New Applications for Foam Composites of Polyurethane and Recycled Rubber

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ABSTRACT: In Portugal, most end-of-life tires are recycled through a process involving a cryogenic grinding technology. The purpose of this work was to envisage new applications for recycling rubber from end-of-life tires. In this work, rubber was supported in a polyurethane matrix generating two new products of distinct characteristics and properties. The choice of these products was ruled by the requests of potential clients: (a) Floating trays to withstand the load of plants capable of cleansing polluted water from lagoons, ponds, or basins; (b) Compression-absorbing buoys to dampen the shocks and the compressive stresses between ships and docks. The polyurethane formulations developed herein were based on methylene diphenyl diisocyanate and a trifunctional polyol such that the final foam would be flexible. As the floating trays' density should be lower than the water density, the best formulation found comprised 150% of rubber, 4% of water (relative to the polyol mass), with an isocyanate index of 105% and a density of 89 kg m^{-3}. The foam that presented the optimal compression behavior to be applied in compression absorbing buoys, comprised 200% of rubber, 3% of water, with an isocyanate index of 105% and a density of 121 kg m^{-3}. In both cases, the composite foam materials obtained showed final properties compatible with the envisaged applications, pointing out that the implied methodology may be used in the future to recycle rubber from end-of-life tires. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2873–2881, 2013

INTRODUCTION

Recycling of End-of-Life Tires

It is estimated that 1 billion end-of-life tires (ELTs) are generated each year, and yet only 4 billions are currently in landfills and stockpiles worldwide.[1] ELTs represent a serious problem because of the large volumes occupied and also because rubber natural decomposition lasts for hundreds of years. Moreover, stockpiled ELTs may burn out easily for months emitting gases harmful to the environment, and public health. Even when ELTs are disposed off in landfills toxic gases may accumulate and explode.[2] Therefore, ELTs' disposal in an environmentally safe and productive manner is a high priority aim and plenty of initiatives have been launched worldwide to address it, supported by the government authorities, and the tires industry.[1] For instance, the European Directive 1999/31/EC (April 26, 1999) prohibits ELTs' disposal in landfills and obliges the Member States to properly manage ELTs' collection and treatment, for example, by the following strategies:[3]

i. Retreading: reconstructing an ELT to resume its use for its original purpose,
ii. Energy recovery: burning out ELTs instead of coal for energy production, yielding an equivalent power, though less expensive and polluting,
iii. Reuse: reuse of an ELT, which may still be used for its original purpose, or reuse of an ELT without any processing for other purposes,
iv. Recycling: processing ELTs for any purpose other than the original, especially as raw materials to incorporate into new products.

As for the reuse of ELTs for other purposes,[3] there is a wide variety of applications, in particular the reuse of whole tires.

Because of their structural strength, the whole ELTs can be used in civil engineering applications, for example, landfills, tunnels and retaining walls, permeable floors for roads, and drainage layers in platforms and warehouses. Tires may be used as barriers for collision, erosion, rainwater runoff, boats, piers and marshes protection, and as sound barriers between roadways and residences, as well. The rubber of old tires (without steel) can still be used to manufacture shoe soles, strips for sofas upholstery, rubber circles for trawling nets, bowls, and so on. Although such applications have little relevance at present, they are an emerging market with great growth potential.

As for the recycling of ELTs,[3] the whole or sliced ELTs are the raw materials to be processed and produce rubber pellets of several particles size, mainly by

i. a mechanical process that consists in crushing and grinding the tires, the steel and the textile being removed by magnetic separation and gravity, respectively. The crumb rubber is separated according to the rubber particles size by sieves of various mesh sizes;

ii. a cryogenic process in which liquid nitrogen and pneumatic hammers are respectively used to freeze and crack the rubber to fine granular rubber. The steel and the textile are separated from the rubber through magnetic separation and aspiration, respectively.

The crumb rubber is used for several applications replacing other construction materials, for example, in the manufacture of floors, in particular soccer fields, basketball courts, tartan tracks, playgrounds, synthetic turf, and so on. The finest granules may be incorporated in Rubber Modified Concrete and Rubber Modified Asphalt, the latter being used for the construction or repair of highways pavements, increasing the roads life span and substantially reducing the noise.[3]

The main drive for this work was the awareness and concern to recycle ELTs. In Portugal, Recipneu uses a cryogenic grinding technology to produce rubber granulates of various grading. The grading of the rubber granulate used in this work (particles size in the range of 0.18–0.60 mm) is not currently used in any production process, that is, it is envisaged as industrial garbage. This work aimed to assess the application of this rubber granulate in two useful products, namely floating trays and compression-absorbing buoys.

