



CHARTER II

BACKGROUND IN EVA FOAMING PROCESS

2.1 Foaming Process

2.1.1 Theory of the Foaming Process

The foaming(1) process consists of three steps:

step 1 Bubble Initiation : the creation of small discontinuities or cells in a fluid or polymer-phase.

step 2 Bubble Growth : the growth of these cells to a desired volume.

step 3 Bubble stabilization : the stabilization of the resultant foam structure by physical or chemical means.

1) Bubble Initiation

This process is occurred by serveral sources:

a) Dissolved gases that are normally present in the liquid or polymer solution and force into supersaturation by increased temperature.

b) Low boiling liquids that are incorporated into the system as blowing agents and force into gas phase by increased temperature or decreased pressure.

- c) Gases produced as blowing agents.
- d) Chemical blowing agent that decompose thermally to form a gas.

Bubble nucleation is affected by a number of condition. Physically, the effect of temperature, pressure, and in some case humidity are fairly obvious. Other important parameters are surface smoothness of the substrate, surface characteristics of filler particles, presence and concentration of certain surfactants or nucleators, size and amount of second-phase liquid bubbles, and the rate of gas generation. The number and size of these gas bubbles may be another important factor in bubble development.

2) Bubble Growth

The initial bubble is ideally a sphere that grows as a result of interaction of the difference pressure (ΔP) between the inside and outside of the cell and the interfacial surface tension (γ) the radius (r) of the bubble at equilibrium is related to these factors as shown in equation

$$\Delta P = 2\gamma / r$$

The differential pressure is larger for a small bubble at a fixed surface tension. Accordingly, smaller bubbles tend to equalize these pressures by growing faster, breaking the wall

separating the cells, or by diffusion of the blowing agent from the small to the large cells as indicated by equation.

$$\Delta P_{1,2} = 2\gamma (1/r_1 - 1/r_2)$$

The rate of growth of the cell depends on the viscoelastic nature of the polymer phase, the blowing agent pressure, the external pressure on the foam, the cell size, and the premeation rate of blowing agent through the polymer phase.

3) Bubble Stabilization

Maintaining bubble distribution at a low level as in high density foams favors the lowest surface energy spherical cell that is readily stabilized. At lower densities the cell-wall stability required to produce a polymer foam is achieved by careful control of the factors that influence membrane thinning. One of the factor is a viscosity factor. The viscosity can be increased by several ways such as, by chemical reactions which molecular weight is increased through polymerization or by cross-linking or by temperature reduction

2.1.2 Effect of Foaming Process on Properties

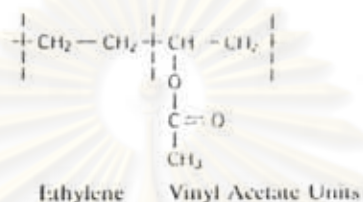
The properties of a foamed polymer depend on parent polymer, additives and form structure. The conditions or states, of the polymer phase, eg,

orientation, crystallinity, previous thermal history, and its chemical composition, determine the properties of that phase. Density has the most important influence on mechanical properties of polymer foam of given composition. The cell structure of a particular polymer would require the size, shape, and location of each cell. Cell size has been characterized by measurements of cell diameter. Cell shape is governed predominantly by final foam density and external forces exerted on the foam structure before its stabilization in the foaming state. In a foam prepared without external forces the cells tend to be spherical or ellipsoidal at gas volume less than 70-80% of the total volume, and exhibit the shape of packed regular dodecahedra at greater gas volumes. In the presence of external force, the cells may be elongated or flattened.

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2.2 Ethylene-Vinylacetate Copolymers

When ethylene (3) is copolymerized with vinylacetate, a special rubber is obtained, namely ethylene-vinylacetate or EVA. Its polymer structure is shown below.



Presence of vinylacetate units in this polymer chain suppresses the crystallization of polyethylene and also its melting point. The EVA copolymers with 5-40% vinylacetate content become progressively more flexible and rubbery. At higher vinylacetate content up to 40-70% , they are amorphous rubber-like materials. However, other structural features, particularly the average molecular weight and short chain branching, also have an important effect on the properties. The ability to vary the degree of crystallinity of EVA copolymer is one of the most importance in controlling properties for particular end-uses. Impact strength, stress crack resistance and swelling resistance will be increased when increasing vinylacetate contents.

