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Techniques and parameters investigations on crosslinked rubber foam formations

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Abstract

Single Stage, Heat Transfer and Heat and Chill techniques were applied to determine suitable methods for crosslinked rubber foam formation. Various parameters such as expansion temperature and blowing agent concentration were also investigated. All samples were characterized to determine their curing time, foam density, gel content, cell size and compression strength. From the results obtained, it indicates that only Heat Transfer technique can produce crosslinked rubber foam. From this technique, it shows that increasing expansion temperature from 140 ^{0}C to 160 ^{0}C, no significant changes in gel content was observed. However, cell size decreased and foam density increased. Furthermore, increases blowing agent concentration from 4 phr to 8 phr, the foam density decreased follow by the increased in cell sizes with no changes in gel content. The compression properties found to be highly dependent on foam density.

Keywords: Rubber foam, Heat transfer, Crosslinked, Blowing agent and Gel content

Introduction

There are two major generic foam types that has been produced namely crosslinked and non-croslinked polymeric foams. However, crosslinked polymeric foam has gained wide acceptance and been extensively studied [1]. Crosslinking gives a considerably higher heat resistance and the material behaves as a thermoset compared with the base polymer (such as polyethylene, ethylene-vinyl acetate and polypropylene) which is thermoplastic in nature. The main areas of application of polymer foams depend upon density reduction. As the density decreases, improvements are seen in energy absorption, thermal conductivity and strength to weight ratio [2]. Another factor is that closed-cell foams exhibit buoyancy, which may be used in combination with other factors above to enable them to penetrate many markets [1]. The major application of polyolefin foams is in thermal insulation, packaging, construction and sports and leisure industries [3].

The most widely used crosslinked foam is based on crosslinked polyolefin and it is believed that its market will substantially increase due to further development and environmental concerns of physical blowing agents (PBAs) used in non-crosslinked polyethylene foam manufacture. Historically, chlorofluorocarbons (CFCs) were widely used as PBAs in non-crosslinked polyethylene foam manufacture [4]. The usage of CFCs has been dramatically reduced and they have been phased-out in the developed world following international legislation [5] designed to reduce the rate of destruction of the earth's ozone layer [6].

Most polymer can be crosslinked by chemical or irradiation methods, involving free radical generation, which can result in intermolecular covalent bonding and three-dimensional network formation [7]. However, different base polymers used in crosslinked polymeric foam manufacturing give different physical and mechanical properties and affect their processability [8].

Globally the majority of crosslinked polymeric foam sheet is produced by four processes developed by Furukawa Electric Co [9], Sekisui Chemical Co [10], Toray Industries Inc [11] and Hitachi Chemical Co [12]. The Sekisui and Toray processes rely on irradiation crosslinking while Hitachi and Furukawa processes employ chemical crosslinking. However, Furukawa Electric Company was one of the first companies which advanced the compression moulding

process for chemically crosslinked foam. These techniques can be generally classified into two groups namely single and two-stage expansion process. The single stage process completes crosslinking and thermal decomposition of the blowing agent under pressure in the mould. Opening the press allows instantaneous expansion and ejection of the moulding from the mould cavity. The two-stage expansion process is divided into heat transfer and heat and chill process. In the heat transfer process, the first stage is identical to the single stage process (except for using a somewhat lower temperature) but on opening the press the expanded blank is immediately transferred to a circulating hot air oven at a higher temperature. The first stage of the heat and chill process is identical to the single stage process except that when the predetermined dwell time is reached, the mould is held under pressure whilst rapidly cooling the platens to ambient temperature. This blank is immediately transferred to a circulating hot oven at a selected temperature. Therefore in this research, it is the intension to explore and attempt to develop crosslinked rubber foams using various techniques and the effect of expansion temperature and blowing agent conetration.

