Laporan Akhir Projek Penyelidikan Jangka Pendek

Development And Properties Of Chemically Crosslinked Rubber Foams

No. Akaun Geran : 304/PKIMIA/634154

Disediakan oleh :

Coswald Stephen Sipaut @ Mohd Nasri
Pusat Pengajian Sains Kimia,
Universiti Sains Malaysia

Tempoh penyelidikan : **1 Jun 2003 hingga 19 April 2005**

Tempoh asal yang diluluskan : **1 Jun 2003 hingga 31 Mei 2005**

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Kandungan

Y. Bhg. Dato' Prof. Muhammad Idris Saleh
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RCMO

April 19, 2005

Y. Bhg. Dato' Prof.,

Laporan Akhir Projek Penyelidikan Jangka Pendek :
Development and Properties Of Chemically Crosslinked Rubber Foam
No. Akaun Geran : 304/PKIMIA/634154

Sukacita saya ingin majukan laporan akhir projek penyelidikan jangka pendek di atas untuk tindakan pihak Jawatankuasa Penyelidikan Universiti.

2. Saya ingin merakamkan setinggi terima kasih kepada pihak Jawatankuasa Penyelidikan Universiti terutamanya Jawatankuasa Sains dan Teknologi yang telah memberi peluang dan bantuan kewangan untuk melaksanakan projek penyelidikan ini.

3. Untuk makluman Dato' Prof., tempoh asal projek ini ialah 1 Jun 2003 hingga 31 Mei 2005. Bagaimanapun projek ini dapat disiapkan sepenuhnya pada 19 April 2005.

4. Saya amat berbesar hati untuk menyerahkan laporan akhir bersama satu hasil penerbitan daripada projek ini.

Sekian, terima kasih.

Yang benar,

....
(Coswald Stephen Sipaut @ Mohd. Nasri)

Perakuan daripada Pengerusi Jawatankuasa Penyelidikan Pusat Pengajian Sains Kimia

Projek telah disempurnakan dgn-jayanya.

23/4/05

Tandatangan Pengerusi
Jawatankuasa Penyelidikan
Pusat Pengajian Sains Kimia.

PROF. DR. BOEY PENG LIM
TIMBALAN DEKAN
(PENGAJIAN SISWAZAH & PENYELIDIKAN)
PUSAT PENGAJIAN SAINS KIMIA
UNIVERSITI SAINS MALAYSIA
11800 PULAU PINANG

Penemuan projek/Abstrak

Kesan penggunaan natrium hidrogen karbonat ($NaHCO_3$) sebagai agen peniupan dalam pengeluaran atau pembentukan span getah berangkaisilang secara kimia berasaskan SMR (getah semulajadi) dan EPDM (getah etilena propilena telah dipertimbangkan.

Terdapat tiga teknik pemprosesan digunakan dengan parameter dan keadaan pemprosesan yang berbeza. Kesan ini telah dicirikan sebagai fungsi kepekatan relatif dalam peringkat pepejal dan peringkat dispankan. Daripada data yang diperoleh, teknik pemprosesan "pemindahan haba" memberikan produk span yang baik dan tidak bergantung kepada asas bahan getahnya berbanding dengan teknik-teknik process "pemanasan-penyejukan" dan "pemanasan terus", keputusan juga mencadangkan bahawa suhu pematangan adalah 80 °C selama 10 minit dan suhu pengembangannya pula 140 °C – 160 °C selama 30 minit merupakan keadaan optimum dalam penghasilan span getah. Ia juga didapati bahawa pada kepekatan agen peniupan yang sama, kandungan gel yang meningkat (sebagai contoh kandungan sulfur meningkat) akan meningkatkan ketumpatan span dan menurunkan saiz sel. Tambahan lagi, pada kepekatan kandungan gel yang sama, peningkatan kepekatan agen peniup akan menunjukan penurunan ketumpatan busa dengan saiz sel yang membesar dan kebanyakannya ia menghasilkan struktur sel terbuka. keputusan juga mencadangkan bahawa pada kandungan gel yang minima (darjah rangkai-silang) bersesuaian untuk penghasilan busa (sebagai contoh 50% kandungan gel), Kepekatan agen peniup adalah optimum pada 3.5 phr yang mana ia menghasilkan saiz sel terkecil (0.311± 0.012 mm), homogen dan mempunyai struktur sel terbuka. Ia juga didapati bahawa ketumpatan busa bergantung kepada modulus lebur, nisbah pengembangan dan ketumpatan rangkai silang. Span dengan berstruktur sel tertutup ditunjukkan mempunyai set kemampatan yang rendah iaitu pembalikan asal yang cepat dengan modulus kemampatan yang tinggi berbanding dengan sel terbuka.

Kata kunci: Span (busa), rangkai silang, getah, saiz sel dan struktur sel.

Abstract

The effect of introduction of sodium hydrogen carbonate ($NaHCO_3$) as a blowing agent in the production or formation chemically crosslinked rubber foam based on SMR (natural rubber) and EPDM (ethylene propylene rubber) was considered. Three processing techniques were employed with different parameters and processing conditions. Their effects were characterized as a function of relative concentration in solid and foamed state. It is shown that heat transfer processing technique could obtain relatively good foam product independent of rubber based materials. It also suggested that curing temperature of 80 ^{o}C for 10 minutes and expansion temperature ranging from 140 ^{o}C – 160 ^{o}C for 30 minutes was the optimum conditions in the rubber foam production. It was found that at a similar blowing agent concentration, increasing in gel content (i.e. increasing sulphur content) will increased foam density and decreased in cell sizes. Furthermore, at similar gel content, increasing blowing agent concentration shows a decreased in foam density with larger cell size and produce mostly open cell structure. It was suggested that at a minimum gel content suitable for foam production (i.e. 50 %), the optimum concentration of blowing agent is 3.5 phr which produce significantly homogenous smaller cell size (0.311± 0.012 mm) with closed cell structure. It was also found that foam density highly dependent on melt modulus, swell ration and crosslink density. Moreover, foam with close cell structure showed significantly lower compression set (i.e. exhibit faster compression recovery) with higher compression modulus compared to open cell structure.