2.2.1 Compounding of EVA Copolymer

The properties of EVA copolymer can be modified by compounding and vulcanization for commercial products (3). It is possible to blend EVA with diene polymers like NR or SBR, to improve the weather resistance of the latter. Since EVA is a fully saturated polymer, it can not be cross-linking with sulphur and accelerators. Instead, peroxide have to be used and their suitability depends on the processing conditions (decomposition, temperature, odour). Peroxides alone do not usually give a sufficient state of cure, and therefore, special coactivators have to be used. Some coagents or coactivators, such as triallyl cyanurate, triallyl phosphate, has to be used to improve cross-linking density and give a sufficient state of cure without raising the peroxide concentration. Some reinforcing fillers, such as neutral kaolin, have to be used when EVA compound is formulated due to its lack of self-reinforcing properties. Since the EVA have a relatively low viscosity, the high filler loadings should be avoided. In general, no protective agents are required while the use of softeners is necessary. Paraffinic oils with very low unsaturation are most frequently used, while very highly saturated paraffinic oils are particularly well suited. Ester and ether-based plasticizers such as dibutylphthalate, dioctyladipate and dioetylsebacate are used to improve low temperature

flexibility, filler dispersion, and the extrudability or calenderability. Stearic acid, pentaerythritol tetrastearate as well as fatty alcohol residues are also used.

2.2.2 Properties of EVA Vulcanization

Properties of EVA vulcanizates (3) depend on the influence of components in the formulation. With reinforcing fillers, high tensile strengths can be obtained, whereas the tear resistant leaves much to be desired. The abrasion resistance also, does not compare with that of good diene rubber vulcanizates, and the elasticity of EVA vulcanizates is oftenly obscured by a stiffening effect due to the thermoplastic character of the copolymer. The compression set is also influenced by the residual thermoplastic behavior, and it is therefore poor at room temperature. At higher temperature, however, the compression set becomes extremely low. EVA vulcanizates have an excellent degradation resistance in hot air and extremely good weather and ozone resistances. For many applications, EVA vulcanizates are sufficiently resistant to swelling in aliphatic oils and this resistance can be improved by increasing the vinylacetate content. Because of the polar nature of EVA, its electrical resistivity is considered only in some applications. By using hydrated alumina as filler, halogen-free compounds can be formulated for cable insulations with a good flame resistance.

2.3 Chemical Blowing Agents

The term "blowing agent", in the broadest sense denotes an inorganic or an organic substance used to incorporate in a polymeric materials to produce a foam structure. Chemical blowing agent are stable at room temperature, but decompose at higher temperature with liberation of gaseous products. The decomposition procees is generally exothermic and irreversible and takes place within a specific, narrow temperature range.

The primary criterion (4) governing a choice of blowing agents, for expanding a particular plastics material is its decomposition temperature. The blowing gas must be evolved within a defined temperature range, which should not be too large, and related to the processing temperature of the plastics material. The blowing agent must not decompose too spontaneously, as in the case of an explosive, otherwise heat build up and combustion could occur due to the heat generated by the exothermic reaction. The gas formed should, if possible, consists of nitrogen and contain no explosive constituents. The blowing agent should be easy to incorporate and to disperse evenly in the plastic materials concerned. Neither the blowing agent nor its decomposition products should be any health hazardous, adversely affect the thermal stability or mechanical strength of the plastic or have a corrosive effect. The

decomposition residues should be compatible with the plastic and not exude or cause discoloration. Finally, the blowing agent should have a high gas yield and be economical to use. In view of all these conditions, it is obvious that no chemical blowing agent is ideal in every respect. Certain of these demands, however, are not necessarily relevant to the manufacture of every type of foam.