Composites of Polyurethane and Recycled Rubber

In the synthetic polymers area, the polyurethanes chemistry represents one of the main highlights. Although polyurethane is a very well-known product, the discovery of which occurred decades ago,[4,5] it is still under investigation because of its many distinct applications. Eight patents and three scientific works on composites of polyurethane and recycled rubber were found in the literature as follows, although none of them for the two applications aforementioned.

i. Desiccated rubber particles can be mixed with a polyol and an isocyanate to form a polyurethane precursor blend, which is substantially free of water or other blowing agent. Recycled rubber products may be easily em-

bedded into a polyurethane matrix to produce a material of high strength and wear resistance, which can be used in tires, shoes, or boots.[6]

ii. An aqueous dispersion of an anionic polyurethane pre-polymer (reaction product of a diisocyanate and a sulfonated polyester polyol, a hydroxyl carboxylic acid, and an aliphatic diol), blended with an acid reactive cross-linking agent or a polyisocyanate crosslinking agent shows adhesive properties. These adhesives may be used for various substrates (e.g., styrene-butadiene rubber), in shoes, fiberglass, and automotive applications. They have good water resistance and stability at low pH, long life span, and improved heat resistance.[7]

iii. The methodology COMBI-Highcycling uses widely ranging wastes as raw materials, for example, polyurethane foam, rubber, plastics fiber, mixtures, and so on, to make recycled plastic products, to housing resisting climatic extremes and natural disasters.[8]

iv. A composite board for re-roofing a roof deck can be produced using a polyurethane foam filled of rubber-tire vent, polyurethane scrap, and/or scrap rubber from recycled tires.[9]

v. A treated crumb rubber for producing recycled rubber products (e.g., resilient surfacing or mat) can be prepared from rubber particles coated with cured polyurethane resin (binder).[10]

vi. Shock-absorbing layers can be produced from a composite of granulated recycled rubber in a polyurethane resin, compacted and cured *in-situ* to form a flat pad upon which the synthetic carpet is laid. The effects of the binder content, bulk density, layer thickness, and rubber size distribution on the shock-pad energy restitution, impact behavior, and tensile strength were assessed.[11]

vii. The properties of a composite material, comprising recycled rubber from ELTs or rubber factory leftovers, and polyurethane (binder), were determined to assess its use in the manufacture of rubber mats and pads for antivibration tracks.[12]

viii. Flame-retarded thermoplastic polymers were prepared with recycled rubber tires, low-density polyethylene, ethylene vinyl acetate copolymer, and additives using waste polyurethane foam and ammonium polyphosphate. The new thermoplastic rubber showed excellent handling for the building construction.[13]

ix. High oil-absorbing polyurethane foam comprises isocyanate, polyol, catalyst, foam stabilizer, foaming agent, trapping agent, fire retardant, silicone rubber micropowder, and coupling agent. This foam is simple to prepare and it is used for absorbing and recycling oils and oil soluble organics from surface and groundwaters.[14]

x. A composite rubber fence may be prepared from multiple units of rubber, and a polyurethane film plated on each unit. The fence is durable, light-weight, and shows high pressure resistance, and elasticity.[15]

xi. A polyurethane and rubber composite material can also be prepared using toluene diisocyanate, polyether polyalcohol, recycled waste rubber powder, foaming agent, two

crosslinking agents, and a filling agent. This foam composite material has physical–mechanical properties similar to plastics properties, contains easily available and cheap raw materials, and ensures simple preparation.[16]

Floating Trays

The floating trays are objects capable of floating while holding certain plants, the roots of which carry out the treatment of polluted water from lagoons, ponds, or basins, for example, disposed wastewaters from the mining industry.

