Research Article

Preparation and Properties of HGBTPU Composite Foam for Football Protection

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Football is a very dangerous sport. In order to reduce the injury of athletes, we must have corresponding protective articles, and the materials used are very important. Foam material has attracted the attention of all circles for its light weight, high strength, strong absorption impact load, and good heat insulation performance. However, the mechanical properties of foam materials will decrease with the decrease of density, which limits their application in sports, especially in some sports occasions, such as motorcycle competition, football, and other sports protection. In this paper, HGB/TPU foam materials are mainly studied. The material not only has good shock absorption performance but also has light weight and good mechanical properties. It can be used as protective equipment for football. In this paper, HGB/TPU composite foam materials were prepared by extrusion foaming method using TPU and HGB as raw materials. The effects of HGB surface modification, foaming agent content, and HGB content on the cellular structure and mechanical properties of composite foams were also investigated. The experimental results show that when the foaming method is extrusion foaming, the content of HGB is 3% and the content of foaming agent is 1.5%. It has better resistance to external forces, which helps to protect athletes from serious injuries.

1. Introduction

Foamed plastic is a widely used polymer material. Its polymer matrix contains a large number of bubbles, so it is also a composite material filled with gas. Compared with pure plastics, it has many excellent properties, such as light weight, high specific strength, strong ability to absorb impact load, good heat, and sound insulation performance, so it has been widely valued by all walks of life. Therefore, foam plastics have received more and more attention in various industries. There are many kinds of foam plastics, which can be used to make foam materials, such as polyurethane foam, epoxy foam, phenolic foam, polystyrene foam, and polypropylene foam. As an important polymer material, foams are widely used in transportation, building materials, automobiles, sporting goods, and other fields. Although foam plastics have been studied for quite a long time, their mechanical properties have been reduced due to the existence of foam. Therefore, they must be reinforced to adapt to special situations such as high strength, low density, and anti-interference.

Thermoplastic polyurethane (TPU) is an elastic polymer with high strength, high elasticity, high wear resistance, shock absorption, and chemical resistance. Its molecule is rich in carbamate group (NHCOO−), which is a good sport protective material. TPU has good elasticity, which is mainly due to the orderly arrangement of soft and hard segments in the molecular structure, rather than covalent crosslinking, so it can be reprocessed. Thermoplastic polyurethane material can be treated by foaming process, which can reduce its quality and improve its properties. Hollow glass bead (HGB) is a kind of inorganic nonmetallic material with light weight. It is a hollow spherical structure composed of N₂, CO₂, and other inert gases. It has high filling amount, low density, stress concentration, and low thermal conductivity. By adding thermoplastic polyurethane, it can prepare foamed materials with porous structure, which can improve the properties of foamed materials to a certain extent. It also reduces production costs. In this paper, HGBs are combined with thermoplastic polyurethane. The composite foamed plastic is prepared by foaming process. The prepared
material has excellent properties such as cushioning, damping, absorbing impact load, thermoplastic elastomer, high elasticity, high strength and low density and high compressive strength of HGBs. It can effectively absorb the energy caused by external pressure and impact for a long time and can be used for high-intensity sports protection. It can give consideration to both protection and comfort. First, through the surface modification of HGB, the HGB/TPU composite foam was prepared by extrusion foaming process. On this basis, this paper systematically analyzes and discusses various factors affecting the whole HGB/TPU system. It is hoped that it can provide a theoretical reference for the subsequent foaming molding process.