2.3.1 Product Classes and Modes of Action

The chemical blowing agents(1) in industrial use are azo compounds, hydrazine derivative, semicarbazides, tetrazoles and benzoxazines. Azodicarbonamides and their modifications account for about 95% of all chemical blowing agents. Of the remaining 5%, approx. 2% are sulfohydrazides, 2% are what are known as high-temperature blowing agents and 1 % are other compounds.

a) Azo Compounds

Azodicarbonamide (1) is the most important substance in this group. Azodicarbonamide is an orange to pale yellow, crystalline powder with a density of 1.65 g/cm^3 and a decomposition temperature in air of 205 to 215°C With its gas yield of approx 220 ml/g, it is virtually insoluble in most organic solvents and plasticizers. The thermal decomposition of dry azodicarbonamide (1) in air gives rise to the following proportions of decomposition products:

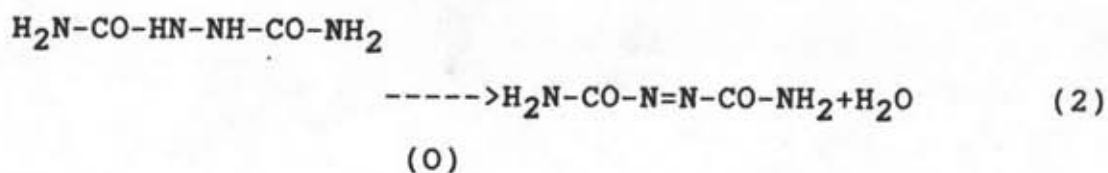
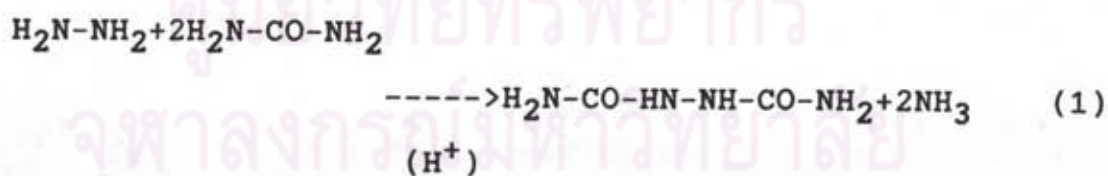
gaseous products: 32 % by wt
 Solid residues: 41 % by wt
 sublimate: 27 % by wt

The gaseous products consist of:

nitrogen (N₂) : 65 % by vol
 carbon monoxide (CO): 32 % by vol
 carbon dioxide (CO₂): 3 % by vol

The solid residues and the sublimate are composed mainly of urazole (39%), cyanuric acid (26%), hydrazodicarbonamide (2%) and cyamelide (1%). The percentages are calculated on the quantity of azodicarbonamide used.

The decomposition of azodicarbonamide appears to follow one of two reaction mechanisms, depending on the formulation of the polymer, compound and the temperature.



Moisture affects the decomposition of azodicarbonamide. In the presence of acids or bases at high temperatures, it may hydrolyze to form hydrazodicarbonamide, nitrogen, carbon dioxide and ammonia.



The various possibilities that exist for influencing the way azodicarbonamide decomposes (5) are of considerable importance in foam manufacture. Although the decomposition temperature of pure azodicarbonamide is very high, it can be reduced by means of a number of kickers also used in the compounding of polymer. Effective kickers include polyols, urea, amines, certain organic acids and bases and also a large number of metallic compounds, particularly basic lead, zinc, and/or cadmium compounds used mainly as stabilizer, certain fillers and pigments are also suitable. By using zinc oxide about 50 percent of azodicarbonamide(1), the decomposition temperature can be lowered by some 20-30 C and the decomposition rate increases at constant temperature.

The decomposition rate of azodicarbonamide can be influenced not only by various kickers but also by the particle size of blowing agent. Since activation takes place in a heterogeneous system, the specific surface, and therefore the particle size, obviously has

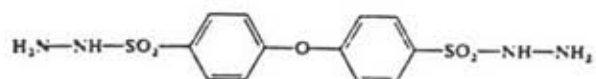
a decisive effect on the decomposition rate. Azodicarbonamide of small particle size is more easily "kicked" than coarser materials.