Keywords: Foam, crossliked, rubber, cell size and cell structure.

Penghargaan

Saya ingin mengucapkan syukur ke hadrat Allah SWT dengan izinNya, saya telah berjaya menamatkan projek penyelidikan ini pada masa yang ditetapkan. Setinggi penghargaan kepada ibu bapa saya (di Ranau, Sabah), isteri dan anak-anak saya atas kesabaran, ketabahan dan sokongan yang diberikan selama ini walaupun kadang-kala berjauhan dengan mereka. Rakaman setinggi-tinggi terima kasih saya ditujukan kepada Pengerusi and Ahli-Ahli jawatanKuasa Penyelidik Universiti, Universiti Sains Malaysia kerana peluang yang diberikan kepada saya untuk melaksanakan projek penyelidikan ini. Bantuan kewangan dan sokongan daripada bahagian penyelidikan dan pembangunan Universiti Sains Malaysia amat saya hargai. Seterusnya jutaan terima kasih saya ucapkan kepada Dr. Mohamad Nasir Mohamad Ibrahim diatas bantuan serta panduan dalam merangka kewangan penyelidikan ini dan Dr Zulkifli Ariff atas bantuan pengadunan sampel. Akhir sekali terima kasih saya ucapkan kepada pembantu pelajar yang bekerja dalam projek ini iaitu Cik Zakiah Abdullah dan Cik Norhayati Ahmad serta pelajar projek tahun akhir di bawah penyeliaan saya pada sidang akademik 2003/2004 dan 2004/2005 iaitu Salmah Bacosa, Shamsul Azila, Wan Ramlah, Che Nor Aini, Anisah dan Lai Yan Boon.

Laporan Kewangan

Hampir kesemua peruntukan yang diberi berjaya dibelanjakan bagi projek ini. Penyata perbelanjaan peruntukan kewangan yang diperoleh sehingga 31 Disember 2005 dari Unit Pembayaran, Jabatan Bendahari, USM adalah seperti berikut:

VOT	Diluluskan / RM	Perbelanjaan / RM
Vot 11000	2,047.00	3,102.35
Vot 21000	1,491.00	1,603.50
Vot 23000	300.00	7.35
Vot 27000	9,750.00	13,014.19
Vot 29000	5,500.00	1,119.60
Peruntukan yang diluluskan	19,088.00	18,846.99
Baki		RM 241.01

Output dan Faedah projek

(a) Penerbitan

Seminar : International Conference On Chemical and Bioprocess Engineering 27th – 29th August 2003, Universiti Malaysia Sabah, Kota Kinabalu.

(b) faedah-faedah lain

Penemuan teknik penghasilan span menggunakan pengembang bahan kimia tidak merbahaya iaitu natrium hidrogen karbonat (digiunakan dalam pembuatan kek) dan memandangkan penggunaan pengembang asal iaitu azodiacarbonzmide tidak dapat memasuki malaysia, maka cara ini menjadi satu altenatif untuk penghasilan span secara kimia dapat dilaksanakan.

(c) Latihan Gunatenaga Manusia

- (i) Pelajar Prasiswazah
  - Salmah Bacosa
  - Che Nor Aini
  - Shamsul Azila
  - Wan Ramlah
  - Anisah
  - Lai Yan Boon

Penerbitan I

C. S. Sipaut and G. L. A. Sims: "Effect of triallyl cyanurate on dicumyl peroxide crosslinking of low-density polyethylene foam formulation", Proceedings of International Conference On Chemical and Bioprocess Engineering 27th – 29th August 2003, Universiti Malaysia Sabah, Kota Kinabalu.

Proceedings of International Conference On Chemical and Bioprocess Engineering
27th – 29th August 2003, Universiti Malaysia Sabah, Kota Kinabalu

Effect of triallyl cyanurate on dicumyl peroxide crosslinking of low-density polyethylene foam formulation

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Abstract

This study investigates peroxide crosslinking of two low-density polyethylene grades of similar number-average molecular weight but differing molecular weight distribution. At gel contents typically associated with dicumyl peroxide (DCP) crosslinked foams, melt tensile properties of the solid matrix, foaming behaviour and foam properties were not significantly different. Further when crosslinking by DCP alone, stable foam formation is only achieved at gel contents higher than 50 % and foam density can be predicted on the basis of gel content for both LDPE grades.

The main work compared the effects of crosslinking systems based on DCP alone and DCP with the polyfunctional monomer, triallylcyanurate (TAC). The presence of TAC allowed specific gel contents to be achieved at significantly reduced DCP concentrations compared with DCP alone. It was also determined that cost-effective use of TAC was limited to approximately 0.5 – 0.75 parts per hundred resin.

When comparing results of solid and foamed samples of identical gel content, the presence of TAC significantly increases the melt modulus and reduces extensibility of the solid matrix compared with DCP alone and promotes a higher nucleation density in foam. This is considered to be due to a higher crosslink density in the network fraction which introduces complications in prediction of foaming behaviour if gel content alone is considered.

Keywords:

Gel content, melt, crosslink density and foam

Introduction

The major application of polyolefin foams is in thermal insulation, packaging, construction and sports and leisure industries [1]. Factors which enable them to penetrate many markets include closed-cell foams which exhibit buoyancy [2] and most importantly density reduction as improvements are seen in energy absorption, thermal conductivity and strength to weight ratio [3].

The most widely used crosslinked polyolefin foam is based on crosslinked polyethylene 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.

Traditionally, polyethylene can be crosslinked by peroxide involving free radical generation, which can result in intermolecular covalent bonding and three-dimensional network formation [4]. This molecular crosslinking is the most important structural modification [5] when used in the manufacture of polyolefin foams, which stabilises the cellular structure during expansion above the melting point of the polymer.

This work studies the effect of introducing polyfunctional monomer, triallyl cyanurate (TAC), into dicumyl peroxide (DCP) crosslinked low-density polyethylene (LDPE). Formulations were varied, the effect of crosslinked polymer matrix properties by gel content and melt strength. Selected formulations of similar gel content (with and without polyfunctional monomer) were foamed and matrix polymer physical and mechanical properties were compared with foaming behaviour and foam properties in an attempt to correlate the results.