There are commercial floating trays comprising polypropylene tubes bonded to a quadrangular metal mesh in between them. Fours patents on floating devices for similar purposes but materials other than composites of polyurethane and recycled rubber were found in the literature:

i. A tray or basket placed inside a floating ring consisting of a polypropylene tube encapsulated in fibers, to grow water plants in ponds, plants to feed fishes, or water birds nests.[17]
ii. A floating ring from polyethylene for floating, and supporting drinks inside glasses, bottles, or cans in pools, lakes, or ponds, without the need of trays.[18]
iii. A floating tray from expanded polypropylene for supporting glasses or beverage containers in pools or lakes, to prevent beverage spills from flowing into the water.[19]
iv. A floating bed comprising plastic water bottles and polyvinyl chloride sleeves.[20]

In this work, flexible composite foams of polyurethane and recycled rubber were investigated to assess the application of this new material in the manufacture of floating trays. As the trays loaded with the plants must show a density smaller than 10^3 kg m^{-3} to float on water, and the plants generally weight nearly 20 kg m^{-2} of surface area, the effect of the components of the flexible foam composites on their density was studied.

Compression-Absorbing Buoys

Freighters and ships moored in docks require buoys capable of acting as cushions and dampen strong compressions and shocks in between them and against the docks. The inflatable buoys (Figure 1) consist of an outer layer of vulcanized rubber filled with air. Whenever such a buoy is subjected to a compressive stress, the air contained therein is compressed against the rubber, thus it may rip because of rubber wear and/or strong compressive stresses, its maintenance, or replacement being too expensive. Hence, compression absorbing buoys with foam padding (instead of air) have been developed. Their main advantages in comparison with the inflatable buoys are

i. the rubber outer layer is cheaper because it must not be so resistant to compression (pressure exerted by air compression > pressure exerted by an equivalent foam compression),
ii. a ripped foam buoy still acts as a floating dampener even if water soaks it somewhat, because the foam density is lower than the water density; anyway, in such a case the foam compressibility drops, thus its maintenance is highly recommended.

Figure 1. Inflatable damper buoy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Several companies have been commercially producing and selling compression-absorbing buoys and fenders for ports, docks, and ships. For instance, Marine Fenders International (MFI) has over 30 years of experience in the marine and polyurethane industries. Therefore, it may be ranked on the cutting edge of marine fendering and buoyancy technologies, and its advances in the strength and durability of polyurethane elastomers are outstanding. MFI manufactures the Ocean Cushion^{TM} foam-filled fender with chain and tire nets, which is the toughest netted foam-filled fender currently available. This fender comprises (i) an external chain, aircraft tires, and rubber tubing net, leading to its strength and resilience; (ii) a skin of thick nylon filament embedded into a polyurethane layer, making it extremely durable; and (iii) a closed cell foam core, which is energy absorbing and cannot be ruptured.[21] No scientific works were found on compression-absorbing buoys.

In this work, the ability of the flexible composite foams of polyurethane and rubber (prepared previously for the density measurements of potential floating trays) to absorb compressive stresses was studied, in order to assess its application in the manufacture of compression-absorbing buoys. It is well-known that the mechanical properties of composite polyurethane blends are strongly affected by the nature and amount of fillers.[22]

EXPERIMENTAL

First, samples of composite polyurethane foam with granulated rubber were produced to investigate their subsequent application as floating trays and/or compression-absorbing buoys. The isocyanate index of these foams, defined as

$$\text{Isocyanate index } (\%) = \frac{-\text{NCO mass}}{-\text{OH mass}} \times 100$$
$$= \frac{-\text{NCO real mass}}{-\text{NCO theoretical mass}} \times 100$$

should be nearly 100% such that the foams are flexible. When too much water is added to a formulation, too much of gaseous CO_2 is formed by the reaction with the isocyanate group. In such a case, the bubbles of CO_2 in the froth may grow too

much, and if the polymer is not too viscous yet, these bubbles may rise through the foam, destroying its cellular structure at their passage and producing "chimneys" (vertical holes) in the foam. Therefore, the water content never exceeded 5% to prevent "chimneys" formation during the foam expansion.

An isocyanate index of 105% was set to account for the moisture on the polyol and other components, and the masses of all components used to synthesize the composite foam were calculated. The basic formulation consisted of 3% of water to produce CO_2 (expansion agent) by the reaction with the isocyanate, 30% of rubber with particles of grading within the range 0.18–0.60 mm, and an amount of MDI (methylene diphenyl diisocyanate, Lupranat M50, BASF) to yield an isocyanate index of 105%. To stabilize the foam formation, we used silicone oil Tegostab B8225 (Evonik) 0.6% as surfactant agent. DABCO (1,4-diazabicyclo[2,2,2] octane, 33LV, Air products) 0.086% and DBTL (dibutyltin dilaurate, T12, Air Products) 0.25% were used as amine and organotin catalysts, respectively. The amine catalyst is meant for the reaction of isocyanates with polyols and water, whereas the organotin catalyst is meant specifically for the condensation of isocyanates with polyols. The percentages reported throughout this work are relative to the mass of polyether polyol (F-5521, Repsol, 3000 Da) added, that is, they were calculated as: mass of additive (silicon oil, water, DABCO, DBTL, and rubber)/ mass of polyol × 100%. This is the standard procedure for reporting formulations of polyurethane foams.