Experimental

Raw Materials

All formulations were based on Standard Malaysian Rubber 10, (SMR 10), supplied by River Tek. Sulphur was selected as crosslinking agent in a fixed concentration of 0.5 phr (part per hundred resin). Steric acid of 2.0 phr was used as an initiator. The chemical blowing agent used was sodium hydrogen carbonate, ($NaHCO_3$), and the concentration was varied in the range of 4.0 phr to 8.0 phr. Zinc oxide of 4.0 phr was used as a stabilizer. A fixed concentration of 1.0 phr cyclohexylbenzotiazylsulphamide and 2.5 phr tetramethylthuram disulphide was used as an accelerator.

Sample preparation

Mixing was conducted on two-roll mills. 200 g of rubber were mill until it produce rubbery band. The stabilizer, initiator and accelerators was added first and mixed by cutting and folding for 5 minutes, follow by progressive addition of blowing agent (where applicable) over a period of 10 minutes. Sulphur was added last and mixing was continued for a period of 3 minutes.

Foam productions

Foaming was carried out by a single stage, heat and chill and heat transfer techniques in a 10 mm deep mould. After charging, the foamable compounds were compressed moulded at 14 MPa for 8 minutes. In the case of single stage process, the sample was compressed at 140 °C and the

pressure was released at specified time. However, for heat and chill process, the sample was compressed at 100 °C at specified time and water cooled under pressure to 30 °C. After release of pressure, the sample was immediately transferred in an oven at 140 °C for 20 minutes. For heat transfer process, the sample was also compressed at 100 °C at specified time but the pressure was released without cooling and the partially expended sample was immediately transfer in an oven at 140 °C, 150 °C and 160 °C for 20 minutes.

Curing behavior measurements

Approximately 2 g of compounded rubber sample without blowing agent were placed in rheometer and charged at different temperature of 140 °C, 150 °C and 160 °C for 30 minutes or until the value of tork become constant. The curing time of the compound was estimated using equation 1.

$$T = t_{10} + 90(t_{90} - t_{10}) \qquad (1)$$

Foam characterizations

Gel content
Gel content was determined by refluxing in a stainless-steel mesh cage in boiling xylene for 24 hours and expressing the weight of the vacuum-dried insoluble fraction as a percentage of sample weight before extraction [13].

Foam density
Foam density was determined from the weight and volume of regular parallelepiped samples (50 x 50 x 20 mm) free of skin, voids or other irregularities [14].

Cell imaging and cell size determinations

Cellular structures of foam specimens were assessed from Scanning Electron Microscope (SEM) images. The mean apparent cell size was obtained from SEM images by a modified cell count method described elsewhere [15].

Foam compression properties

Parallelepiped specimens (free of defects and skins) 50 mm x 50 mm with an average thickness of 10 mm were cut from bulk foamed samples. Compression measurements were performed on an Instron Universal Testing Machine fitted with a compression cage at a crosshead speed of 20 mm min[1] and compressing the samples to 80 % of their original thickness. Elastic compression modulus was calculated from the initial linear portion of the stress-strain curve and the compressive stress at 50 % strain was recorded.

Results and discussions

Curing or crosslinking time

In the formation of crosslinked polymeric foam, it is very important to determine curing time of solid polymer matrix. The material must have sufficient elastic strength to retain the pressure from gas release by blowing agent. Therefore crosslinking must occur at certain time before the expansion stage or decomposition of blowing agent proceeds. Figure 1 shows the effect of increasing charging temperature on curing time using a compound without blowing agent. From the results, it indicates that the curing or crosslinking time decreased with increasing charging temperature from 140 °C to 160 °C. This possibly cause by the faster dissociation of initiator and crosslinking agent at higher temperature to complete the crosslinking reaction. Futhermore, this also hinted that a subsequent crosslinking generally takes place during the first 5 to 6 minutes depending on the curing temperature. However, to ensure that the compression moulding time was long enough to complete the reaction, an 8 minutes cycle was used for all subsequent work.
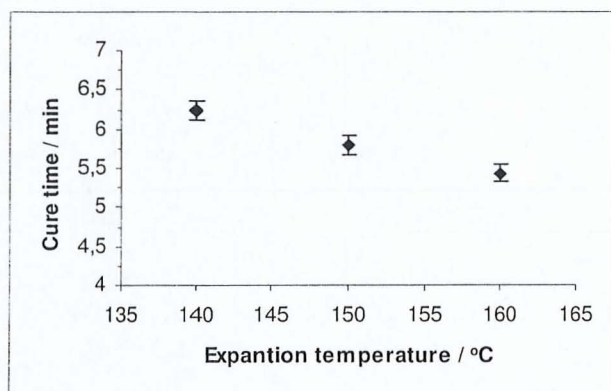