Experimental

Materials

Base polymer

Formulations were based on Stamylan 1808 supplied by DSM which is highly branched low-density polyethylene with a density of 918 kg m^{-3} and melt flow index of 8 dg min^{-1}.

Crosslinking agent

The crosslinking agent used was dicumyl peroxide (DCP) selected for its suitable decomposition attributes with a half-life of 10 hours at 115 °C and 1 minute at 171 °C [2]. This provides convenient dissociation behaviour for compounding into the polymer with little or no decomposition and a satisfactory rate of crosslinking for both batch and continuous processing at elevated temperature. DCP was used in a modified form. Perkadox BC-40kd, manufactured by AKZO Chemicals, consisted of 40% DCP in inert clay carrier.

Polyfunctional monomer

The polyfunctional monomer used was triallylcyanurate (TAC) with three nominal functional group and manufactured by Degussa with a melting point of 27.3 °C.

Blowing agent

The chemical blowing agent used for foaming studies was DP45/1, manufactured by Bayer AG. It is based on activated azodicarbonamide (ADC) and formulated for blowing polyolefins by compression moulding techniques. The system was reported (6) to contain ZnO as activator and a co-blowing agent (oxybisbenzenesulphonylhydrazide) to reduce the ADC decomposition temperature from approximately 220 °C (2) to more suitable levels (approximately 165 °C). All foaming studies used a fixed concentration of 8.0 phr DP45/1.

Sample preparation

Compounding

Mixing was conducted on a thermostatically controlled, electrically heated two-roll mill with front and back rolls rotating at 20 and 24 rpm respectively. Roll temperatures were initially 115°C (slightly higher than the melting point of LDPE) to melt and continuously band the LDPE charge. Roll temperatures were then reduced to 105°C (just below the melting temperature) to form a rubbery opaque LDPE band which facilitated handling during compounding. Polyfunctional monomer was added (where applicable) cutting and folding for 5 minutes, followed by progressive addition of the blowing agent (where applicable) over a period of 10 minutes. DCP was added last to minimise premature dissociation and crosslinking over a period of 3 minutes with continuous cutting and folding.

Solid Crosslinked Matrix for Melt Tensile Measurements

45 g of compound were placed in a square plate mould pre-heated at 165°C to produce sheet approximately 1.5 mm thick, both inner surfaces of the mould being covered with PTFE foil to obtain good release and surface finish. Samples were then compression moulded at 14 MPa for 20 minutes (unless otherwise stated). The mould was then water-cooled to 30°C under pressure. The crosslinked polyethylene sheet was then removed from the mould and stored at 23 ± 2°C and 50 ± 5 % relative humidity for a period of 24 hours before testing.

Foam production

Foaming was carried out by a two stage heat and chill technique in a pre-heated 10 mm deep mould lined with PTFE foil. After charging, the foamable compound was compression moulded at 14 MPa for 20 minutes at 165°C after which it was water-cooled under pressure to 30°C. After release of pressure, the partially expanded moulding was immediately transferred to a circulating hot air oven at 130°C for 20 minutes to gradually complete the expansion.

Characterisation

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 [7].

Melt tensile measurements

Melt tensile behaviour of the solid crosslinked matrix was performed at 130°C (the final expansion temperature in the heat and chill process) to assess expansion resistance. Dumbbell specimens, die cut from solid crosslinked matrix, were placed in the jaws of an Instron tensile testing machine fitted with an environmental chamber set at 130°C. Samples were conditioned for 10 minutes before commencing the test. The gauge length was set at 30 mm and the crosshead speed at 20 mm min^{-1}. Results allowed assessment of melt modulus (Young's modulus of the melt), ultimate strength and elongation at break of the matrix.

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 [8].

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Cell imaging and cell size determination

Cellular structures of foam specimens were assessed from Scanning Electron Microscope (SEM) images [9]. The mean apparent cell size was obtained from SEM images by a modified cell count method described elsewhere [10].

Foam compression properties

Parallelepiped specimens (free of defects and skins) 50 mm x 50 mm with an average thickness of 20 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 were reported as the mean of ten measurements.

Results and Discussion

Croslinking behaviour on traditional LDPE/DCP system

Initially, moulding or curing time of crosslinked LDPE samples was determined by using 0.5 phr DCP alone and maintaining moulding temperature of 165 °C and pressure of 14 MPa whilst cycle time was varied up to 60 minutes. Figure 1 shows that increasing moulding times resulted in a sharp increase in gel content up to 10 minutes which levelled off after longer times. This suggested that full dissociation of DCP and subsequent crosslinking generally takes place during the first 10-15 minutes. To ensure that the compression moulding time was long enough to complete the reaction, a 20 minute cycle was used for all subsequent work which is in agreement with other workers [11].

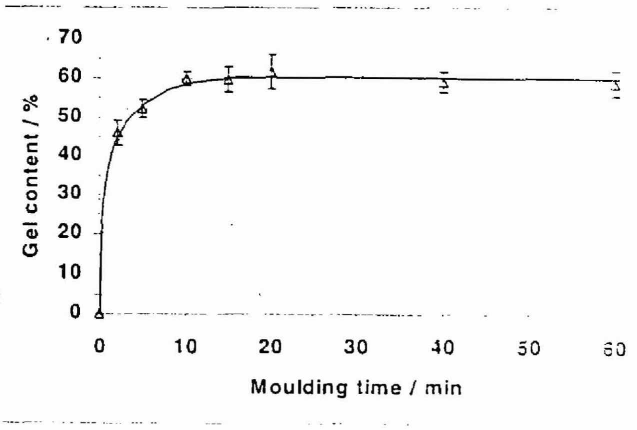

Figure 1- The dependence of gel content on moulding time

To establish the crosslinking behaviour of traditional crosslinking system, the results of gel content for crosslinked LDPE samples as a function of DCP concentration (after curing) are shown in figure 2. Generally the results showed that increasing DCP concentration is accompanied by an increase in gel content.