All the formulation components, were weighted by a technical balance, and all of them but MDI were poured to a beaker, and stirred with a blade mixer for at least 1 min. Afterward, the mass of MDI required to get an isocyanate index of 105% was added, the components were mixed for 30 s, after which the liquid mixture was poured into a 10 L mould. The foam was allowed to freely rise and cure for at least one week before testing.

Floating Trays
The bulk apparent density was determined for each and every foam formulation obtained by varying the water and rubber contents (0.5%, 1%, 2%, 2.5%, 3%, 4%, and 5%, as for the water content, and 30%, 60%, 70%, 80%, 90%, 100%, 125%, 137.5%, 150%, and 200%, as for the rubber content), because these two components are mainly responsible for the bulk apparent density of the foams. For this determination, cylindrical samples with 45 mm of diameter were cut from each foam formulation, their geometrical volumes were calculated, and their masses were weighted by an analytical balance (AE240, Mettler), the bulk apparent density being the ratio of the mass by the volume of each cylinder. The uncertainty of repeated determinations was approximately ± 2.5 kg m^{-3}.[23]

The cream time is the time comprised between the end of the mixing and the start of the foam expansion, that is, the time for the liquid mixture to attain a viscosity large enough to become an emulsion (or cream). After the cream time elapses, the mixture should be kept still such that it may freely expand without external disturbances that would ruin the foam. The cream time corresponds to the maximum time for pouring the

Figure 2. Samples of polyurethane foams. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mixture into the moulds. A long cream time means a long time to distribute the liquid mixture into the mould and obtain a homogeneous expansion. For a short cream time, the mould filling is heterogeneous, producing a foam with heterogeneous expansion rates and densities. As the cream time is a relevant parameter for the homogenization of the foam expansion and distribution into the mould, this parameter was studied by varying the content of DABCO catalyst from 0.02% to 0.13%.

Compression-Absorbing Buoys
Compression tests were conducted on each and every sample of the polyurethane foams obtained for the study of the floating trays, to optimize them as compression-absorbing buoys. Parallelepiped samples of 5 cm × 5 cm × 2.5 cm were cut from each foam sample (Figure 2), and the compression tests were carried out by an equipment Ingstrom 5566 (Figures 3 and 4) using the standard method ASTM D3574-81.[24] Each sample was subjected to four identical consecutive compressions to check the data reproducibility. The uncertainty of the experimental determinations of the nominal compression stresses was below 1%. The Young's modulus corresponded to the slope of the elastic region in the experimental curves determined by this equipment.

RESULTS AND DISCUSSION
Floating Trays
Effect of the Water Content. Two main chemical reactions (gelation and expansion reactions) occur simultaneously during the polyurethane foam formation. The gelation reaction is the condensation of the isocyanate MDI with the polyol, that is, the reaction between —NCO and —OH groups to produce the urethane bond. The expansion reaction is the reaction between the water and an —NCO group to form gaseous CO_2 and an amine. Subsequently, the amine reacts with another —NCO group to form urea bonds. The balance between these two reactions is crucial to obtain stable foams. As the expansion and the gelation reactions occur simultaneously in the presence of water, the CO_2 produced is retained within the polyurethane foam, causing its expansion and reducing the foam apparent density.[25]

Figure 3. Equipment Ingstrom 5566. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
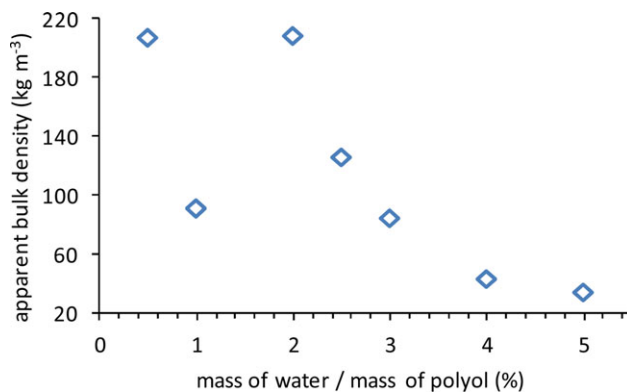

