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Effect of additives on flexible PVC foam formation

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ABSTRACT

In this study, effects of Ca/Zn stearate and organotin heat stabilizers and zeolite, $CaCO_3$, cellulose and luffa flours fillers, and their concentrations (2.5, 5, 10 and 20% by weight) on production of flexible PVC foams by chemical blowing agent, azodicarbonamide were investigated. Foam morphology, foam density, compressive mechanical properties and water uptake capacities of samples were determined. Morphology of the sample without any filler showed that employment of Ca stearate and Zn stearate heat stabilizers instead of organotin stabilizers increases foam formation and decreases pore sizes and regularity in pore size distribution. Foams having organotin stabilizer were more resistant to heat than the ones with Ca/Zn stearate for long heating periods. Foams, including organotin-based heat stabilizers, have compact structure. It was observed that, samples containing zeolite, $CaCO_3$, cellulose or luffa flour had lower pore volume but higher Young's modulus and stress values compared to unfilled samples.

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1. Introduction

Use of polymeric foam in today's technology continues to grow at a rapid pace throughout the world. Numerous reasons for this growth include the light weight, excellent strength/weight ratio, superior insulating abilities, and energy absorbing performance and comfort features of polymeric foams. Foams can be prepared from virtually any polymer; all that is necessary is the introduction or generation of a gas within the polymer matrix. Selection of polymers suitable for industrial foam applications depends upon their properties, their ease of manufacture and the economics of the foaming system. Application areas of polymeric foams are furniture, transportation, bedding, carpet underlay, packaging, textiles, toys, gasket, sport applications and insulation appliances. Mechanical properties of foamed polymers change according to different additives. Initiators are the additives, that cause the foam formation (Berins et al., 1982; Brathun and Zingsheim, 1991).

Foams can be flexible or rigid due to their glass transition temperature, which in turn depends upon their chemical composition, the degree of crystallinity and the degree of cross-linking. The cell geometry may be opened or closed cell. The open cell foams are best for car seating, furniture; bedding and acoustical insulation, among other uses, and are generally flexible. The closed cell foams are most suitable for thermal insulation and are generally rigid (Gaechter and Müller, 1993; Hensen, 1997; Matuana et al., 1998).

Additives which are used in the production of the foams improve the endurance and hardness, and protect foams from the environmental effects. The cellulose-based fillers (such as cellulose, wood flour, luffa, etc.) generally used for increasing biodegradability of plastics. The inorganic-based fillers (i.e. calcium carbonate, zeolite, clay, etc.) used for developing the structure of foams. In order to compensate for the lowered impact strength and ductility of wood flour composites due to the incorporation of wood flour in the PVC matrix, Matuana et al. (Matuana et al., 1998) successfully

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introduced a microcellular-foamed structure using a batch process. The mechanical properties of these materials indicated that the microcellular structures improved the impact strength of rigid PVC/wood flour composites dramatically while lowering the density of the artificial wood to the desired range of 0.6–0.8 g/cm^3 (Matuana et al., 1998; Mengeloglu and Matuana, 2001; Patterson, 2001; Saechtling, 1987; Yanez-Flores et al., 2000).

Since PVC undergoes dehydrochlorination by heating, heat stabilizers should be added especially mixed metal soap heat stabilizers such as Ca/Zn stearates or organotin compounds. The heat stabilizers also affect the rate of decomposition of chemical blowing agents (Arkiş and Balköse, 2005; Balköse et al., 2001).

The objective of this study is to investigate effects of different fillers on the foam formation, density, mechanical properties, water uptake and morphology of the flexible PVC foam. Moreover, it was aimed to investigate effects of different heat stabilizers which are Ca/Zn stearate and organotin. For this purpose, different compositions of fillers; zeolite, $CaCO_3$, cellulose powder or luffa flour were added to PVC plastisols that consist of PVC base, dioctyl phthalate (DOP, plasticizers), azodicarboxamide (AZD, blowing agent) and Ca–Zn stearate or organotin heat stabilizers. These foams were compared with flexible PVC foam without any filler to observe the effects of concentration of the filler. Thus, tailoring the properties of the flexible foams would be possible.