This phenomenon can be explained as the sharp initial increase in gel content was attributed to higher amounts of crosslinking agent (DCP) generating primary and secondary polymer radicals in sufficient concentrations to significantly increase the probability of network formation (rather than significant proportions of two-dimensional molecular extension that was suspected at low DCP concentrations) thus leading to the higher gel content.

The levelling off in gel content as the DCP concentration increased to 1.0 phr was assumed at this stage to be due to increased crosslinking primarily as a result of an increase in intra- rather than inter-molecular crosslinking. Similar trends have been observed by other workers [12]. This hypothesis is supported by the increase in melt modulus and reduction in elongation at break as the DCP concentration increased from 0.5 to 1.0 phr as illustrated in figure 3.

Having established the crosslinking behaviour with DCP alone (traditional system), the work was extended to assess the effect of the addition of triallyl cyanurate (TAC), a polyfunctional monomer containing allylic double bonds which form radicals that are more stable than alkyl radicals [13].

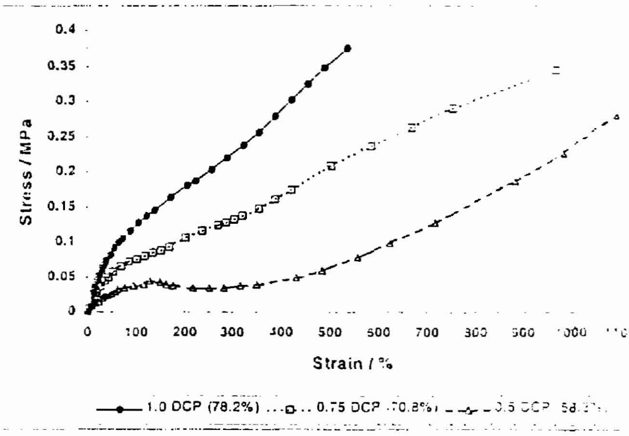

Figure 2- Effect of DCP concentration on gel content

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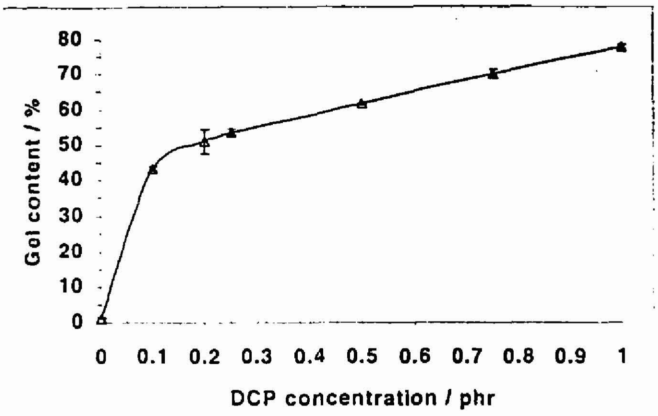

Figure 3- Effect of DCP concentration on stress-strain curves (DCP concentration in ppm, gel contents in parentheses)

Effect of introducing TAC into crosslinking system

The effect on gel content of varying peroxide concentration at a fixed TAC concentrations of 0.5, 2.0 and 5.0 phr are shown in figure 4 (includes data from figure 2). The results show that all formulations incorporating TAC showed a higher crosslinking level at each particular DCP concentration than when using DCP alone. The increase in gel content was relatively rapid up to 0.1 phr DCP, whereas it was much more gradual at higher DCP concentrations. The initial steep rise in gel content suggested a significant increase in the probability of three dimensional network formation. At a DCP concentration of 0.1 phr in the absence of TAC a gel content of approximately 42 % was achieved (figure 2), whereas in the presence of 0.5 phr TAC the gel content was 54 %. It was evident that TAC acted as a crosslinking promoter because of the dramatically increased crosslinking efficiency. This suggested that the presence of TAC increased the crosslinking level by making more effective use of radicals generated by DCP and that TAC possibly incorporated into the polyethylene structure.

This is supported by other workers [14] who suggested that TAC was very efficient in producing high yields of radicals during irradiation and, as a result, this helped in achieving better graft copolymerisation of monomer to polyethylene and enhanced the crosslinking efficiency. This trend was also observed by Simunkova *et al* [15] who generally showed that by using similar concentrations of DCP in crosslinking polyethylene with and without TAC, the sample containing TAC gave higher crosslinking levels than DCP alone.

However within the limits of experimental error, the results tended to indicate that at a specific DCP concentration (in the presence of TAC), the gel content appeared to be relatively independent of the TAC concentration in the range 0.5 to 5.0 phr. This has potential implications on the commercial use of TAC as a crosslinking promoter in that a concentration greater than 0.5 phr appears to offer no great advantage. Further, higher TAC concentrations are later shown to be less effective.

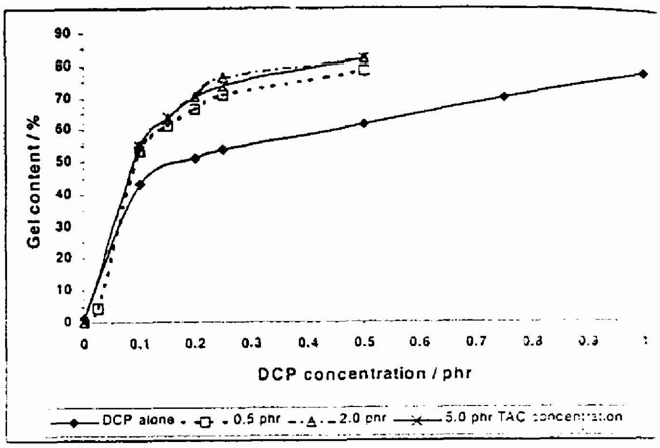

Figure 4 - The effect of TAC and DCP concentration on gel content

The phenomenon seems to suggest that as the TAC concentration is increased above a critical concentration, no corresponding meaningful increase in gel content is obtained. This would strongly suggest that some form of TAC oligomerisation has occurred. It is envisaged that, dependent on the intimacy of the mix, TAC would be added into the chains either as single, double, or treble molecules or possibly TAC polymerisation occurred. This hypothesis was supported by separate studies, which showed that compression moulding TAC alone gave a gel content of only 1 % whereas compression moulding of TAC and DCP (in the absence of polymer) in the ratios 1: 8 and 1: 20 gave gel contents of 97.6 and 98.8 % respectively. These findings strongly suggest that TAC itself is not a crosslinking agent but promotes crosslinking by being able to act as a radical trap and stabiliser which is capable of being incorporated efficiently into the network in the presence of free radicals produced by dissociation of DCP.