Figure 5. Effect of the water content on the foam apparent density (30% of rubber, 0.6% of Tegostab B8225, 0.086% of DABCO, and 0.25% DBTL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The polyether polyol used in this work produces a flexible polymer, because of its high molecular weight (3000 Da) and its few —OH groups per molecule (trifunctional polyol). In such circumstances, it is expected that most of the foam cells are open as the cells walls may easily rupture because of the inner pressure.[23]

To study the effect of the water content on the foam apparent density, we set a fixed composition, namely, 30% of rubber, 0.6% of Tegostab B8225, 0.086% of DABCO catalyst (1,4-diaza-bicyclo[2,2,2]octane), and 0.25% DBTL catalyst (dibutyltin dilaurate), whereas the water content was varied (0.5%, 1%, 2%, 2.5%, 3%, 4%, and 5%), and MDI content was also varied accordingly to obtain an isocyanate index of 105% in all formulations.

The results obtained are presented in Figure 5. The increase of the water content beyond 2% caused the foam density to decrease, mainly because of the retention of CO_2 produced inside the foam causing its expansion.

For water contents up to 2%, the foam density showed fluctuations because of the lack of water to promote the foam expansion. In such a case, the production of CO_2 and amines occurred in small amounts, thus the foam cells did not expand and the reticulation occurred in smaller degree, allowing the CO_2 produced throughout the cure to escape, causing the foam contraction. Hence, it was hard to obtain reproducible data for water contents up to 2%.

Effect of the Rubber Content. The influence of the rubber content on the foam apparent density is also significant. This effect was studied for fixed water contents of 3%, 4%, and 5%, and for each of these water contents, the rubber content was varied, namely, 30%, 60%, 70%, 80%, 90%, 100%, 125%, 137.5%, 150%, and 200%.

The results achieved are shown in Figure 6. In general, the increase of the rubber content led to the rise of the apparent bulk density, although some positive fluctuations were noticed. For the water content of 3%, sharp fluctuations occurred between the rubber contents of 80% and 150%. For the water
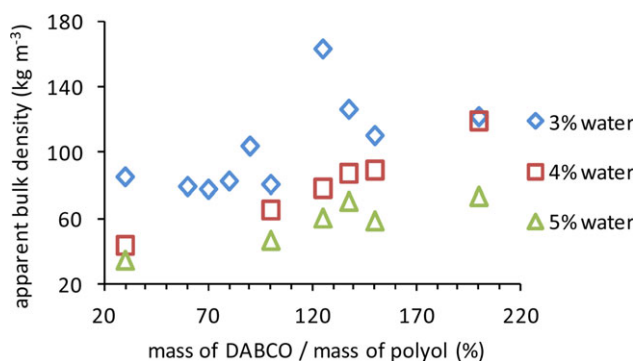
Figure 4. Sample of polyurethane foam under compression stress. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. Effect of the rubber and water contents on the foam apparent density (0.6% of Tegostab B8225, 0.086% of DABCO and 0.25% DBTL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. Effect of DABCO and water contents on the cream time (30% of rubber, 0.6% of Tegostab B8225, and 0.25% DBTL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

content of 4%, no significant fluctuations were observed, whereas for the water content of 5%, smooth fluctuations occurred between the rubber contents of 125% and 150%.

These fluctuations imply that the rubber content is responsible for two opposite effects. In general, the increase of the rubber content raises the surface tension of the open cells, causing their partial collapse and/or the formation of "chimneys," both phenomena promoting the release of CO_2, and in turn the increase of the foam apparent density. For the foams with 3% of water, the effect of the rubber content was most critical. In the range of rubber content 90–137.5%, the foams exhibited a highly unstable behavior because of the partial collapse of the cellular structure. However, beyond a rubber content of 150%, the foams seemed to exhibit a more stable behavior without the partial collapse of the foam structure, probably because of an increase of the mechanical stability of the froth of the polymer blend (polyurethane and rubber). This might explain the decrease of the foams apparent density with 137.5% and 150% of rubber content.