Azodicarbonamide-containing additives of any kind must be regarded as a modified azodicarbonamide(1). The additives facilitate the dispersion of the blowing agent and kicker lower the decomposition temperature. Some modified azodicarbonamides have developed by modify the usual decomposition of azodicarbonamide and suppress the formation of cyanuric acid, which causes of plate-out on the surface of molds, dies and screws. The additives such as zinc oxide or silicic acid with a low water content, also act as nucleating agents, giving a cell structure of uniform fineness. Another possible method of modifying azodicarbonamide is to mix it with other chemical blowing agent, e.g. from the sulfohydrazide group. These "auxiliary blowing agents" decompose at lower temperature than azodicarbonamide. The decomposition products formed, as well as the water split off when sulfohydrazides decompose, accelerate the decomposition of azodicarbonamide. Here, too, the formation of cyanuric acid is suppressed.

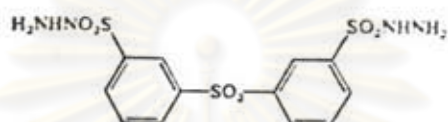
There have also other groups of blowing agent which should be summarized here as followed.

2) Hydrazine Derivatives

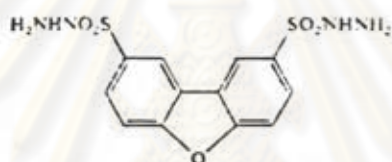
4,4' - Oxybis (benzene sulfohydrazide)



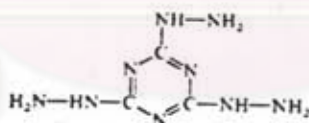
Diphenylsulfone-3,3'-disulfohydrazide



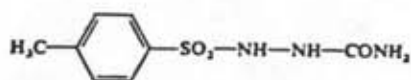
Diphenylene oxide-4,4'- disulfahydrazide



Trihydrazinotriazine

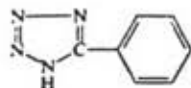
3) Semicarbazides

P-Toluenesulfonyl semicarbazide

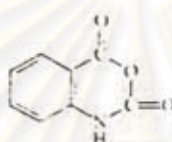


4) Tetrazoles

5-Phenyltriazole

5) Benzoxazines

Isotaic anhydride



The decomposition temperature in air and the gas yield of all aboved blowing agents are given in Table 2.1

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Table 2.1 Common chemical blowing agents according to decomposition range, gas yield and principal uses(1).

Chemical description	Decomposition range in air (°C)	Gas Yield (ml/g)	Used mainly for
Azodicarbonamide	205 to 215	220	PVC, PE, PP PS ABS, PA
Modified azodicarbonamide	155 to 220	150 to 220	PVC, PE, PP EVA, PS, ABS
4,4'-Oxybis(benzene sulfohydrazide)	150 to 160	125	PE, PVC, EVA
Diphenylsulfone-3,3' disulfohydrazide	155	110	PVC, PE, EVA
Diphenylene oxide-4,4' disulfohydrazide	175 to 180	120	PE, PVC, EVA
Trihydrazinotriazine	275	225	ABS, PE, PP, PA
P-Toluenesulfonyl semicarbazide	228 to 235	140	ABS, PE, PP, PA PS
5-Phenyltetrazole	240 to 250	190	ABS, PPO, PC, PA PBTP
Isotatic anhydride	210 to 225	115	PS, ABS, PA, PPO PBTP, PC

2.4 Organic Peroxides as Cross-linking Agents

Using organic peroxides as cross-linking agents has been reported for the first time in 1915 but gained importance for the vulcanization of natural rubber and with the development of the saturated synthetic rubbers. Parallel to its applications as elastomers, interest was being shown in the use of peroxides for the cross-linking of thermoplastics. The decomposition temperature of organic peroxide is the main determinant for scorch temperature and cure rate. For this reason, the composition of the peroxide determines its usefulness as a cross-linking agent.