Consequently it seems logical to assume that a certain limiting concentration of TAC is required to effectively increase the crosslinking efficiency but at higher concentrations, dimerisation to polymerisation of the TAC molecules occurs thus the additional TAC is not effective in further network formation. This aspect required further investigation but the hypothesis is generally supported elsewhere [15]. They found that simultaneous polymerisation of TAC monomer occurred especially at higher TAC contents. This then diminishes the crosslinking effectiveness.

To investigate the limiting effect of the addition of TAC, crosslinked polyethylene samples were made using a fixed concentration of 0.25 phr DCP and varying the crosslinking promoter concentration in the range of 0.1 to 5.0 phr. The

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concentration of 0.25 phr DCP was selected due to the fact that a reasonable degree of crosslinking was obtained with DCP alone (approximately 53 % gel content). Figure 5 appears to indicate that there are three regimes of gel content behaviour as the concentration of the crosslinking coagent increases.

Up to 0.5 phr of TAC, the gel content rises approximately linearly suggesting efficient use of the crosslinking promoter. In the second regime, from approximately 0.5 to 2.0 phr TAC, the gel content continues to rise but at a markedly reduced rate. This suggests that for cost-effectiveness, a concentration ranging from 0.5 to 0.75 phr would most suitable. Finally there is a strong indication that, within the limits of experimental error (± 3 % of the mean), higher concentrations of TAC (5.0 phr) actually result in a marginal decrease in gel content. The reduction was more significant when the TAC concentration was increased to 10.0 phr which resulted in a gel content of approximately 67 %. However, such a high concentration is of no further interest in this work.

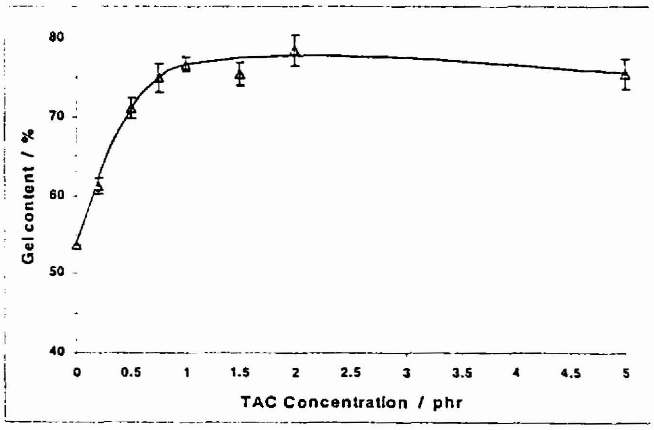

Figure 5- Effect of TAC concentration on gel content using a fixed concentration of 0.25 phr DCP

These findings strongly suggest that at a relatively low concentration (~ 0.5 phr) the TAC is evenly spatially dispersed amongst the polymer chains and thus contributes most efficiently to a gel content increase. On the other hand, it was previously shown that TAC has the propensity to polymerise in the presence of free radicals. It may therefore be envisaged that, above the limiting spatial concentration, higher local concentrations of TAC molecules could result in oligomerisation within the network. These additional TAC molecules are therefore wasted and do not contribute to increased efficiency of crosslinking. This hypothesis explains the levelling off and slight reduction in gel content at TAC concentrations greater than 1.0 phr.

To illustrate this phenomenon further, figure 6 shows that when varying the DCP concentration at TAC concentrations of 0.0, 0.5, 2.0 and 5.0 phr at any specific gel content, melt modulii increased significantly with increasing TAC concentration. However, at gel contents above 70 %, the system containing 5.0 phr TAC appears to divergently increase. The results suggested that the increased melt modulus are attributed to higher three dimensional network formation i.e. higher crosslink density which gave better stress distribution in the sample.

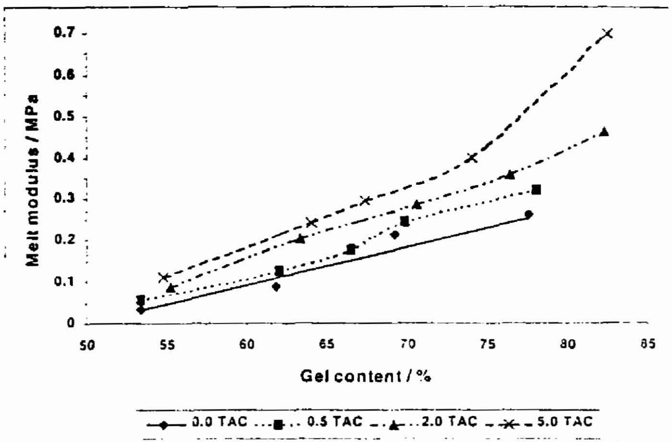

Figure 6 – Dependence of melt modulus on TAC concentration (using 0.25 phr DCP)

Foaming and their dependence on gel content and melt modulus

Traditionally, other workers [9,11,16] generally used gel content as a basic indicator to determine foam density. They showed that on traditional crosslinking (i.e. crosslinked with peroxide alone), different base polymers gave approximately similar foam density at a similar gel content. Figure 7 shows the basic curve of foam density as a function of gel content on LDPE crosslinked with DCP alone. The curve indicates a progressive decrease in foam density as the gel content increases to 53 % followed by increases in foam density as the gel content increases further. The high foam density at 53 % gel content was attributed to insufficient melt strength to retain the bulk of the gas i.e. crosslinking was not sufficient to stabilise the foam against thermal collapse. These results supported those of other workers [16] who indicated that stable foam formation is only achieved at gel contents higher than 50 %.