2. Related Work

In recent years, researchers from various countries have been studying the preparation and properties of composite foam materials. The microstructure and properties of the flexible composite foam were studied by Lee G. H. The thermal properties of flexible composite foam were measured by double probe method and compared with other insulating materials. The thermal conductivity and diffusivity coefficient of the flexible composite foam were calculated to be 0.053 W/m·K and 0.097 mm²/s, respectively. And it has low heat exudation, so it can be applied to the thermal insulation layer of environmental protection buildings [1]. Ashrith discussed the effect of wall thickness and cutting parameters on the drilling of glass microspheres/epoxy composite foam composites. As the thermal stability of the composite foam increases, increasing wall thickness will significantly reduce the surface roughness, cylindricity, and roundness error. He used gray relational analysis (GRA) to explore the optimal combination of process parameters to obtain the drilling quality with the best efficiency. Gray correlation analysis shows that the combination of higher particle wall thickness and feed rate, lower cutting speed, and bit diameter can produce better drilling quality [2]. In order to improve the controllability and mechanical properties of foamed aluminum foams, A356-based composite aluminum foams were prepared by Wang N. using improved stirring casting process. In the molten A356 alloy, the Al₂O₃ hollow spheres with diameter of 3–5 mm were added, and the composite foam aluminum was obtained by stirring and compaction. Compared with other conventional aluminum foams, the composite foamed aluminum has robust mechanical properties and flexible adjustment of cell size [3]. Kartal conducted an in-situ experimental study of the composite foam failure mechanism based on X-ray microcomputerized tomography. Under different compressive strain, he used X-ray microcomputerized tomography to scan hollow glass microsphere composite foam and obtain three-dimensional (3D) image of its internal microstructure. It is found that there is a certain relationship between the volume fraction of hollow glass microspheres and the compressive strain applied. [4] Liu H. developed a composite foam composed of silicone modified resin and hollow polymer microsphere for the application of composite cross arm. He tested the physical properties, electrical conductivity, and hydrolysis resistance of the composite foam. The test shows that the composite foam has excellent permeability and hydrolysis resistance. It can be used as an internal insulation material for the composite cross arm, and it is applied in the field of electrical insulation [5]. In order to improve the structure and properties of HGB composite and improve its dispersibility, Afolabi applied HGB composite to foam composites with improved degassing technology. He analyzed and studied foam composites by means of scanning electron microscope, transmission electron microscope, and density measurement. The analysis results show that the improved degassing technology can significantly reduce the porosity of composite foams [6]. Wu et al. discussed the preparation and mechanical properties of carbon fiber reinforced polyphase epoxy composite foam. He used CFR-HEMS, EP curing agent system, and hollow glass microsphere (HGMS) to prepare polyphase epoxy composite foam plastics (ESF) through the “compression molding method.” He studied the influence of CFR-HEMS and HGMS type and content accumulation volume fraction, wall thickness, and inner diameter on ESF energy in EP hardener system [7]. ESF with relatively good performance in the experiment can be used in 2673 m deep water and provide 490 kg/m³ buoyancy, which is helpful to prepare buoyancy materials in deep-sea exploration system and oil production system.

3. Thermoplastic Polyurethane and Hollow Glass Beads

3.1. Thermoplastic Polyurethane (TPU). Polyurethane is a polymer material containing carbamate groups (NH–COO–) in the molecular backbone. Its molecular main chain is composed of flexible segments (soft segments) below room temperature and rigid segments (hard segments) above room temperature. It has a wide variety of synthetic raw materials. It can select the composition and proportion of reaction raw materials according to the purpose of the product, so as to obtain the performance indexes of various materials. It has been widely used in plastics, elastomers, fibers, foams, paints, adhesives, artificial leather, and so on. It has become one of the most widely used polymer materials [8].

Among many polyurethane materials, thermoplastic polyurethane (TPU) is a kind of polyurethane with both plastic and rubber properties. It shows high elasticity at room temperature and plasticity of ordinary plastics at high temperature. It can be secondary treated by general thermoplastic process and can be recycled. It is an environmentally friendly polymer, which is the most promising polyurethane material [9, 10]. Thermoplastic polyurethane elastomer is prepared by catalytic polymerization with polymer diols, isocyanates, and chain extenders as raw materials. The reaction formula is as follows:

$$RNCO + R' – OH \rightarrow RNHCOOR'.$$  (1)