Figure 1 – Dependence of expansion temperature on cure time

Techniques of rubber foam production

Three different techniques were employed in the formation of crosslinked rubber foam namely single stage, heat and chill and heat transfer. To investigate to efficiency of these techniques, 4.0 phr blowing agent were mixed into the compound during millings at a fixed concentration of other materials. It is highlighted here that single stage and heat and chill process is not sufficient techniques to form crosslinked rubber foam with no expansion behaviour or partially expanded but produce defect with a big hole in the middle of the compound. However, heat transfer process can produced crosslinked rubber foam with the good and uniform expansion characteristics.

Therefore only heat transfer process was employed to investigate the effect of expansion temperature and blowing agent concentration on crosslinked rubber foam properties. The expansion temperature was varied from 140 °C up to 160 °C by using 4.0 phr blowing agent concentrations in the formulation and the loading of blowing agent were also varied from 4.0 phr up to 8.0 phr.

Rubber foam properties

Various workers [15, 16] assume that the mechanical properties of crosslinked polymer matrix play a significant role in controlling expansion resistance in foaming processes. They therefore contribute to the physical and mechanical properties of the foam produced. The most common method of physical assessment of crosslinking level of a polymer can be determined by gel content measurements, which represent the insoluble portion of the resin i.e. the percentage of three-dimensional network.

Effect on gel content

Figure 2 illustrates the effect of varying expansion temperature from 140 °C up to 160 °C on gel content. From the results obtained it shows that no significant different on gel content with increasing expansion temperature at the second stage heat transfer process. This suggested that the selected expansion temperature give no contribution on the degree of croslinking. Furthermore, figure 3 shows the effect of varying blowing agent concentration from 4.0 phr to 8.0 phr on gel content. The results also indicate that no effect on the gel content as the blowing agent concentration increased. Both these findings support those of other workers [8, 16] who indicated that the gel content depend on extent of reaction of the peroxide crosslinking agent and this is controlled by time and decomposition temperature of croslinking agent.
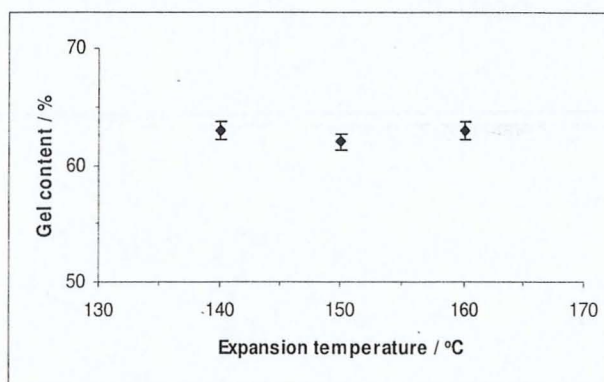

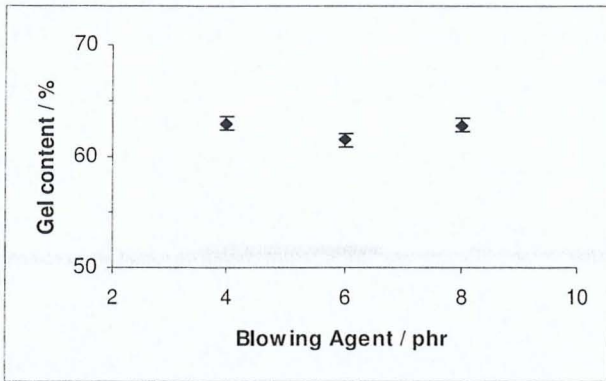
Figure 2 – Effect of expansion temperature on gel content