The slight increase in foam density above 53 % gel content is related to higher gel content giving higher melt modulus and thus greater resistance to expansion with increasing peroxide concentration. Consequently, density reduction was limited in accordance with the principles propounded by Mahapatro *et al* [17]. This interpretation is supported by the melt tensile measurements as described earlier (figure 3).

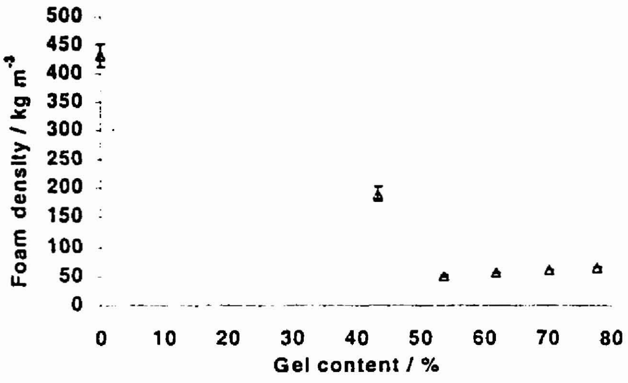

Figure 7 – Effect of gel content on foam density for DCP crosslinked LDPE

The theory propounded by Mahapatro *et al* [17] suggested that foam density is directly related to melt modulus at equilibrium expansion. To examine the validity of this theory, formulations crosslinked with DCP alone over the range of foamable gel contents (figure 8) show that the gel content has an approximately linear relationship to melt modulus. This indicates that above the limiting gel content for foam formation (shown to be approximately 50 % gel which agrees with the previously quoted minimum for stable foaming), either gel content or melt modulus should give a reasonable indication of foam density for material crosslinked by DCP alone.

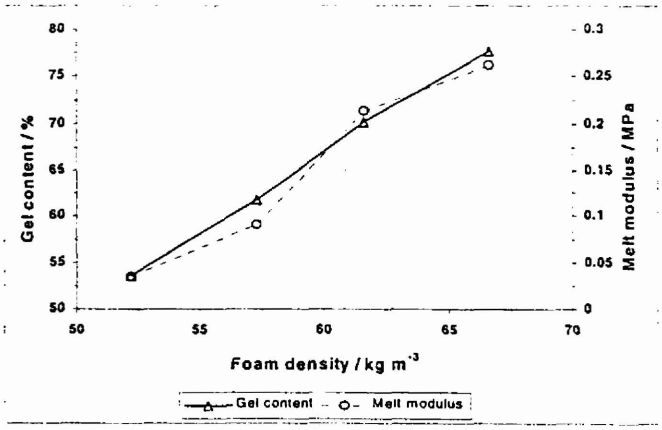

Figure 8 – Effect of gel content and melt modulus on foam density

To assess the phenomenon further, the densities of foam formulations giving gel contents of approximately 62 %, 70 % and 77.5 % for crosslinking system containing DCP alone and DCP/TAC are shown in figure 9. Generally, within the limits of experimental error, at any specific gel content, the higher the TAC concentration, the higher the foam density. The results also showed that when using DCP alone or with 0.5 phr TAC, an approximately linear response was observed between foam density and gel content. In the presence of 2.0 phr TAC, the slope of the curve up to approximately 70 % gel content is similar to DCP alone. However, at higher gel contents, the slope appears to divergently increase (compared with DCP alone).

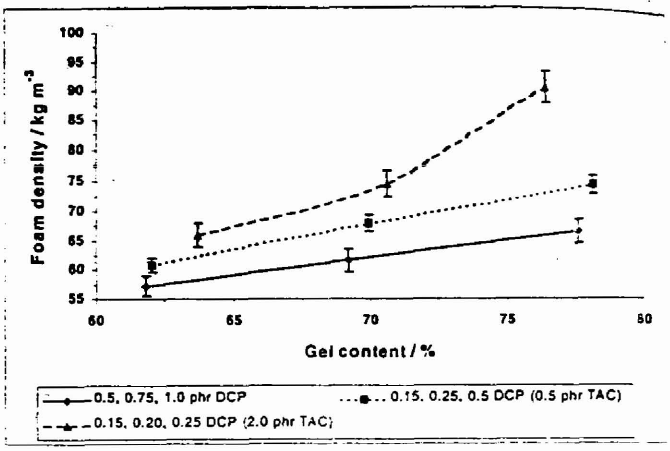

Figure 9 – Effect of formulation on foam density at similar gel content

Thus gel content is not a suitable parameter to define foam behaviour when TAC is introduced into the system. The foam density increases with increasing TAC which strongly suggests that increasing TAC at any specific DCP concentration seemed to give higher crosslink density. This in turn would explain the increases in melt modulus (restricting cell expansion and limiting foam density reduction) with increasing TAC concentration as indicated in figure 10.

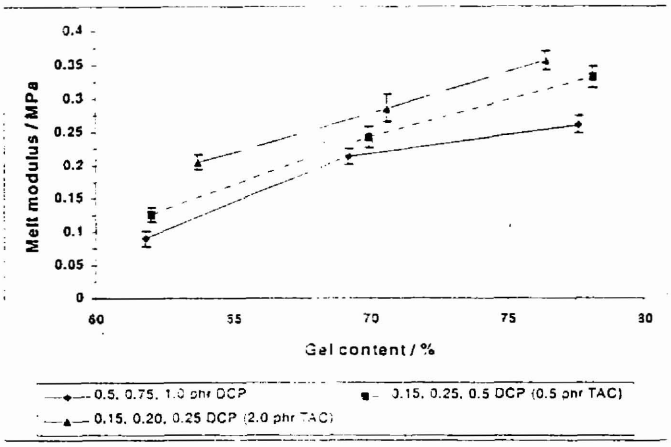

Figure 10- The effect of formulation on melt modulus at similar gel content

Figure 11 gives a wealth of information. It is important to understand that each series of three separate results at each nominal gel content represents an adjustment in DCP concentration to give the nominal gel content in the presence of 0, 0.5 and 2.0 phr TAC (increasing TAC concentration produces progressive increase in melt modulus and foam density). The result positively indicates that gel content is not a suitable indicator to predict foam density (as previously suggested). However, if all data points could be considered as part of a mastercurve then the Mahapatro theory appears to hold some validity.