3.1.1. Polymer Diol. Polymer diols contain a reactive hydroxyl group at the end of their molecular chain, which is the basic raw material for the synthesis of polyurethane
elastic materials. Generally, diols can be divided into polyester and polyether according to their main chain structure. Polyester diol is a kind of high molecular diol, and its molecular structure contains a large number of ester groups (-COO-) [11]. Due to the large polarity of ester group, it is easy to combine with intermolecular hydrogen bond. It increases the force between polymer chains, so as to improve the strength, wear resistance, and oil resistance of products. However, its disadvantage is that it is easy to react with water, which reduces its hydrolysis stability [12]. Common polyester diols include polycarbonate diols and polycaprolactone diols. Polyether diols are polymer diols that contain a large number of ether bonds (-O-) in the main chain of molecules. It has more ether bonds on the molecular chain. Due to the large elasticity of its molecular chain, the products have excellent low temperature resistance and good processing ability. However, because there is no ester group on the macromolecular main chain, its mechanical properties are poor, but it has good hydrolysis stability. For example, the commonly used polytetramethylene ether glycol (PTMG) contains a large number of flexible ether bonds in the molecular main chain. The material not only has good elasticity and high toughness, but also has excellent mold resistance [13].

3.1.2. Diisocyanate. Diisocyanate is a part of the hard segment of TPU, and its stiffness has a great impact on the performance of the final product. At present, there are two kinds of isocyanates used most: aromatic isocyanates and aliphatic isocyanates [14, 15]. Both have their own advantages and disadvantages. Comparison of reaction activity: aromatic isocyanate > aliphatic isocyanate. Aromatic isocyanates are a kind of isocyanates whose molecular structure is benzene ring. The elastomer material has high strength because its molecular structure contains a rigid benzene ring. However, due to the existence of benzene ring, the optical stability of the product is very poor, and it is easy to turn yellow. The common aromatic diisocyanate is methyl diisocyanate (TDI) with molecular weight of 174.16 [16]. TDI has two isomers, 2,4-TDI and 2,6-TDI. The structure is shown in Figure 1.

It can be seen from the TDI structural formula that the chemical reaction activities of the two NCO groups in the molecular structure of 2,4-TDI are different. Due to the steric hindrance effect of adjacent methyl groups, the reaction activity of 2-nco group is lower than that of 4-nco group. The research shows that the reaction activity of 2-nco group is 2~3 times different from that of 4-nco group. In addition, TDI is a flammable substance with explosion risk, so more attention should be paid to safety during use [17, 18].

4,4-Diphenyldiisocyanate (MDI) has a molecular weight of 250.26. MDI has lower toxicity than TDI because of its high molecular weight and low volatility. However, when using MDI, we must pay attention to the storage problem. Since MDI will self-polymerize to form dimer at room temperature, it needs to be stored at low temperature. Generally, the storage temperature is below –5°C [19]. MDI structure is shown in Figure 2.

There are two NCO groups in the molecular structure of MDI, and its reaction activity is high. The molecular structure of MDI is a high-strength elastomer, and its molecular structure is symmetrical [20].

The prepared material has excellent resistance to UV yellowing because it contains aliphatic ring and isocyanate [21]. Isophorone diisocyanate (IPDI) is commonly used, and its structural formula is shown in Figure 3, including dicyclohexylmethane diisocyanate (hmdi) and 1,6-hexamethylene diisocyanate (HDI).

3.1.3. Chain Extender. Chain extender is a small molecular compound containing active hydrogen in the molecular structure, which can extend and expand the molecular chain and react with isocyanate to form the hard segment of TPU. The selection of chain extender directly affects the hard segment in TPU system, the internal microstructure of the system, and finally the macro properties of the material. The
commonly used chain extenders are amine chain extenders and alcohol chain extenders.

3,3′-Dichloro-4,4′-diphenylmethane diamine (MOCA) is an amine chain extender commonly used in polyurethane synthesis. The structural formula is shown in Figure 4. The molecular structure contains rigid benzene ring, so the strength of the product is high. However, MOCA has high toxicity and high reactivity of amine chain extenders, so attention should be paid to the control of reaction conditions.

The molecular viscosity of alcohol is relatively low and the reaction activity is relatively low due to its short hydrogen chain. It can be used as chain extender. It can react with isocyanate quickly before polyol, so as to expand the chain. Common chain extenders of small molecular diols include ethylene glycol (EG), 1,4-butanediol (BDO), and 1,6-hexanediol (HD).

