IMPROVED CONSTRUCTION MATERIALS FOR POLAR REGIONS USING MICROCELLULAR THERMOPLASTIC FOAMS

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Abstract

Microcellular polymer foams (MCF) are thermoplastic foams with very small cell diameters, less than 10 microns, and very large cell densities, 10^9 to 10^{15} cells per cubic centimeter of unfoamed material. The concept of foaming polymers with microcellular voids was conceived by Dr. Nam P. Suh in 1979 to reduce the amount of material used for mass-produced items without compromising the mechanical properties. The reasoning behind this concept was that if voids smaller than the critical flaw size pre-existing in polymers were introduced into the matrix, they would not affect the overall strength of the product. MCF polycarbonate (PC), polystyrene (PS), and polyvinyl chloride (PVC) were examined to determine the effects of the micro-structure towards the mechanical properties of the materials at room and arctic temperatures. Batch process parameters were discovered for these materials and foamed samples of three densities were produced for each material. To quantify the toughness and strength of these polymers, the tensile yield strength, tensile toughness and impact resistance were measured at room and arctic temperatures. The feasibility of MCF polymers has been demonstrated by the consistent and repeatable MCF micro-structures formed, but the improvements in the mechanical properties were not conclusive. Therefore the usefulness of the MCF polymers to replace other materials in arctic environments is questionable.

Purpose and Scope

The purpose of this experimental research was to show that microcellular thermoplastic foams have similar or improved mechanical properties to solid thermoplastic materials at arctic temperatures. MCF thermoplastics have shown better fracture toughness, impact strength, and fatigue in previous tests performed at room temperatures for various materials.

This experimental research focused on three materials: polycarbonate (PC), polystyrene (PS), and polyvinyl chloride (PVC). These materials were foamed using the batch microcellular foaming process. This process creates a microcellular foam structure by inducing a thermodynamic instability in the materials with an inert gas (non-CFC). The resulting cell structure incorporates a 10^{10} to 10^{13} void per cm^3, at an average size of 0.1 to 2.5 microns. The tensile strength and toughness and the impact resistance were examined to demonstrate the change in mechanical properties.

Background

Plastics have long been the material of choice in design due to the excellent combination of such advantages as low cost, ease of manufacturing, and outstanding properties as a function of weight. Many of the advancements in materials development over the past 50 years have been in the field of plastics, resulting in hundreds of different types and thousands of grades and alloys.

Thermoplastics are those polymers that have a melting point and solidify by cooling after processing. Thermoplastics have been characterized as having a dramatic reduction in their toughness at low temperatures. This is usually experienced in materials that are examined across their glass transition temperature (Tg). The glass transition temperature is where a polymer experiences a semi-phase change from a glassy state to a rubbery state. All of the polymers examined in this experiment were already

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below their Tg, so a great reduction in toughness was not expected to come from crossing this phase. An increase in toughness per amount of material was expected to come from the microcellular foam structure. "The rationale is that if bubbles smaller than the flaws that naturally occur in polymers were created in sufficient numbers, then the material density could be reduced without compromising the mechanical properties." <Ref. 1>

Microcellular Foams (MCF) are polymers in which very small voids ranging in diameter from 0.1 to 25 microns, and are present in very large numbers, in the range of 10^9 to 10^{15} voids per cubic centimeter (cc). The densities of these polymers have been reduced to as low as 0.04 g/cc in batch processing, which is an expansion of about 30 times the original volume. The invention of this foaming process that creates microcellular structures in polymers was pioneered by the Massachusetts Institute of Technology.

Nearly all polymers can be processed having a microcellular structure. It is accomplished by inducing a thermodynamic instability after the polymer has been saturated with an inert gas through a sudden change in pressure and/or temperature. In batch processing this is done by exposing solid samples to gaseous or super-critical fluid N_2 or CO_2, for example, under pressure until completely saturated, depressurizing them, and providing enough heat to allow the polymer matrix to deform and allow cell growth. Polymers may gain as much as 20% super-critical CO_2 fluid by weight. Process parameters have been established empirically and theoretically for many polymers. Continuous processing, such as extrusion, requires super-critical N_2 or CO_2 to form a homogeneous solution with the polymer melt and the pressure drop of the melt exiting the die allows cell growth.