2.4.1 Advantages and Disadvantages

The advantages and disadvantages (5) of peroxide vulcanization are summarized as following:

Advantage :

- scorch free storage of compounds
- the rapid vulcanization at high temperatures
- possibility to apply high vulcanization temperatures without reversion
- good balance between processing properties and crosslink density
- simple formulation
- low compression set even at high temperatures

- good electrical properties, no copper corrosion
- good high temperature stability
- no discoloring
- no bloom
- easy covulcanization with other polymer,
also with plasticizers

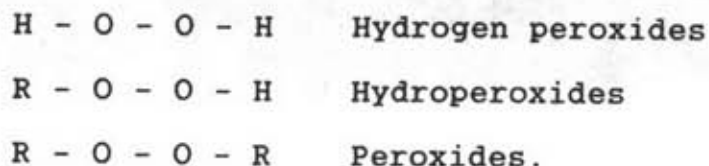
Disadvantage:

- limited compounding, because of reactions of
compounding ingredients with peroxides.
(e.g. antioxidants, plasticizers, resin etc.)
- sensitivity of vulcanization reactions to oxygen
- at low temperatures long vulcanization times
- mostly lower tensile strength, lower tear
strength
- lower abrasion resistance
- higher swelling
- frequently disturbing odors and toxicity of
fragments
- mostly higher costs.

2.4.2 Classification and Characteristic of

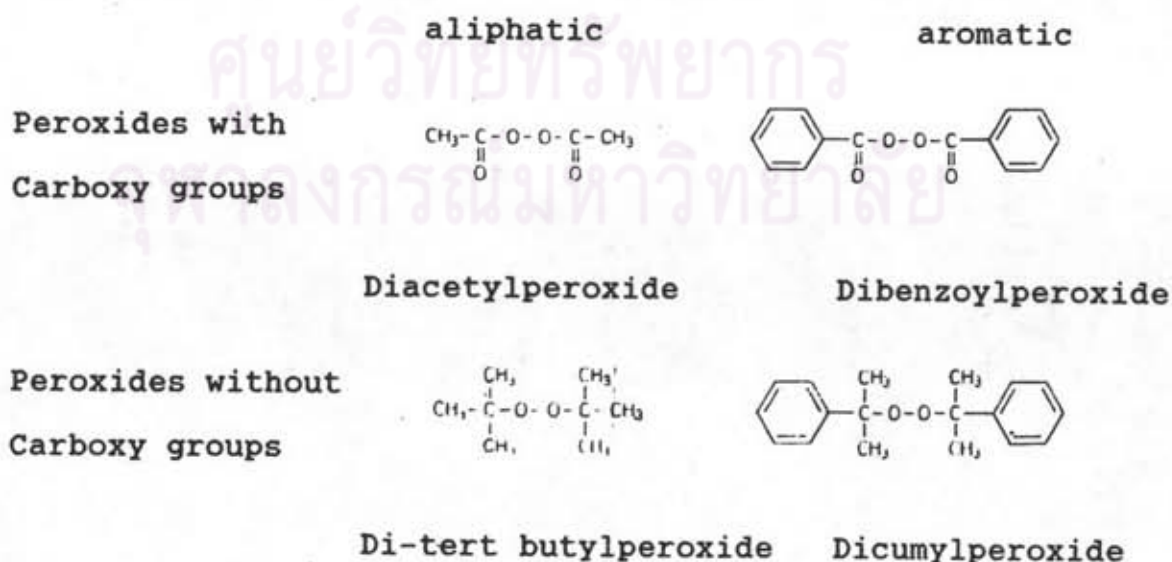
Peroxides

The formulas of all peroxides (5) can be derived from hydrogen peroxide, the single substituted products are the hydroperoxides, the double substituted products are the peroxides.

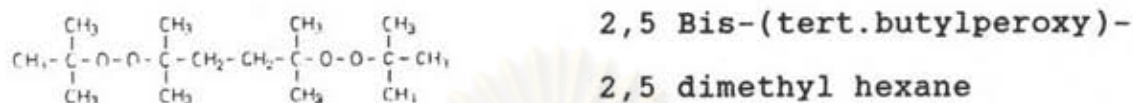


Hydroperoxides do not lead to the formation of crosslinks, but can interfere with the cross-linking capacity of other peroxides. However they can degrade polymer molecules. They are therefore not important in the crosslinking of rubber.