3.2. Hollow Glass Beads (HGB). Glass bead is a new kind of micron material made of borosilicate and other raw materials. Its particle size ranges from a few microns to a few millimeters. It has the characteristics of light weight, low heat conduction, and high strength. After special treatment, its surface can be well dispersed into organic matter. At present, there are mainly four methods for industrial production of glass beads: powder method, droplet method, spray granulation method, and sol-gel method. Glass beads mainly include solid glass beads, porous glass beads, and HGBs. Because the density of HGBs is smaller than other kinds of glass beads and the thermal conductivity is low, it is a kind of glass beads processed by special technology. Generally speaking, HGBs have a wall thickness of 10–250 microns, a wall thickness of 1–2 microns, and a particle size of 0.1–0.25 g/cm³. It is a new lightweight material with excellent performance and bright application prospect.

HGBs were first produced by Emerson and Cumming in the early 1960s. The manufacturing process is to pass the foam containing particles through the high temperature zone, dissolved or softened in the high temperature zone, which then forms gas in the softened glass, and these particles will become hollow particles due to the expansion of the gas. HGBs are a new type of inorganic lightweight nonmetallic materials with diameters ranging from a few microns to hundreds of microns. Its appearance is gray, with soft texture and good fluidity. Under microscope observation, the appearance color of HGBs is gray or white, showing the shape of hollow thin-walled sphere. The shell contains inert gases such as N₂ or CO₂, and its wall thickness is 8% to 10% of its diameter, as shown in Figure 5. In the early days, hollow glass microspheres were widely used in cutting-edge scientific and technological fields such as aerospace and national defense and military, such as aircraft, lifeboats, submarines, and seaplanes. With the progress of science and technology and the industrialized production of HGBs, HGBs have gradually become a new material with low price and rich resources. At present, HGBs have been widely used in military and civil fields, such as thermal insulation, insulating materials, emulsion explosives, composites, and chemical product additives.

Table 1: Chemical composition of HGB.

| Component | Content (%) |
|-----------|-------------|
| SiO₂      | 55–65       |
| Al₂O₃     | 26–35       |
| Fe₂O₃     | 0.2–1       |
| Na₂O      | 0.5–4       |
| K₂O       | 0.5–4       |
| CaO       | 0.2–0.6     |
| MgO       | 1–2         |
| TiO₂      | 0.5–2       |

Table 2: Physical properties of HGB.

| Properties          | Figure |
|---------------------|--------|
| Practical size range | 5.0–200μm |
| Average practical size | 26–35μm |
| Bulk density        | 0.08–0.64g/cm³ |
| Surface area        | 1.92m²/g |
| Moisture rate       | <1%    |
| Sphere rate         | >95%   |
| Melting point       | 1450   |
| Specific heat       | 1.13kJ·g⁻¹K⁻¹ |
addition, HGBs also have excellent physical and chemical properties, such as good fluidity, low density, low thermal conductivity, low thermal shrinkage coefficient, high compressive strength, acid and alkali corrosion resistance, and good thermal stability. The physical properties of HGBs are shown in Table 2. It has excellent physical and chemical properties. It is a new silicate material. Those with a diameter of less than 0.8 mm are called microspheres, and those with a diameter of more than 0.8 mm are called fine spheres. Glass beads with different particle levels have great differences in different industries. They can be widely used in deep-sea exploration, aerospace, hydrogen storage, drug diagnosis, and other fields. Hollow glass beads have broad application prospects in filling materials, chemical industry, construction engineering, and so on.

As a new lightweight material with excellent performance, HGBs have the following main characteristics:

1. Low density: the bulk density of HGBs is between 0.1 and 0.3 g/cubic centimeter, while the actual density is between 0.1 and 0.5 g/cubic centimeter. The density of the material itself can be significantly reduced when the HGB/TPU composite foam is manufactured.

2. The surface modified HGBs have good wetting effect and are easy to disperse. They can be widely used in polyester, polyurethane, epoxy resin, and other epoxy resins.

3. Good fluidity: HGB is a kind of small hollow ball. Its fluidity is better than other forms of filler, so its filling effect is very good. The sphere of HGBs is isotropic, which will not cause inconsistent shrinkage in different parts of the molded product due to orientation, so as to ensure the dimensional stability of the final product.