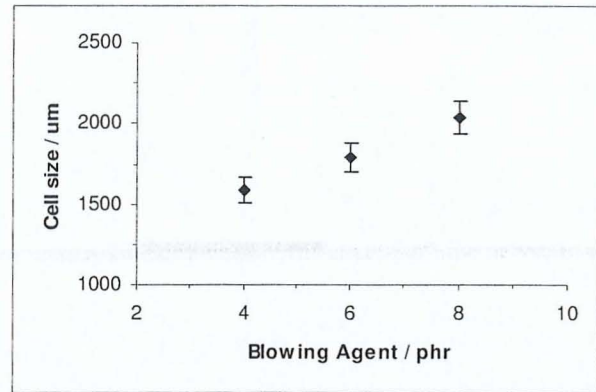*Figure 3 – The effect of increasing blowing agent concentration on gel content*

Effect on foam density and cell size

Result shows that foam density decreased with increasing expansion temperature from 140 °C to 160 °C at the final stage of heat transfer process as illustrated in figure 4. The decreased in foam density at higher expansion temperature attributed to higher rate of nucleation giving less nucleation concentration due to more rapid dissociation of gases (at a fixed 4.0 phr blowing agent concentration). Therefore the foam produced has lower cell concentration but bigger size as shown in figure 5.
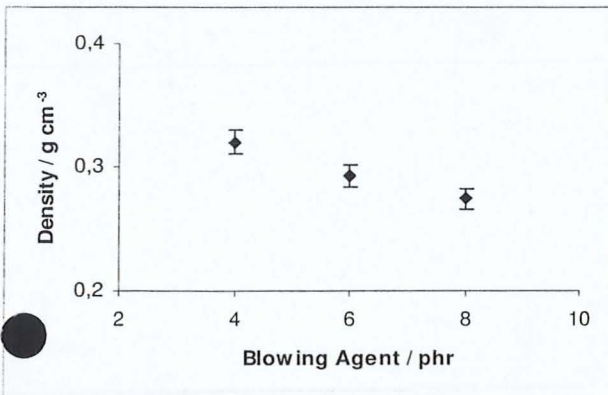

Figure 4 – Blowing agent concentration versus foam density

Figure 5 – Increasing blowing agent concentration on cell sizes

Figure 6 showed the effect of increasing blowing agent concentration on foam density and cell sizes. The results indicate that foam density decreased and cell size increased with increasing blowing agent concentration from 4.0 phr to 8.0 phr. This finding is in agreement with the work of Sims and O'connor [17] which suggested that the decreased in foam density follow by the increased in cell sizes due to the more nucleation of gas occurred in the matrix and higher volume of gas evaporated as the blowing agent concentration increases.
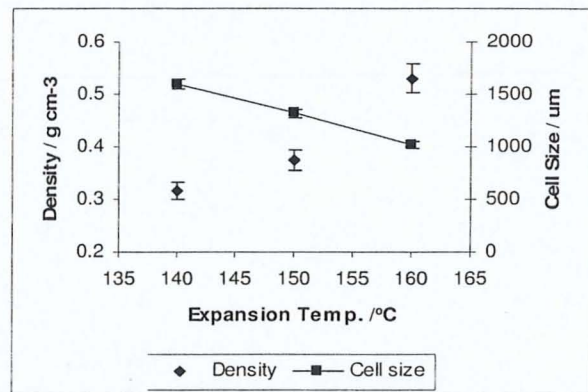