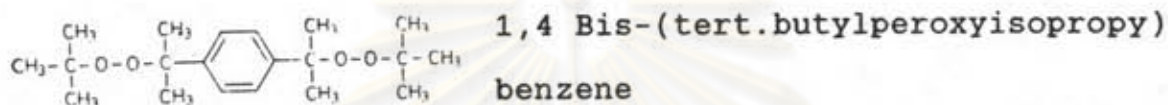
Peroxides can practically be used for the cross-linking of polymer, should be stable and not dangerous during the usual handling, and that, on the other hand, decompose sufficiently fast at customary curing temperatures. For that purpose, peroxides with tertiary carbon atoms are justified. Peroxides bonded to primary and secondary carbon atoms are less stable. One can distinguish two groups of organic peroxides that are stable enough for rubber processing.



Almost all peroxides can be derived from these basic types. Peroxides containing more than one peroxy group are called polymeric or polyvalent peroxides, for example



OR



The peroxides in the different classes (5) have the following characteristics:

Carboxy group peroxides:

- . low sensitivity to acids
- . low temperature of decomposition
- . high sensitivity to oxygen, therefore, cure problems in the presence of carbon black.

Peroxides without carboxy groups:

- . sensitivity to acids, aliphatics better than aromatics
- . higher temperature of decomposition
- . lower sensitivity to oxygen than peroxides with carboxy groups

For the curing of elastomers those peroxides are preferred that form the following radicals.

2.4.3 Mode of action

Decomposition of peroxides (5) can occur under the influence of the following factors : by heat, by light or high energy radiation, or reactions with other materials. Preferably the decomposition can occur at the peroxy groups. It can be affected by other compounding ingredients, that can lead to reduced radical yield and thereby influence the cross-link density. A peroxide that decomposes at low temperatures would be desirable because of rapid vulcanization and high production rate. These advantages however are countered by decreased processing safety. Because of production problems and high reject production rates, peroxides with short half-life can frequently not be used. The stability of the peroxide is of course important for the choice of the vulcanization temperature. For example, compounds with dibenzoylperoxide can only be heated to 45°C without scorching. Compounds with dicumyl peroxides can tolerate approx. 110°C without scorching danger. The stability of the peroxide also determines the maximum curing temperature that one can use; it shouldn't exceed about 130°C for dibenzoylperoxide and 170°C for dicumylperoxide. The radical yield and the crosslink density depend very much on the temperature. One can not draw conclusion from the behavior of a peroxide in a given polymer to the behavior of the same peroxide in a different polymer. Acceleration is only possible within

limits by an increased temperature and it is not possible to activate peroxides with metal oxides, like ZnO, or stearic acid. Crosslink density can be considerably increased by using coactivators. Here we are dealing with polyvalent compounds (for example di or triallyl compounds, maleic acid or reactive acrylic derivatives) that produce several consecutive reactions with one peroxydic initiation. Different coactivators are recommended for different polymers.

2.4.4 Selection of Peroxides

Selection of a peroxide (6) is primarily determined by the polymer to be cross-linked and its processing conditions such as residence time and temperature and by the requirements that have to be met by the finished article. A further factor is that the degree of cross-linking is a function of the peroxide quantity, whereas the rate of the cross-linking reaction is determined by the temperature. The amount of peroxide required depends on the structure of the peroxide, the polymer to be cross-link and the presence and quantity of other additive. Data on the amounts of peroxide required for the cross-linking of important polymer are list in table. Satisfactory mechanical properties can already be obtained with the lowest quantity of peroxide. However, permanent set (polymer foam) does not improve until fairly high quantities of peroxide are used. The mechanical properties generally deteriorate

contains substance that can scavenge free radicals, higher quantities than the minimum are likewise necessary.

Table 2.2 Amount of peroxide needed for cross-linking of polymers.

Polymer	Parts per weight peroxide per 100 part polymer		
	A	B	C
EPDM, EPM	6.8 to 11.3	6.1 to 10.1	3.8 to 6.3
NBR	2.6 to 4.5	2.4 to 4.1	1.5 to 2.5
PE	1.5 to 7.6	1.4 to 6.8	0.8 to 4.2
EVA	2.6 to 5.3	2.4 to 4.7	1.5 to 3.0

A : 1,1 ditert. butylperoxy - 3,3,5 trimethylcyclohexane
(40% active material)

B : Dicumyl peroxide (40% active material)

C : Bis (tert. butylperoxyisopropyl) benzene (40% active material)

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