4. The oil absorption rate is low, the specific surface area of HGBs is the smallest, and the oil absorption rate is very low. Adding HGBs can reduce the amount of thermoplastic polyurethane and increase the output by 10% ~ 20%.

5. Good heat resistance and thermal decomposition of HGBs at more than 1450 degrees Celsius: as a filler in composite foams, the flame retardancy of finished products can be improved.

6. Excellent heat insulation performance: there will be a small amount of gas filled in the inner cavity of HGBs, so it has good sound insulation and heat insulation performance. It is usually used as the filler of various heat insulation and sound insulation products.

3.3. Performance Test and Characterization of Composite Foam Materials. It is assumed that the failure of the composite is caused by the load acting on the effective part of the matrix, and there is no stress transfer and stress concentration between the particles and the matrix. Then the strength of the composite can be expressed by the following formula:

$$
\delta_c = \delta_m \cdot \left(1 - aV_f^n\right).
$$

Among them, \(\delta_c\), \(\delta_m\) is the yield strength of composite material and matrix, respectively; \(V_f\) is the volume fraction of filled particles; \(a\) and \(n\) are constants. It depends on the shape and arrangement of the particles.

Considering the different stress distribution on the stressed section, the stress concentration factor \(s\) is introduced here, after considering the different stress distributions, a stress concentration factor \(S\) is proposed.

$$
\delta_c = \delta_m \cdot \left(1 - aV_f^n\right) \cdot S.
$$

When there is no adhesive force between filler and matrix, the expression of composite strength is as follows:

$$
\delta_c = \delta_m \cdot \left(1 - 1.21V_f^{2/3}\right).
$$

The above formulas do not take into account the bonding state between particles and matrix, so they are only used to predict the tensile strength of composites, tensile strength, and compressive properties of ordinary foams.

The compressive strength of the composite foam can also be expressed in the following way according to the loading of the resin matrix and the accumulation of beads.

$$
\delta_c = \delta_m \cdot \frac{1 - V_f}{A\left(1 + V_f\right)} \cdot \exp\left(\beta V_f\right).
$$

In the formula, \(\delta_c\), \(\delta_m\) is the strength of the composite foam and the strength of the matrix resin. \(A\) is a constant, which is related to the shape of the filler. For spherical beads, \(A = 2.5\); \(\beta\) is a constant that indicates the effect of interface adhesion. When \(\beta = 0\), the filler and the substrate are unbonded, and the filler is the same as the air bubble, which is pure foam material. When \(\beta \geq 3\), they bond well, and the addition of filler helps to improve the strength of matrix material. \(V_f\) is the volume fraction of beads. For three-phase composite foams, the influence of air bubbles on the strength of composite foams should be considered. Therefore, the strain of Formula (1)–(4) is Formula (1)–(5).

$$
\delta_c = \delta_m \cdot \frac{1 - \phi}{A\left(1 + \phi\right)} \cdot \exp\left(\beta\phi\right).
$$

Among them,

$$
\phi = V_f + V_{air}.
$$

For bubble \(\beta = 0\), therefore

$$
\delta_c = \delta_m \cdot \frac{1 - \phi}{A\left(1 + \phi\right)} \cdot \exp\left(\beta V_f\right).
$$

During the test, the instrument synchronously measures the tensile force and tensile deformation of the material, and the engineering stress and engineering strain of the material are as follows:
\[
\sigma = \frac{F_t}{A_0},
\]
\[
\epsilon = \frac{\Delta l_t}{l_{t0}}. \tag{9}
\]

\(F_t\) is the tensile force, \(A_0\) is the cross-sectional area of the gauge section of the material sample, \(\Delta l_t\) is the elongation of the gauge section of the sample, and \(l_{t0}\) is the original length of the gauge section of the sample.