Figure 6 – Effect of expansion temperature on foam density and cell size

Effect on compression properties

Mechanical properties are known to be strongly density dependent [2] and at this stage mechanical properties of foams are assessed by compression-load deflection. Parameters such as compression modulus and compressive stress at 50 % strain were determined. Figure 7 shows the effect of expansion temperature on compression properties. Initially, density differences were ignored to obtain a picture on stress-strain curves. Each curve illustrated a linear

elasticity regime at low stress with a hint of a yield point followed by a long collapse plateau and ultimately by a regime of densification above 70 % strain in which stress began to rise more steeply.
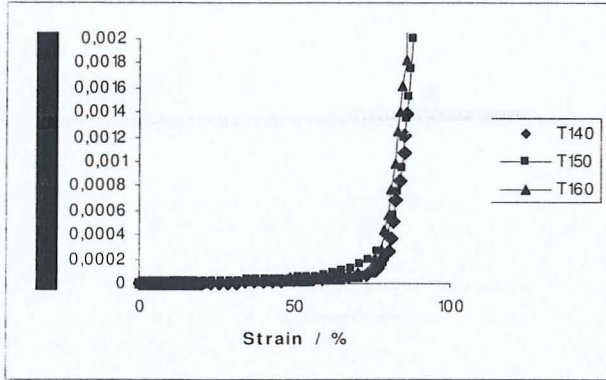

Figure 7 – stress-strain curves of increasing expansion temperature

Similar curves were also observed by Sims and Khunniteekool [16] who generally concluded that on the first loading, the cell walls bend and buckle giving linear elasticity but when a critical stress is reached the foam begins to collapse by stretching and yielding of the cell walls. At higher strains, significant contribution from internal cell gas compression is evident and the opposing cell walls start to touch thus continued compression becomes more and more like compressing the solid material. This results in the final steep rising portion of the curve as densification progresses [2].

Figure 8 and 9 shows the effect of density on compression modulus and compressive stress at 50 % strain for formulations with varying expansion temperature and blowing agent concentration respectively. Results indicate that compression modulus and compressive stress decreased with increasing expansion temperature (i.e. increased foam density). Moreover the result also showed that compression modulus and compressive stress increased with increasing blowing agent concentration (i.e. reduced foam density). Similar behaviour were also observed by other workers [16, 17] and showed that the compressive stress and compression modulus increased with increasing density. This phenomenon was attributed to a reduction in void fraction and a corresponding increase in polymer fraction. This results in an increase in the thickness of the cell walls and greater resistance to cell wall bending and cell collapse [2]. Compression modulus is calculated from the linear elastic region in stress-strain curves. It is controlled by bending of cell edges, elastic stretching of cell faces and enclosed gas compression, all of which are reversible. This finding highly suggested that compression properties of foam dependent on foam density.
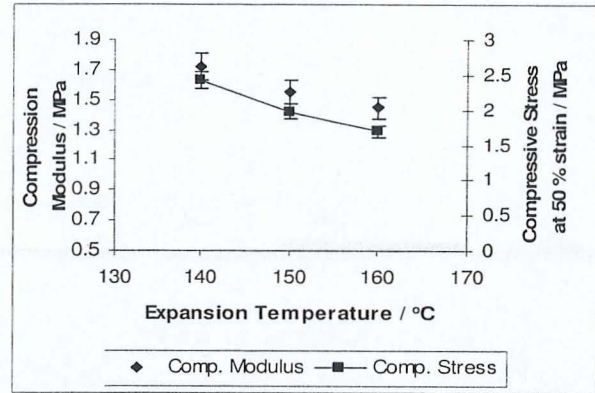

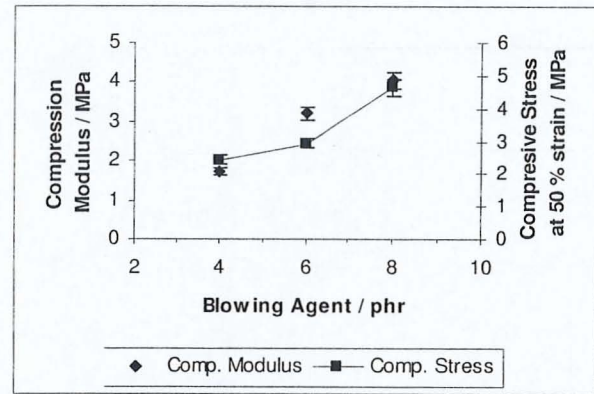*Figure 8 – Effect on expansion temperature on compression properties*