Tensile elongation, tensile toughness, and tensile strength measurements are among the most important indications of strength in a material and are most widely specified properties of plastic materials. Tensile strength, in a broad sense, is a measurement of the ability of a material to withstand forces that tend to pull it apart and to determine to what extent the material stretches before breaking. Tensile modulus, an indication of the relative stiffness of a material, can be determined from a stress-strain diagram. Different types of plastic materials are often compared on the basis of tensile strength, elongation, and tensile modulus data. Many plastics are very sensitive to the rate of strain and environmental conditions. Therefore, the data obtained by a method cannot be considered valid for applications involving load-time scales or environments widely different from the method. The tensile property data are most useful in preferential selection of a particular type of plastic from a large group of plastic materials and such data are of limited use in actual design in the product. This is because the tensile test does not take into account the time-dependent behavior of plastic materials.

The impact properties of polymeric material are directly related to the toughness of the material as well. Impact resistance of a material is the ability to resist fracture under stress applied at high speed. That is to say, impact strength is a measure of the ability of a material or structure to withstand the application of a sudden load without failure, to prevent crack propagation through the sample. Furthermore, it is defined as the ability of a polymer to absorb applied energy that is related to the toughness of plastic materials. The toughness of a material is proportional to the area under the stress-strain curve, the tensile toughness. Impact is mathematically defined as I = Force x Time. Thus, impact strength is related to the load as well as to the speed of the application.

In contrast to impact resistance, the fracture toughness of a solid polymer is much better defined for a given set of environmental conditions. Theoretically, the impact strength/brittleness of a material is related to micro-mechanical fracture in the matrix. Under shock loading, the matrix tries to readjust in a short time. Material will not fracture if energy applied is absorbed completely in this readjustment of molecules. For example, rigid polymers such as polystyrene and acrylics take a longer time to readjust than flexible polymers such as plasticized PVC. Flexibility of the molecules depends upon the chemical structure or molecule, type and amount of additives, temperature, time span of application (very short application time of load makes flexible polymers behave as solids), and possibly the cell structure. <Ref. 2>

The effects of the micro-cells in the polymer matrix were not expected to debilitate the tensile properties, because they were smaller than the critical flaw size to initiate a crack. Theoretically, the tensile strength and toughness of a MCF polymer should be the same as a solid polymer of equal weight. A small increase in impact strength was expected through the blunting of the crack tip primarily at open cell regions.

Experimental

Materials and Equipment

Materials:
  Polystyrene (PS) GP crystal PS neat, Westlake Co.
  Polyvinyl Chloride (PVC) Type I clear, Huls America
  Polycarbonate (PC) Cryolan ZX 9034, Cylko Ind.
  Polyamide (Nylon) Nylon 6/6 neat, EI DuPont
  Carbon Dioxide gas

Equipment:
  Hydropak gas intensifier
  Autoclave Engineering 600 in^3 pressure vessel
  Heated water baths
  Instrom Tensile testing machine 6025
  TMI Izod testing machine 43-1
  Setra 100 Scale 150.000 grams

Procedure

The research plan consisted of examining the foaming parameters of microcellular foamed thermoplastic materials, discovering the micro-structure of these materials, and discovering the mechanical properties of these MCF polymers at room temperature and at an arctic temperature.

The first task of this research was to examine the gas absorption of the polymer materials to determine when they were completely saturated. These material specimens were saturated with super-critical CO_2 at 3500 psi and 40°C for different lengths of time to yield the data necessary to determine the gas absorption verse time curve for each material.

The second task of this experiment was to examine the foaming parameters. Each specimen after being completely saturated with super-critical CO_2 was submersed in glycerin oil at different temperatures, ranging from 30°C to 65°C, then measured to determine the void fraction. This data was used to correlate the void fraction with temperature in order to predetermine the foaming temperature to achieve a specific foam density.

The third task was to foam precut specimens using the saturation and foaming conditions discovered in the previous tasks to achieve 10, 20, and 30% void fraction. The foamed test specimens were intended to be the same size as the unfoamed baseline ones.