The main parameters describing the performance of materials in the elastic stage include Young’s modulus, proportional limit, and elastic limit, where Young’s modulus is the slope of the curve in the elastic stage:

\[
E = \frac{\sigma}{\epsilon}. \tag{10}
\]

The proportional limit is the stress at the point where the stress-strain curve begins to deviate from the straight line. After exceeding this stress, the material load deformation relationship will no longer follow Hooke’s law, and its expression is as follows:

\[
\sigma_p = \frac{F_{tp}}{A_0} \tag{11}
\]

\(F_{tp}\) is the load at the linear deviation point of the tensile curve.

The elastic limit is the maximum stress of reversible elastic deformation of the material. Within this stress range, the material can completely recover to the initial length after unloading the load. Its expression is as follows:

\[
\sigma_c = \frac{F_{te}}{A_0} \tag{12}
\]

\(F_{te}\) is the load that the tensile curve changes from elasticity to plasticity.

The yield limit of the material is the maximum stress that the material can bear. Beyond this stress, it is considered that the material will have unrecoverable plastic deformation, which can be expressed by the following formula:

\[
\sigma_s = \frac{F_{ty}}{A_0} \tag{13}
\]

\(F_{ty}\) is the load corresponding to the yield point.

For elastic-plastic materials, yield limit is usually used as the criterion of structural design, while for brittle materials, tensile strength is more suitable as the criterion of material structural design.

Tensile strength refers to the stress corresponding to the maximum load before the specimen breaks, which is commonly expressed by the following formula:

\[
\sigma_b = \frac{F_{tb}}{A_0} \tag{14}
\]

\(F_{tb}\) is the maximum load that the sample can bear.

In practical application, the fracture elongation and section shrinkage coefficient of the material are mainly used as the plasticity evaluation indexes, and the calculation formula is as follows:

\[
\delta = \left(\frac{l_k - l_{t0}}{l_{t0}}\right) \times 100\%, \tag{15}
\]

\[
\phi = \left(\frac{A_0 - A_k}{A_0}\right) \times 100\%.
\]

\(\delta\) is the elongation of the material after fracture, \(l_k\) is the total gauge length of the sample after fracture, \(\phi\) is the reduction of area, and \(A_k\) is the minimum cross-sectional area of the sample after fracture.

Some round bar samples and thin plate samples may be used for torsion test. According to the material mechanics formula, the shear modulus is the slope of the elastic section of the torsion curve, and its expression is as follows:

\[
G = \frac{Ml_{t0}}{\phi_I l_t}. \tag{16}
\]

Among them, \(G\) is the shear modulus of the material, \(M\) is the torque load on the sample, and \(l_{t0}\) is the original length of the gauge section of the sample. \(\phi_I\) is the torsional angle of the gauge section of the sample, and \(l_t\) is the torsional moment of inertia of the section.

For circular section and rectangular section, \(l_t\) is

\[
l_t = \frac{\pi d_s^4}{64}, \tag{17}
\]

\(d_s\) is the section diameter of the round bar sample, \(\beta\) is the size coefficient of the thin plate sample, which is related to the values of \(h\) and \(b\), \(h\) is the width of the rectangular section of the thin plate sample, and \(b\) is the thickness of the rectangular section of the thin plate sample.
4. Preparation of HGB/TPU Composite Foam Material

The raw materials for the preparation of HGB/TPU composite foam include thermoplastic polyurethane TPU, HGB, silane coupling agent KH550, azo two formamide AC-K, ethanol, sodium hydroxide, and propanamine. The required instruments include vacuum drying oven, high-speed mixer, injection molding machine, flat vulcanizer, infrared spectrum analyzer, and others, as shown in Table 3 for specific equipment types.

The main component of HGB is silica, and its surface contains some organic substances. If HGB is directly added to TPU, because there is no adhesion between HGB and matrix, it is easy to produce interface defects, which makes it unable to effectively transfer stress, thus reducing its performance, so it must be modified. It can reduce the gap left on the interface and greatly improve the adhesion between HGB and TPU.

4.1. Modification of Hollow Glass Beads. HGB hollow glass beads were screened through 300 mesh and 400 mesh screens, and hollow glass beads with particle size of 35–55 microns were screened. Then, the vacuum drying oven is used for drying treatment, and the temperature of the drying oven is set to 120°C, and the drying time is set to 3H. After drying, cool down naturally and finally put it into the drying oven for standby.