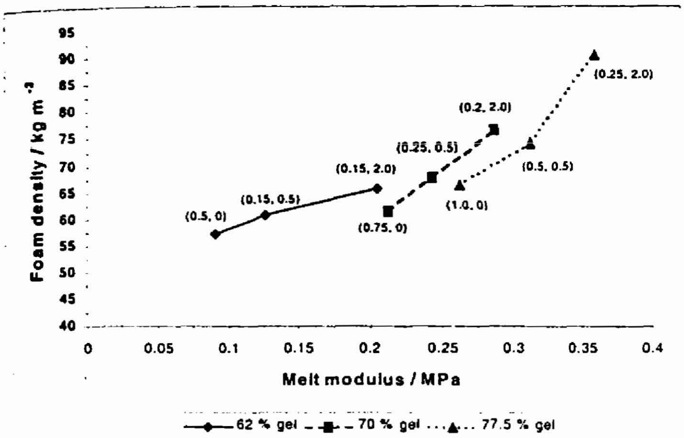

Figure 11 – The dependence of foam density on melt modulus at specific gel contents (DCP.TAC ratios[phr] shown in parentheses)

However, when experimental errors are taken into account, three separate curves are strongly suggested. It appears that the Mahapatro theory may be valid in the presence of TAC but only at a specific gel content. Overall, however, the incorporation of TAC in the crosslinking system seems to invalidate general application of the Mahapatro theory. It is considered at this point that crosslink density may contribute to this phenomenon which is the subject for further investigation.

Foam properties

Since properties are density dependent, further investigation attempted to compare various parameters of selected formulations at similar foam density as shown in table 1. Generally, within the limits of experimental error, formulations containing DCP/TAC or DCP alone showed no significant difference in foam mechanical properties or cell size at any specific foam density (nominally 57, 62 and 67 kg m^{-3}). There was however, a slight hint that cell size may reduce with increasing TAC concentration. Table 1 summarises a number of points, the most important of which is that foam density appears to control compression modulus, compressive stress at 50 % strain and cell size irrespective of formulation. When first viewed, this appears to be a strange result as at any specific density, the gel contents vary significantly. However, at specific foam densities and similar cell sizes, not only is the volume of polymer in the foam the same but also cell walls should be of similar thickness given typical pentagonal dodecahedral cell structures.

The results also indicate, as was expected, that an increase in foam density was accompanied by a significant increase in compression modulus and compressive stress at 50 % strain and reduced mean cell size. It is also noted that foam density was not related to gel content when TAC was introduced into the formulation. This graphically confirms that gel content alone is not a suitable parameter to predict foaming characteristics when crosslinking promoters are used. Similarly, the results also show that melt moduli do not correlate with foam density. This strongly suggested that the theory of Mahapatro *et al* [17] was inadequate to define foaming behaviour when the components of the crosslinking system are changed and more specifically when crosslinking promoters are used in the formulation.

Table 1 Effect of formulation on foam properties at similar foam density

DCP / phr	TAC / phr	Gel content / %	Density / kg m^{-3}	Compression modulus /MPa	Compressive stress at 50% strain / MPa	Cell size / mm	Melt modulus / MPa
0.500	None	61.4 ± 1.6	56.3 ± 1.2	1.17 ± 0.06	0.173 ± 0.007	0.169 ± 0.012	0.090 ± 0.004
0.125	0.5	56.2 ± 1.6	57.3 ± 0.9	1.19 ± 0.05	0.176 ± 0.005	0.157 ± 0.010	0.090 ± 0.003
0.750	None	69.2 ± 1.8	61.6 ± 1.7	1.52 ± 0.07	0.203 ± 0.005	0.135 ± 0.010	0.213 ± 0.012
0.150	0.5	61.4 ± 1.8	60.9 ± 1.4	1.55 ± 0.06	0.210 ± 0.003	0.130 ± 0.013	0.126 ± 0.011
0.100	2.0	55.2 ± 1.6	62.0 ± 1.4	1.55 ± 0.04	0.210 ± 0.004	0.130 ± 0.011	0.090 ± 0.003
1.00	None	77.6 ± 1.6	66.6 ± 1.6	1.81 ± 0.08	0.255 ± 0.010	0.115 ± 0.009	0.262 ± 0.013
0.25	0.5	69.9 ± 1.5	68.0 ± 1.1	1.95 ± 0.09	0.268 ± 0.009	0.108 ± 0.011	0.243 ± 0.008
0.15	2.0	62.3 ± 2.0	66.0 ± 1.2	1.90 ± 0.08	0.254 ± 0.008	0.102 ± 0.012	0.208 ± 0.009

Conclusions

It can be concluded that introduction of the polyfunctional monomer, TAC, into the crosslinking system allows significant reduction in peroxide concentration to achieved specific gel contents. Foaming behaviour cannot be predicted on the basis of gel content or melt modulus when triallylcyanurate is included in the crosslinking system. Significantly, the limiting TAC concentration for cost-effective usage ranges from 0.5 to 0.75 phr in the presence of 0.25 phr DCP. The difference in foaming behaviour of LDPE crosslinked with or without TAC may be attributed to crosslink density. Furthermore using higher proportions of TAC in the formulation can result in self-polymerisation of TAC which significantly reduces the efficiency of TAC usage in promoting crosslinking.

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Lampiran Abstrak-abstrak Penyelidikan Projek Tahun Akhir

Abstrak I: Kajian Terhadap Kesan Peroksida-peroksida Ke Atas Pembentukan Rangkaisilang Polietilena Ketumpatan Rendah (LDPE).

Abstrak II: Mengkaji Parameter-parameter Optimum Campuran PVC Dengan DINP Bagi Penghasilan PVC Busa.

Abstrak III: Mengkaji Kesan Monomer Pelbagai Fungsi Terhadap Rangkaisilang LDPE Dengan Peroksida, DCP.

Abstrak IV: Kesan Dibenzoil Peroksida Terhadap Pembentukan Busa Polivinil Klorida (PVC) Berangkaisilang.