The test specimens were foamed in heated water baths for more than 10 minutes to insure full cell growth. They were unrestrained and evenly heated to promote even cell growth. All of the test specimens were out-gassed in a vacuum chamber for 2 to 8 days to remove the residual CO_2.

The mechanical properties, namely the tensile strength and toughness and the impact resistance, were measured following ASTM D638-87b, "Standard Test Method for Tensile Properties of Plastics," and ASTM D256-84, "Impact Resistance of Plastics and Electrical Insulating Materials." Sample preparation and testing procedures followed the ASTM requirements. Tensile Type I samples were used for the

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tensile testing and 0.125 inch wide by 0.5 inch thick, notched impact bars were used for the Izod impact testing.

The cell size and cell density were determined by examining the Scanning Electron micro-graphs taken. The cell size was measured using the scale present on the micro-graph. The cell density was determined by counting the cells in a measured area, calculating the area density, and taking the square root of that, and then cubing the result. This assumes isotropic bubble distribution.

Discussion of Results

The examination of the MCF specimen's micro-structure was done with an SEM. The cell sizes of the MCF PS and PVC specimens were remarkably small, 0.1 to 0.3 microns in diameter and the cell density was high, 10^{12} to 10^{13} cells per cubic centimeter of original material (See Charts). The skin thickness for the MCF PS specimens was approximately 2 microns and PVC specimen's skin thickness was less than 1 micron. MCF PC specimens had larger cells, 2 to 2.5 microns and consequently lower cell densities. The skin thickness for the PC specimens was about 25 microns. Both the MCF PVC and PS specimen's cells were spherical, but the PC specimen's cells were cavernous like, with numerous smaller cells throughout the larger cells. Cell densities were relatively uniform throughout the thickness of each specimen.

The mechanical property data was collected and analyzed for each material and foam density. The final testing specimens were all the same size to maintain uniformity, that is the 30% foamed specimens had 30% less material than the unfoamed ones.

The unfoamed sample data are presented in each chart to provide a base point for comparison. Since the unfoamed specimens were not processed with super-critical CO_2 and not put through the same processing procedures, it is biased to directly relate the foamed and unfoamed results. Gas saturation of the polymers caused annealing in the specimens and possible molecular and additive degradation. The effect of super-critical CO_2 to the polymers is not fully known, but visual inspection of some polymers shows evidence of degradation. It appeared that the MCF PS specimens that were saturated longer than 48 hours under went this degradation, the smooth surface features common to MCFs were destroyed and the material seemed to be very brittle. This could have been from the CO_2 reacting with the polymer matrix and possibly breaking the polymer chains.

In general, the foamed micro-structure of each sample did not debilitate the mechanical properties. While some properties improved for some materials, other properties decreased. Data taken from "Structural Design with Plastics," Ref. 3, for typical thermoplastic structural foams shows that MCFs have the same or better tensile strengths than structural foams.

The tensile yield strength of each MCF material significantly decreased from the unfoamed sample. This could be attributed to the effect of super-critical CO_2 towards the polymer. To provide a relevant unfoamed baseline, some specimens were saturated but not placed in the heated bath. Unfortunately, the chamber temperature during saturation provided enough heat to promote cell nucleation and foam growth. The yield strengths of the MCF samples show a decrease in strength roughly proportional to the decrease in the amount of material.

It was found that the cold temperature (-30°C) testing results were generally higher than the room temperature (21°C) results. This occurrence was expected for amorphous materials below their Tg, because the cold temperature constricts the polymer matrix. This constriction brings the polymer chains closer together creating a larger influence of the steric hindrances due to the interaction of the side chains elements. Close to 20% increases in tensile yield strength were observed in PC and PVC due to the cold temperature. PS specimens displayed slight increases in yield strength, probably from the fact that the benzene side molecules exhibit near their maximum steric hindrance even at room temperature.