Preparing 200 ml of 0.5 mol/L NaOH solution, adding 5 g of HGBs, heating at 90°C, refluxing and stirring for 2 h, then washing with distilled water for 2–3 times, and then filtering until the pH of the solution is neutral, it dries and gets ready for use. Add 5 g of silane coupling agent KH550 and 0.1 g of n-propylamine to 100 ml of cyclohexane to make a mixed solution, then add dried HGBs, heat to 70°C, and reflux for 2 hours. In addition, it needs to be cleaned with alcohol twice and distilled water three times. Finally, put the mixed solution into a vacuum furnace at 80°C and dry it for 2 hours.

4.2. Extrusion Foaming. According to a certain proportion, after the surface modified HGB and TPU are stirred evenly by the high-speed mixer, the foaming agent is added and poured into the twin-screw extruder for extrusion foaming molding to obtain the style of extrusion foaming. The formula parameters are shown in Table 4 and the process flow is shown in Figure 6.

5. Properties of HGB/TPU Composite Foam

This part mainly analyzes the technological process of extrusion foaming material, discusses the influence of its formulation and technological conditions on the microstructure and properties of the foam material, and concludes the technological conditions of the best foaming effect. In this paper, the infrared spectrum of HGB before and after treatment with silane coupling agent KH550 is shown in Figure 7. Figures 8 and 9 are the variation trend of internal cell size and cell density of foamed samples under different AC and HGB contents. Figure 10 shows the effects of different AC and HGB contents on the tensile properties of foamed samples.

As can be seen from Figure 7, at the wavelength of 3480 cm$^{-1}$, the infrared peak shows the superposition peak of -NH$_2$ and -OH stretching vibration, which is the characteristic spectral line of amino and hydroxyl groups in silane coupling agent. After HGB is treated with KH550, there is a -CH$_2$ stretching vibration peak at the wavelength of 2440 cm$^{-1}$, which is the characteristic spectral line of the chemical component of KH550. At the wavelength of 1640 cm$^{-1}$, there is a -NH$_2$ bending vibration peak, and at the wavelength of 1275 cm$^{-1}$, there is a Si-O-Si bond, which is the component spectral line of HGB. It can be seen from the infrared spectrum that KH550 silane coupling agent exists on the surface of HGB, indicating that silane coupling agent can effectively improve the surface of hollow glass beads. Adding the modified HGB to TPU can change its bonding form with resin from mechanical bonding to organic bonding, so as to greatly enhance the bonding strength.

It can be seen from Figure 8 that when the amount of AC blowing agent is 0.5%, the bubble size and bubble density of the foam sample are all smaller (75.2, 2.23 g/cm$^3$). When the addition amount of AC foaming agent is 1.5%, the minimum cell size reaches 64.7 and the maximum cell density reaches 10.78 g/cm$^3$. Thereafter, with the continuous increase of AC foaming agent content, the cell size began to increase and the cell density gradually decreased. When the AC content increased to 2.5%, the cell size increased to 114.3 and the cell density decreased to 3.06 g/cm$^3$. When the content of AC foaming agent is low, the amount of pyrolysis gas decreases...
Figure 7: Infrared spectra of HGB before and after KH550 treatment. (a) The infrared spectrum of HGB without KH550 treatment. (b) The infrared spectrum of HGB after KH550 treatment.

Figure 8: Graph of cell size and cell density of foamed samples under different AC contents. (a) The effect of different AC content on the cell size of the sample. (b) The effect of different AC content on the cell density of the sample.

Figure 9: Graph of cell size and cell density of foamed samples under different HGB contents. (a) The effect of different HGB content on the cell size of the sample. (b) The effect of different HGB content on the cell density of the sample.
and the internal pressure of the bubble chamber decreases. Therefore, the cell size and density decrease. When the volume fraction of AC foaming agent is 1.5%, the amount of pyrolysis gas increases, the pressure increases, and the bubble nucleation rate increases, forming a suitable gas supply bubble nucleation, so as to achieve the minimum cell size and the maximum cell density. However, with the increase of the amount of AC blowing agent, the gas in the degradation products increased, and the volume pressure increased. The melt strength of TPU decreased, and the gas could not be coated. The volume of the bubble increased and the density of foam decreased. Therefore, to obtain foam samples with good microstructure, the amount of foaming agent cannot be excessive.