The porosity (open cells volume/foam volume) of the foams depicted in Figure 6 is higher than 96%, based on data of a similar formulation with polyether polyol, which produced foams with many open cells and a flexible cellular structure.[23] In that work, the effect of the water content on the open cells volume and the foams' cellular structure was studied. The porosity revealed to be inadequate to distinguish foams with water contents higher than 3%, because the differences between the foams porosities were below the accuracy of the gas picnometry method ($\pm$0.5%). Morever, as the foams have a rather irregular cell shape and size, their porosities cannot be determined by structural images because of large scattering.

Effect of DABCO Content. Bearing in mind the moulding process, it is crucial to investigate the effect of the catalyst content on the cream time. The cream time was determined by a stopwatch as the period between stopping the mixing and the beginning of the froth formation on the liquid mixture surface. To optimize the catalyst content, we intended that the foam expansion and cure did not start too quickly (before spreading the liquid mixture in the mould) nor too late (very slow cure). As
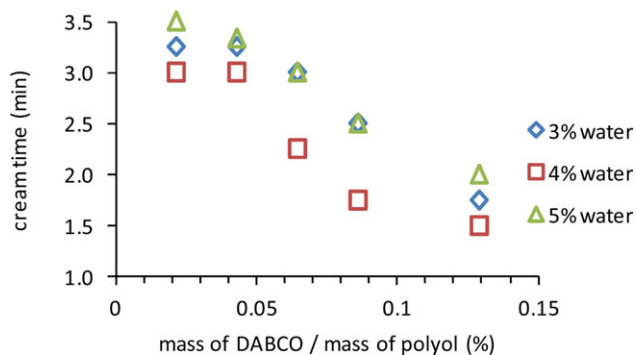
the tertiary amine-based catalysts catalyze both the expansion and the gelation reactions and the organometallic catalysts only catalyze the gelation, the most relevant catalyst for the cream time in this work was the tertiary amine based catalyst, that is, DABCO (1,4-diazabicyclo[2,2,2]octane). Meaning that the addition of more or less DABCO led to the anticipation or delay of the expansion, by shortening or enlarging the gelation reaction time, respectively.

Therefore, it was deemed necessary to study the effect of DABCO content between 0.02% and 0.13% on the cream time, for fixed water contents of 3%, 4%, and 5%, as displayed in Figure 7. In fact, the cream time was sensitive to slight variations of DABCO content, for example, a variation from 0.05% to 0.1% of DABCO content led to a cream time decrease of more than 1 min. Besides, observing the inflection of the cream time curves, we realized that the polymerization was autocatalytic, that is, some products acted as catalysts of the polymerization, as well.

The effect of DABCO content on the foam apparent density, for the water contents of 3%, 4%, and 5%, is depicted in Figure 8. It can be observed that the variation of DABCO content did not lead to a substantial variation of the foam apparent density, that is, most density variations were within the experimental error.
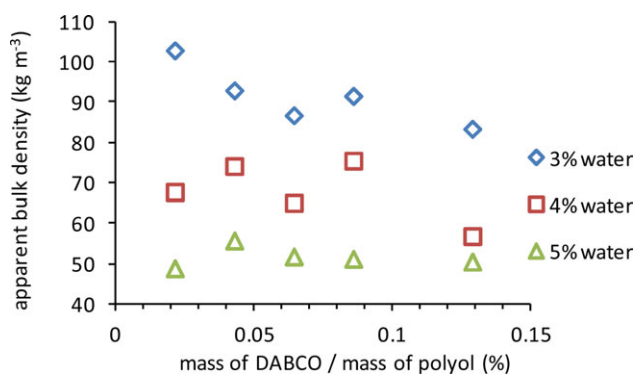

Figure 8. Effect of DABCO and water contents on the foam apparent density (30% of rubber, 0.6% of Tegostab B8225, and 0.25% DBTL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
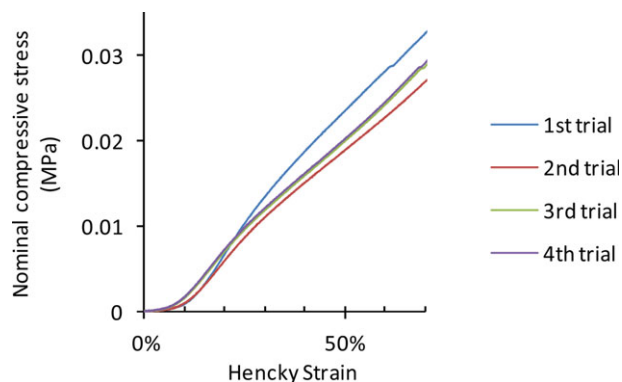
Figure 9. Compression tests of a foam (3% of water, 60% of rubber, 0.086% of DABCO, 0.26% of DBTL, and 0.60% of B8225). [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