Polycarbonate

Property	Units	Test Method ASTM	21oC	-30oC	21oC	-30oC	21oC	-30oC	21oC	-30oC
Density	kg/m3		1200		1044		900		816	
Cell Size	microns		unfoamed		1		2		2.5	
Cell Density	voids/cm3				1.12E+10		4.16E+10		6.4E+10	
Tensile Yield Strength	MPa	D 638	64	74	43	52	44	50	37	46
Tensile Elongation	%	D 638	87	72	105	88	100	83	92	82
Tensile Toughness	Joules	D 638	168	156	206	208	175	211	221	223
Izod Impact Strength	Joules	D 256	6.85	5.71	7.12	2.68	4.99	2.3	2.79	1.9

Polystyrene

Property	Units	Test Method ASTM	21oC	-30oC	21oC	-30oC	21oC	-30oC	21oC	-30oC
Density	kg/m3		1050		914		809		735	
Cell Size	microns		unfoamed		0.2		0.3		0.3	
Cell Density	voids/cm3				2.02E+12		2.33E+12		4.29E+12	
Tensile Yield Strength	MPa	D 638	46	48	29	29	29	29	15	18
Tensile Elongation	%	D 638	2.4	2.6	2.2	1.7	2.2	2.1	1.4	1.2
Tensile Toughness	Joules	D 638	2.44	2.81	1.71	1.29	2.00	1.88	0.69	0.72
Izod Impact Strength	Joules	D 256	0.13	0.15	0.09	0.10	0.07	0.10	0.09	0.11

Polyvinyl Chloride

Property	Units	Test Method ASTM	21oC	-30oC	21oC	-30oC	21oC	-30oC	21oC	-30oC
Density	kg/m3		1400		1218		1148		980	
Cell Size	microns		unfoamed		0.1		0.2		0.2	
Cell Density	voids/cm3				4.69E+13		1.85E+13		5.24E+13	
Tensile Yield Strength	MPa	D 638	79	99	37	53	32	42	32	43
Tensile Elongation	%	D 638	5.4	7.1	10.5	3.8	5.3	3.4	9.4	4.3
Tensile Toughness	Joules	D 638	10.6	18.2	13.6	5.5	6.0	4.2	13.0	6.2
Izod Impact Strength	Joules	D 256	0.20	0.11	0.17	0.27	0.20	0.19	1.87	0.24

The percent elongation was also examined. As expected, the cold temperature results were generally lower than the room temperature results. No significant increases were noticed for any of the MCF materials.

The tensile toughness value was generated through the software testing program. The area under the stress-strain curve was measured and recorded. The toughness measurement is a slow rate applied load. MCF PC specimens showed higher toughness values for all of the foam densities and displayed ductility until failure. The MCF PS and PVC specimens, on the other hand, displayed lower cold temperature toughness results and failed brittlely. The room temperature PVC specimen's toughness was generally the same. Since only MCF PC showed an increase in tensile toughness, it is thought that the foamed micro-structure improves the energy absorption of ductile materials, but not brittle materials.

The Izod impact test was also performed, which is the fast rate applied impact load. This provided the data to analyze the material for sudden impact or shock loading and energy absorption. MCF PC specimen's room temperature impact resistance decreased with a decrease in relative density. This represented PC losing its ductility as the void fraction increased. The cold temperature results initially decreased then remained constant. MCF PS and PVC specimen's impact resistance showed no substantial increase or decrease except for PVC at 30% void fraction at room temperature, which increased nearly 10 times. Instead of a brittle fracture, the PVC specimens exhibited ductile fracture. Since the arctic temperature specimens did not show the same results as the room temperature ones, this behavior is not strictly dependent on the cell size or cell density, but on overall molecular ductility.

Both tensile toughness and impact resistance measure the amount of energy a specimen can absorb before fracture. The results of these two tests should have correlated with each other. This was not the case. Since crack initiation and propagation were not examined in this work, it is difficult to understand how the very small closed celled matrix affects fracture mechanics.

Conclusion

Without examining the micro-mechanics of fracture for MCF, it is difficult to understand the assorted results obtained under this testing. Whereas some mechanical properties increased, others decreased. The micro-structure of the material appears to affect the ductility, and consequently the energy absorption of the samples. The largest effect to the mechanical properties came from the MCF batch processing of the materials. The effect of super-critical fluids on polymers is not well known and degradation was only visibly noticed with MCF PS, but could have affected the other materials.

In general, the cell size and foam densities did not affect the mechanical properties and maintained similar strengths throughout the samples of each material tested as expected. The most notable exception of this is the 30% void fraction MCF PVC specimens that displayed a tremendous increase in impact strength.

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