Abstrak V: Formation Of Crosslinked Polyvinyl Cloride (PVC) Foam In The Presence Of Triallyl Cyanurate (TAC).

Abstrak VI: Polyfunctional Monomer Crosslinking Efficiency In PVC System.

ABSTRACT

This study was carried out to investigate the effect of crosslinking formations by two different peroxide, that are dicumyl peroxide (DCP) and 2,5-dimethyl-2,5-di(tert-butyllperoxy)hexane-3 (T145) on low density polyethylene (LDPE). The temperature and the moulding time of the mixture of 0.5 phr (part per hundred) resin LDPE with each of the peroxide were determined. The results indicated the mixture's properties and were used to compare which one of both modified polymer of LDPE was better in quality. The mixture of LDPE with DCP was heated at two temperatures, 165 °C and 185 °C. But the mixture of LDPE with T145 was heated only at 185 °C because of it's higher half life time. It was been found that for the mixture of LDPE and DCP, the time for the crosslinking to be completed were faster at 185 °C than at 165 °C through the gel content were the same. This showed that the crosslinking of the mixture was more efficiency at 185 °C. LDPE and T145 mixture, the percentage of gel content produced was higher than in the LDPE and DCP mixture at the same temperature. So it was preferable for its quality.

Keywords : LDPE, crosslinking, DCP, T145 and gel content

ABSTRACT

The purpose of this research is to determine the optimum parameters to produce polyvinyl chloride (PVC) foam by mixing PVC powder and di-isononyl phthalate (DINP) as the main materials. The mixing has been done at the room temperature and atmosphere pressure using electric stirrer with the speed of 300 rev/min. From the results, the optimum parameters that were expected in producing PVC foam were in ratio of 10 : 8, PVC with DINP at temperature 120 °C for 20 minutes. The characterization testing shows that percentange of gel content and glass transition temperature (Tg) will increase when the time and temperature of heating were increased. The exact mechanism reaction of PVC and DINP cannot be convinced by using Fourier Transfer Infrared (FTIR) testing.

Keywords : Polyvinyl chloride (PVC), DINP plasticizer, foam, crosslink,DSC.

ABSTRACT

This study investigates the effect of polyfuntional monomers into dicumyl peroxide (DCP) crosslinking systems for low-density polyethylene. The main work compared the effects of crosslinking system based on DCP alone and DCP with polyfuntional monomers, TAC, DALP and TMPTMA into LDPE base polymer. The effect of crosslinking was investigated in term of percentage of gel content. Degree of crystallinity and melt temperature. It is shown that TAC promotes network formation more efficiently than DALP and TMPTMA. The presence of TAC allowed specific gel contents to be achieved at significantly reduced DCP concentration compared with DCP alone. For crystallinity and melt temperature, it is shown that no significant differences in a crosslinked of DCP with or without polifuntional monomers was observed.

KEY WORDS : Crosslinking, LDPE, DCP, polyfuntional monomers, gel content.

ABSTRACT

The purpose of this reseach to determine the effect of peroxide concentration as an agent of crosslinking for Polyvinyl chloride (PVC) foam production. Various parameters in this system also been determined such as blowing agen concentration. heating time and processing temperature. Sampel were characterize using various technique such as, gel content determination, Differential Scanning Calorimeter (DSC). Fourrier Transfered Infrared (FTIR), Scanning Electron Microskop (SEM) and tensile strength. Gel content studies show that as peroxide concentration increased from 0.25 phr to 0.75 phr, gel content increases, however it become constant at higher peroxide concentration. From crosslinked samples, it was observed that heating time suitable for processing is 15 minutes at 120 °C where no degradation occurs. Glass transition temperature value decreasing by increasing peroxide concentration. Futhermore. FTIR studies shows that no difference between crosslinked and non crosslinked sample. In SEM analysis. the production of air bubble (cell) are significantly less. Lastly, there is no significant trend in mechanical properties as the peroxide concentration increased. From the result observed. it can be suggested that mixing method in producing PVC foam has to be improved.

Key words: Polyvinyl chloride (PVC). crosslink. peroxide.

Foam .tensile strength

ABSTRACT

The purpose of this research was to study the formation of croslinked polyvinyl chloride (PVC) foam in the presence of triallyl cyanurate (TAC). Various parameters were considered such as pressing time, peroxide concentration and blowing agent concentration. Gel content percentage, Fourier Transferred Infra Red (FTIR), tensile strength and Scanning Electron Microscope (SEM) were used for samples characterizations. From crosslinked samples, it was observed that curing time suitable for processing is 5 minutes at 170 °C where no thermal degradation occurred. Gel content determination showed that the gel content increased as peroxide concentration increased from 0.25- 0.5 phr as well as TAC concentration of 0.5-1.0 phr. However, the gel content became constant at higher peroxide and TAC concentration. FTIR analysis showed no difference between crosslinked and non crosslinked samples whereas no significant trend in mechanical properties was concluded in the tensile strength. In SEM analysis, the foam collapsed after being heated for 80 minutes at 160 °C in an air oven. From the results obtained, it is recommended that the mixing method in PVC foam formation be improved and usage of chemical blowing agent with higher decomposition temperature.

Key words: Crosslink, Polyvinyl Chloride (PVC), Triallyl Cyanurate (TAC), Foam, Peroxide, Tensile Strength.

ABSTRACT

This study was aimed to understand the efficiency and differences in properties of the PVC sheet of crosslinked using two different polyfunctional monomers, namely triallyl cyanurate (TAC) and trimethylolpropane trimethacrylate (TMPTMA). Initial test was carried out to determine the best curing time for the samples. The samples containing TAC or TMPTMA was cured by hot press at 160 °C at 160 kpa for 10 minutes. The crosslinked PVC sheets were characterized by gel content determination, tensile testing and infrared analysis (FTIR). Results indicating that TMPTMA, a polyfunctional monomer with acrylic group, was better a polyfunctional monomer than TAC, a polyfunctional monomer with allylic functional group.

Keywords: PVC, crosslinking, TAC, TMPTMA, polyfunctional monomer (PFM).