The aim of section Floating Trays was to enlighten about the potential use of recycled rubber in a new material for the manufacture of floating trays. For such a purpose, the composite foam density must be low enough, to ensure the floatability of the trays supporting the grown plants load. On the basis of experimental data presented in the sections Effect of the Water Content to Effect of DABCO Content, we concluded that the most suitable foam composite of polyurethane and recycled rubber was the foam constituted by 150% of rubber, 4% of water, 0.6% of Tegostab B8225, 0.086% of DABCO catalyst, and 0.25% of DBTL catalyst. This foam presented a bulk apparent density of 89 kg m^{-3}.

Compression-Absorbing Buoys

All foam samples prepared in section Floating Trays were investigated to assess the technical feasibility of using them to fill compression-absorbing buoys. To determine the relationship between the compression exerted and the foam samples deformation, we carried out four compression tests for each and every foam sample. For the sake of simplicity, as the results of all foams were somewhat similar, only the data of some representative foams are presented.

According to Figure 9, a sample showed three distinct compression behaviors. For Hencky strains up to approximately 10%, the variation of the nominal compressive stress versus the Hencky strain was linear, that is, obeyed Hooke's law (elastic deformation). In this strain range, the foam deformation was because of air leakage across the open cells. For Hencky strains in the range 10–25%, the nominal compressive stress increased steeply, corresponding to the destruction of some open cells (plastic deformation). For Hencky strains above 25%, the foam displayed the typical rubber behavior, that is, the granulated rubber was compressed.

An interesting observation was the overlap of the 3rd and 4th compression plots, meaning that the 1st and 2nd compression trials promoted the destruction of some closed cells leading to the foam hysteresis,[a] that is, after three plastic deformations the

[a]The hysteresis is the tendency of a material not to retain its initial properties in the absence of the stimulus that changed them.
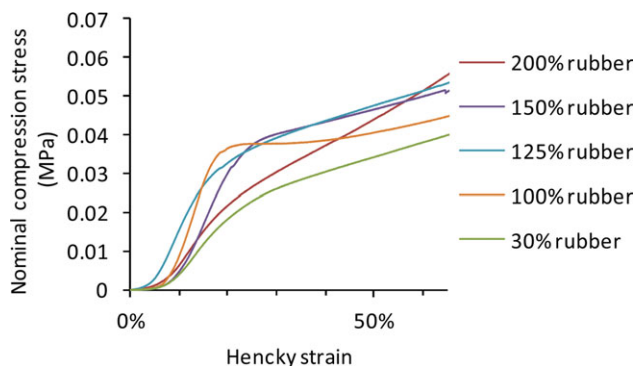

Figure 10. Compression tests for 5% of water content samples (0.086% of DABCO, 0.26% of DBTL, and 0.60% of B8225). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

foam could not exactly return to its original shape/size. Hence, only the results of the 4th trial are presented in Figures 10 and 11. Nevertheless, the gap between the results of the 1st and 4th compression trials was very small, for example, a gap of only 7% at 70% compression, and the gap was even lower at lower compressions, meaning that the variation of the foams cellular structure was not significant. In fact, we did not detect substantial changes in the foams after the compression tests with the naked eye.

To perform a more in-depth study, we conducted compression tests for samples with fixed contents of 0.086% of DABCO, 0.26% of DBTL, and 0.60% of B8225 and variable contents of rubber and water (30%, 100%, 125%, 150%, and 200% of rubber and 3%, 4%, and 5% of water). MDI content was varied accordingly to obtain an isocyanate index of 105%. The results of the compression tests for the three water contents were analogous, thus only the compression test for 5% of water is plotted in Figure 10.

