12% with 60 µm long fibers and by 10% with 65 µm microspheres. Contrary to $E_z$, strength of filled foams decreased at milled fiber content exceeding 3% for both fiber length, and at microspheres content exceeding 9%.

![Figure 2. Compressive strength $\sigma_z$ and $\sigma_x$ (on the right) of 90 kg/m$^3$ foam vs. filler content.](image)

Somewhat different behavior was observed for polyurethane foam characteristics at compression in perpendicular direction. Modulus of elasticity ($E_x$) and strength at compression ($\sigma_x$) increased in a greater degree in foams, filled with short fibers (60 µm). However, increase of $E_x$ by 12% and $\sigma_x$ by 7% was notably fewer then corresponding increase of the same characteristics in parallel direction (Fig. 1, 2). Changes in $E_x$ of foams filled as
with 100 µm long fibers as well as with microspheres was less than of foams filled with 60 µm long fibers. Strength $\sigma_z$ decreased at loading more, than 5% of milled carbon fibers, or more than 16% of glass microspheres. Strength $\sigma_z$ of filled foams became less than the strength of neat polyurethane foam in the case of 100 µm long fibers and glass microspheres.

As far as the foam density decrease, use of filler for enhancing of compressive properties in foam rise direction gradually became less effective. Thus, $E_z$ of rigid 53 kg/m$^3$ polyurethane foam (Fig. 3) after loading of used fillers increase respectively by 18, 10 and 7%. At that, $\sigma_z$ of these foams after filling with fibers and microspheres decreased and became inferior of the neat polyurethane foam characteristic (Fig. 4). It was found that the limiting density, when filled polyurethane foam has the same compressive strength in foam rise direction as neat foam is on the level of 70–80 kg/m$^3$.

In case of filling with microspheres, decrease of the foam density had insignificant influence on compressive properties in perpendicular direction. Completely different situation was found in case of filling with fibers. At loading of 3% of milled carbon 65 µm and 100 µm fibers in rigid polyurethane foam 53 kg/m$^3$ $E_x$ and $\sigma_x$ increased by 27% and 20% correspondingly. Both, strength and modulus of elasticity decreased at fiber contents exceeding 3% (Fig. 3, 4).

The influence of mentioned fillers on foam characteristics at tension in perpendicular direction was completely different. Modulus of elasticity at tension ($E_{tx}$) of 90 kg/m$^3$ filled polyurethane foam increased by 15–20%. In case of 53 kg/m$^3$ foams, slight rise of $E_{tx}$ was revealed only for fiber type fillers. Spherical filler had no practical influence on $E_{tx}$ of 53 kg/m$^3$ foam (Fig. 5).
Figure 5. Modulus of elasticity at tension of 90 and 53 kg/m$^3$ foams vs. filler content

![Graph showing modulus of elasticity vs filler content for 90 kg/m$^3$ and 53 kg/m$^3$ foams.]

Figure 6. Tensile strength ($\sigma_{tx}$) and elongation ($\varepsilon_{tx}$) (on the right) of 90 kg/m$^3$ foam vs. filler content.

Tensile strength of polyurethane foam in perpendicular direction ($\sigma_{tx}$) increased only by 5–7%, but only up to certain limit of filler content (Fig. 6). Higher content of filler – one exceeding 3% for fibrous and 16% for spherical fillers caused decrease of $\sigma_{tx}$ below the strength of analogous neat foams. Tensile strength of the 53 kg/m$^3$ foam decreased on using of all types of mentioned fillers.

The most significant fact was that elongation at break ($\varepsilon_{tx}$) of filled polyurethane foams in all cases was lower than elongation of neat foam (Fig. 6). At that, bigger filler content and lower density caused stronger decrease of elongation. Elongation $\varepsilon_{tx}$ decrease occurred in a greater degree in foams, filled with milled carbon fibers.

3.2 Cellular structure of filled polyurethane foams

Provided studies has shown that the volume content of open cells in polyurethane foams increased with growing of filler content, however filled foams retain in general closed cell structure. Thus, neat polyurethane foam had open cell volume content about 3–4%. At loading of short 60 \(\mu\)m fibers, the content of open cells increased up to 5–7%. However, using longer fibers of 100 \(\mu\)m the content of open cells reached 7-10%. Microspheres content higher than 15% caused increase of open cells content up to 6–8%. The number of defects like air bubbles and open cells at the same filler content increased with decrease of the foam density.