2. Experimental procedure

2.1. Materials

Plastisol consists of emulsion type of PVC (from Petkim, Petvinil 37/74), dioctyl phthalate (Merck Co.) and azodicarboxamide (Merck Co.). Organotin stabilizer (LSN117C) and Ca/Zn stearate (Akdeniz Co.) were added into formulation as heat stabilizers. Pure cellulose (from Aldrich Co., with average particle size of 2 μm), natural luffa fiber (from specialty shops with average particle size between 75 and 150 μm), natural zeolite (Clinoptiolite, from Gördes, with average particle size less than 45 μm) and calcium carbonate (from Aldrich Co., with average particle size of 2 μm) were added to plastisol as fillers.

2.2. Preparation of polymeric foam

In this experiment, PVC foam samples were produced from PVC plastisol. At first, PVC plastisol was prepared in a mechanical stirrer by mixing 100 parts emulsion PVC, 80 parts DOP, 2 parts AZD and 2 parts Ca–Zn stearate heat stabilizers combination or organotin heat stabilizer. Then 2.5, 5, 10 or 20% (by weight) fillers were added and mixed with mechanical stirrer until obtaining a homogeneous mixture.

After preparing the plastisol, mixtures were poured in molds of 5 cm × 5 cm × 2 cm sizes and processed in oven at 190 °C for 25 min. The azodicarboxamide (chemical blowing agent) decomposes during plasticizing, releasing ammonia gas (NH_3) that dissolves in the plastisol. The gas must remain dissolved in the melt until curing is accompanished.

2.3. Density and pore volume

Density of PVC foams was measured by using Sartorius density measurement kit (model YDK01). Ethyl alcohol was used as the liquid causing buoyancy. To determine the sample's buoyancy, float sample was immersed by a sieve. The negative weight displayed by the balance corresponded to the buoyancy acting on the sample in the liquid.

The formed by using following calculation procedure taken from manual of Sartorius AG (Sartorius, 1992). Density of foam samples was calculated by using Eq. (1).

$$\rho = \frac{W_a \rho_{fl}}{0.99983G} + 0.0012 \quad (1)$$

where G is the buoyancy force, ρ_{fl} the fluid density, ρ the foam density and W_a is the dry weight of foam.

The percentage of the volume of pores of the foam samples was calculated by using Eq. (2).

$$V_{\text{total pore}} = \left(1 - \frac{\rho}{\rho_{\text{Theoretical}}}\right) \times 100 \quad (2)$$

The percentage of the volume on the surfaces of the specimen was calculated according to the following procedure. First the geometric volume of the specimen V was calculated by Eq. (3).

The total geometric surface area of the specimen, A, was calculated by Eqs. (2) and (3).

$$A = 2(lw + lh + hw) \quad (3)$$

The percentage volume of the surface cells opened by sample preparation, $V_{\text{surface pore}}$, was determined from Eq. (4).

$$V_{\text{surface pore}} = \frac{At}{1.14} \times 100 \quad (4)$$

where t is the average chord length. It was determined from the relationship between t and the average cell size, d. The average cell size, d, was determined from the SEM micrograph. The relationship is given in Eq. (5).

$$t = \frac{d}{1.626} \quad (5)$$

The open pore volume inside the specimen, in other words the opened channels, $V_{\text{opened channel}}$ in the specimen was calculated with Eq. (6).

$$V_{\text{opened channel}} = \frac{W_{\text{wet}} - W_a}{\rho_{fl}} \quad (6)$$

where W_{wet} is the wet weight of foam.

The total open pore percentages of the foams were calculated by summing open pore volume percentages on the surfaces of the specimen and inside the specimen with Eq. (7).

$$V_{\text{total open pore}} = V_{\text{surface pore}} + V_{\text{opened channel}} \quad (7)$$

The closed pore percentage of the foam is the rest of the total pore volume percentage after subtracting the total open

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