Figure 9 – Effect on increasing blowing agent concentrations on compression modulus and compressive stress

Conclusions

From the foaming techniques selected, only heat transfer foaming techniques is applicable in production of rubber foam. Increasing expansion temperature from 140 °C up to 160 °C in the final stage of the heat transfer process, shows no significant changes in gel content but foam density increased, cell size reduced follow by increased for both compression modulus and compressive stress. However, increasing blowing agent concentration also shows no changes in gel content but density and compression properties decreased follow by increased in cell sizes.

Acknowledgements

References

[1] Klempner, D., and Frisch, K. C. 1991. *Handbook of Polymeric Foams*, Hanser Publishers, New York.

[2] Gibson, L. J. and Ashby, M. F. 1997. *Cellular Solids: Structure and Properties*, Pergamon Press, Oxford

[3] Kirkland, C. 1980. *Crosslinked PE Foam Sheet: New Continuous Process Arrives*, Plastic Technology, 26, 89-92.

[4] Heck III, R. L., and Peascoe, W. J. 1985. *Blowing Agents*, Enc. Polym. Sci. and Tech., John Wiley and Sons Inc., New York, 2, 434-446.

[5] Albouy, A., Roux, J-D., Monton, D., and Wu, G. 1998. *Development of HFC Blowing Agents part I: Polyurethane foams*, Cell. Polym. 17, 75-92.

Rowland, F. S. 1989. *Choloflurocarbons and the Depletion of Stratospheric Ozone*, American Scientist, 77, 36-45.

[7] Sims, G. L. A., and Sipaut, C. S. 2002. *The Used of Polyfunctional Monomers in Compression-Moulded Low-Density Polyethylene Foam Formulations*, Blowing Agents and Foaming Process, Paper 14, RAPRA Technology, Heildelberg Germany.

[8] Sims, G. L. A., and Sipaut, C. S. 2001. *Crosslinking of Polyolefin Foams: I. Effect of Triallyl Cyanurate on Dicumyl Peroxide Crosslinking of Low-Density Polyethylene*, Cell. Polym., 20, 255-278.

[9] Hosoda, K., and Shina, N. 1972. U.S. Pat. 3 651 183 (*to Furukawa Electric Co., Ltd.*)

[10] Sagane, N., Nakata, S., Ueda, H., and Matsumura, T. 1973 U.S. Pat. 3 711 584 (*to Sekisui Chemical Co., Ltd.*)

[11] Shinohara, T., Takahashi, T., and Yamagudi, K. 1971. U.S. Pat. 3 562 367 (*to Toray Industries, Chemical co., Ltd.*)

[12] Asaaka, M., Tori, K., and Yamanaka, E. 1968. Jpn. Kokai Tokkyo Koho 43-22 674 (*to Hitachi Chemical Co., Ltd.*)

[13] ASTM D 2765-95. 1995. *Standard Test Methods for Determination of Gel Content and Swell Ratio of Crosslinked Ethylene Plastics*, ASTM, Philadelphia, Pa.

[14] ASTM D 3575-93. 1993. *Standard Test Methods for Flexible Cellular Materials Made from Olefin Polymers*, ASTM, Philadelphia, Pa.

[15] Sims, G. L. A., and Khunniteekool, C. 1995. *Cell Structure Development in Compression Moulded Polyethylene and Ethylene-Vinyl Acetate Copolymer Foam*, Cell. Polym III, RAPRA Technology, Paper 13, Coventry

[16] Sims, G. L. A., and Khunniteekool, C. 1996. *Compression Moulded Ethylene Homo and Copolymer Foam II. Effect of Processing Conditions and Crystallinity on Cell Structure Development*, Cell. Polym., 15,14 -29

[17] Sims, G. L. A., and O'Connor, C. 1997. *Blowing Agent Systems based on Azodicarbonamide*, Cell. Polym. IV, Paper 1, RAPRA Technology, Shawbury,