For Hencky strains above 60%, the higher the rubber content was, the higher the compressive stress the sample withstood. Therefore, the foam that supported a larger nominal compressive stress (or larger load) was the foam composed by 200% of rubber.
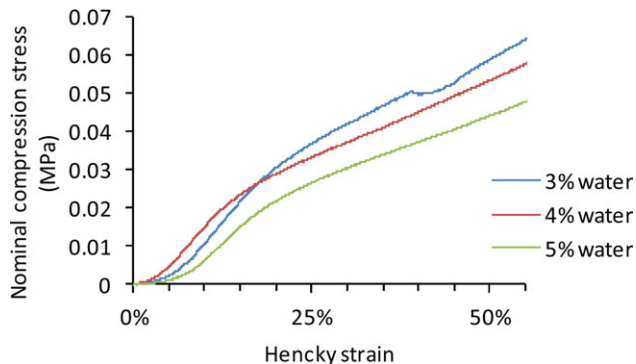

Figure 11. Compression tests of 200% rubber samples (0.086% of DABCO, 0.26% of DBTL, and 0.60% of B8225). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Young's Modulus for the Foam Samples (0.086% of DABCO, 0.26% of DBTL and 0.60% of B8225) Subjected to Compression Tests

	Water content (%)		
	3	4	5
Rubber content (%)	Young's modulus (MPa)		
100	0.016	0.056	0.077
125	0.018	0.059	0.085
150	0.020	0.065	0.106
200	0.039	0.070	0.112

For Hencky strains higher than nearly 25%, regardless of the water content and the plastic deformation, the compressive stress was apparently absorbed by the rubber granulates (Figures 10 and 11).

It was also noticed that for the highest water content (more expanded foam), the destruction of the open cells occurred at smaller Hencky strains and the hysteresis became more striking (Figure 11).

To identify the optimal formulation of the foam composites, the nominal compressive stresses of foams with 200% of rubber content and 3%, 4% and 5% of water content are depicted in Figure 11. The foam composed of 200% of rubber and 3% of water, subjected to a Hencky strain of 60%, supported the largest compressive stress, 0.07 MPa. Whether a compression-absorbing buoy with a surface area of 9 m^2 was subjected to a radial compression, it would withstand a load of 6.2×10^5 N, which is quite similar to the maximum load withstood by a commercial fender, 5.7×10^5 N[26] (deviation of 8%). However, the effect of the buoy shape (tires and chains) on the compressive stress was neglected in this work.

In sum, the optimal formulation for the foam composites of polyurethane and recycled rubber to fill compression-absorbing buoys was 3% of water, 200% of rubber, 0.6% of Tegostab B8225, 0.086% of DABCO catalyst, and 0.25% of DBTL catalyst. This foam presented an apparent density of 121 kg m^{-3}, ensuring the buoyancy of compression-absorbing buoys.

Another relevant data determined in this work was the Young's modulus, shown in Table I. Given that the Young's modulus measures the stiffness of an elastic material, its determination must be done in the range of elastic deformation, that is, where the relationship between the strain and the compressive stress is linear. According to Table I, the Young's modulus increased with the rubber content rise, because the rubber granulates enhanced the foam rigidity. Furthermore, the Young's modulus also increased with the water content rise because the foam bearing higher water content expanded more and had more urea groups in its structure, becoming more brittle and rigid.

CONCLUSION

The results of this work are very promising, as the manufacture of floating trays and compression-absorbing buoys using foam composites of polyurethane and recycled rubber seemed to be

technically feasible, although subsequent scale-up is demanding to optimize the production process.

As for the floating trays, the foam that showed the most adequate bulk apparent density, 89 kg m^{-3}, was the foam composed by 150% of rubber, 4% of water, 0.6% of Tegostab B8225, 0.086% of DABCO catalyst, 0.25% of DBTL catalyst, and an isocyanate index of 105%. Anyway, it will be fundamental to perform pilot/prototype assays, to guarantee the stability of the trays loaded with plants on a water surface.

Concerning the compression-absorbing buoys, the foam composites were optimized as for the ability of open cell foam to absorb compressive stresses. The compression tests on the foam samples pointed out that the foam capable of absorbing the highest compressive stress was composed of 200% of rubber, 3% of water, 0.6% of Tegostab B8225, 0.086% of DABCO catalyst, 0.25% of DBTL catalyst, an isocyanate index of 105%, and a density of 121 kg m^{-3}. Whether this foam was subjected to a deformation of 60%, it would absorb a compressive stress of 0.07 MPa, analogously to a commercial buoy.

It is worthwhile to remark that the rubber granulates are an abundant resource that may be used in the manufacture of floating trays and compression-absorbing buoys, decreasing our ecological footprint, that is, the rubber granulates cannot be ranked as industrial garbage any longer.

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