It can be seen from Figure 9 that when the HGB content is 3%, the foaming effect inside the sample is the best, the minimum cell diameter reaches 62.8, and the maximum cell density reaches 11.37 g/cm³. The concentration of HGB is too high or too low, which will lead to the increase of pore size, decrease of foam density, and decrease of foam quality. When the content of HGB is less than 3%, the number of foaming groups increases relatively, and the content of foaming agent does not change, but the nucleation sites are reduced, so the cell size decreases and the increase of density slows down. Under the ratio of 3%, HGB can be mixed evenly with TPU and to a certain extent as nucleating agent to achieve the best foam effect. When the HGB content further increases, the impact probability of HGB will make the polymerization of the melt more obvious, so as to reduce the strength of the melt, weaken the compressive capacity of bubbles, make bubbles easy to expand, form large bubbles, and cause vaporization or burst. In addition, because the foam effect of the sample is related to the gas concentration in the melt, HGB cannot dissolve the gas after AC decomposition, so the addition of HGB will cause the gas concentration in the melt to decrease and affect the foam effect.

As can be seen from Figure 10, the tensile strength of the foamed sample continues to decrease with the increase of AC foaming agent content. At the same time, with the increase of HGB content, the tensile strength of the specimen increased first and then decreased. When the amount of AC foaming agent was 0.5% to 1.5%, the tensile strength of the specimen decreased from 8.04 MPa to 7.16 MPa, a decrease of 12.29%. In the extrusion foaming process, when an appropriate amount of foaming agent is added, the number of closed pores will increase due to the addition of foaming agent. And the distribution in the resin will become more uniform. When the content of foaming agent is 2.5%, the foam density can be significantly increased. A large number of fusion and collapse further reduce the tensile strength of the sample, with the lowest value of 4.47 MPa, which is 60.17% lower than the original strength. On the whole, the best ratio of AC foaming agent is 1.5%. When HGB content is 3%, the tensile strength of foam material is the highest, reaching 8.2 MPa. This is because when HGB is not added or a small amount of HGB is added, the nucleation point during foaming is very few, the formation of bubbles is uneven and easy to break, resulting in defects in the foamed specimen and reducing its tensile strength. When the content of HGB increased to 3%, the number and distribution of nucleation reached the best value. At this time, the size distribution of bubbles in the foam specimens is uniform, and the tensile strength is significantly improved. However, with the continuous increase of HGB addition, the tensile strength of the material will decrease, because the size and uniformity of bubbles will be reduced. Through comprehensive analysis of HGB process parameters, it is concluded that HGB concentration at 3% is more suitable for extrusion foam process.

6. Conclusion

In this paper, the surface modification of hollow glass microspheres was first carried out. The modified HGB were filled with thermoplastic polyurethane (TPU) and the composite foams were prepared by extrusion foaming process. Based on the study of the tensile properties and its influencing factors, this paper systematically analyzes and discusses the effects of different foaming formulas and process parameters on the cell structure, density, and mechanical properties of foaming materials. The main conclusions are as follows.
(1) In this paper, the surface treatment of HGBs with organosilane coupling agent KH550 can make the HGBs have a good bonding interface in TPU matrix.

(2) With the increase of AC content of foamed agent, the foamed size of the foams increases obviously, and the bubble coalescence and collapse are serious. When the AC content is 1.5%, the foaming effect is good, and the tensile property is the best.

(3) With the increase of HGB content, the size of foamed materials gradually decreased and the number of foam materials increased. The composite foams containing 3%HGB had better pore structure and tensile properties.

Of course, there are still some deficiencies in this paper, which need to be further studied. In addition to extrusion foaming, the foaming process also includes molding foaming and injection molding foaming. The foaming mechanism of each process needs to be further explored.

Data Availability
No data were used to support this study.

Conflicts of Interest
There are no potential conflicts of interest in this study.

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