The average cell dimensions in longitudinal and in transverse directions of the foam with given density demonstrated modest change at loading of relatively small amount of filler ($\leq$5 % for milled fibers and $\leq$9 % for microspheres), also due to the recipe adjustments allowed to keep almost the same density of the foams. Further increase of the filler content caused...
decrease of average size of the cells. With that also increased dimensional inhomogeneity of the cells. Besides, the cellular structure of the foams comprised, besides small air bubbles mentioned before, also big merged cells. However, far more important was the filler distribution in the elements of cellular structure. At low filler content (≤3% for the fibers and ≤9% for the microspheres), it was possible to disperse the filler particles quite evenly in polymer matrix. Completely separated filler particles (fibers or microspheres) were distributed in the cell structural elements such as struts and nodes. At that, the particle location depends on the particle shape and dimensions. Individual microspheres as a rule were located in the cells’ nodes. Only the smallest microspheres of 10-20 µm diameters could be found in the struts, because their dimensions were comparable with the struts thickness of the foams of the given density. Some of the biggest microspheres with diameter 85 µm and more formed the node by themselves where several cells contacted together.

As concerned milled fibers, it was impossible to observe them on the SEM pictures because practically they were completely immersed in the cells’ struts and nodes. It was possible to detect the main features of milled fibers distribution in the polymer cellular matrix by means of transmitted light optical microscopy. More long separated fibers at moderate filler content up to ≤ 3% mostly located in the struts, oriented in foam rise direction. Few long fibers were also found outside the struts. Shorter fibers were found in the struts oriented in other directions. Several short fibers were found as well in the cells’ nodes. Their orientation in the nodes was arbitrary.

Such different modes of long and short fiber distribution in parallel and other directions can explain experimental observation that long fibers (100 µm) enhance the strength of polymer cellular structure in a greater degree in parallel (foam rise) direction. Short fibers (60 µm) had better strengthening effect on cellular matrix in perpendicular direction.

At low filler content separated fibers located only in some struts and nodes. Many struts and nodes of cellular matrix did not have filler particles at all, as it was also noted in the work [11]. However, increase of filler content was accompanied not only by increase of relative number of reinforced struts and nodes. It was not possible to separate all fibers at milled fibers content more then 3% and some part of them remain embedded in cellular matrix as fiber bundles. For this reason significant increase of fiber content did not cause any further increase of compressive properties but, quite the opposite, caused decrease of compressive strength.

Similar pattern with filler particles aggregates was also observed in the foams filled with microspheres, when the filler content exceeds 9%. Pattern of microspheres distribution and character of structural defects remained quite the same in the foams with lower density. At that, more light foams of 52-55 kg/m³, filled with milled carbon fibers, revealed one essential particularity: a number of long fibers were arranged not in the foam rise, but in transversal direction, among others also out of struts. At higher volume content, the fiber bundles disposed mainly in the cells’ nodes. Much of the fibers in the bundles were also oriented preferably in the same transversal direction. These facts explain why compressive strength of the low-density foams filled with fibers increased in perpendicular direction in a greater degree than in the foam rise direction.

The mentioned effects of low-density polyurethane foams filling largely agree with the results described before in other works, for example [10–12]. Nonetheless, it is possible to make important amendment to previously known facts. Generally, in the cited works mechanical properties of filled foams were investigated mainly in the foam rise direction. At that there was short of results regarding filled foam properties in perpendicular direction.
4 Conclusions
Loading of fillers cause increase of compressive properties of rigid polyurethane foams. Properties of foams with density 80–90 kg/m$^3$ increased more significantly in the foam rise direction than in perpendicular direction. Alternatively, 53 kg/m$^3$ foams filled with milled carbon fibers demonstrated bigger increase of compressive properties in perpendicular direction, comparing with properties in the foam rise direction.
The most significant growth of modulus of elasticity and compressive strength in the foam rise direction (30 % and 20% respectively) was found at loading of 100 $\mu$m long milled fibers in polyurethane foam with a density 90 kg/m$^3$.
Increase of the mentioned fillers content caused significant decrease of polyurethane foam tensile elongation. The less was polyurethane foam density the more decreased tensile elongation. Maximal reduction of tensile elongation was observed for polyurethane foams, filled with 100 $\mu$m long milled carbon fibers.
The critical volume content of the filler, over which the foam properties got worse, was 3% for milled fibers and 9% for microspheres.

References