The Effects of Crosslinking on Foaming of EVA

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Department of Mechanical and Industrial Engineering
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Abstract

The effects of crosslinking on EVA foaming are studied in this thesis. A fundamental approach was applied to describe the influences of crosslinking on EVA/gas viscosities, gas solubility and diffusivity in EVA, EVA foaming nucleation and early stage of bubble growth, which leads to a better understanding of the plastic foaming mechanism.

Although crosslinked polyolefin foaming technology has been well applied in industry, more fundamental and thorough studies are demanded to understand the mechanism, which can serve to improve the present technology. The shear and extensional viscosities have been measured for the chemically crosslinked EVA with dissolved gas which could not be found from literature. Furthermore, by controlling the crosslinking agent amount, the polymer melt strength/viscosity can be controlled, so as to obtain optimum foam morphology. The crosslinking also has effects on the diffusivity and solubility of a blowing agent inside EVA. The solubility and the diffusivity of the blowing agent in the EVA decrease with the crosslinking degree increases. The diffusivity decrease makes more gas is utilized for the foaming rather than leak out of the polymer matrix quickly.

This thesis also presents the fundamental studies on the effects of crosslinking on cell nucleation and early bubble growth. Theoretical work and in-situ visualization experimental
results indicate that partial crosslinking leads to higher cell nucleation density and slower bubble
growth, both of which benefit a fine-cell foam morphology generation.

Last but not least, an optimized foaming process was conducted to produce chemically
crosslinked EVA foams with large expansion ratios in a batch system, using a chemical blowing
agent. The results determine that an optimal crosslinking degree is critical for the crosslinked
EVA foaming with maximum expansion ratio. Furthermore, all research results not only benefit
the foaming of crosslinked EVA, but also serve the better production of other crosslinked
polyolefin foams.
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<th>Description</th>
<th>Unit/Dimension</th>
</tr>
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<tbody>
<tr>
<td>$\dot{\gamma}$</td>
<td>Shear rate</td>
<td>$[s^{-1}]$</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Gibbs free energy</td>
<td>$[J]$</td>
</tr>
<tr>
<td>$\Delta G_{\text{hom}}$</td>
<td>Free energy to form critical nucleus during homogeneous nucleation</td>
<td>$[J]$</td>
</tr>
<tr>
<td>$\Delta G_{\text{het}}$</td>
<td>Free energy to form critical nucleus during heterogeneous nucleation</td>
<td>$[J]$</td>
</tr>
<tr>
<td>$\Delta G_V$</td>
<td>Free energy difference between the bubble phase and the polymer phase</td>
<td>$[J]$</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>Pressure drop</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$\Delta P_{\text{exit}}$</td>
<td>Exit pressure drop</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$\dot{\varepsilon}$</td>
<td>Elongation (or extension, or stretch) rate</td>
<td>$[s^{-1}]$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Shear viscosity</td>
<td>$[Pa \cdot s]$</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>Zero-shear-rate viscosity</td>
<td>$[Pa \cdot s]$</td>
</tr>
<tr>
<td>$\eta_\infty$</td>
<td>Viscosity at infinite shear rate</td>
<td>$[Pa \cdot s]$</td>
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<tr>
<td>$\eta^*$</td>
<td>Complex viscosity</td>
<td>$[Pa \cdot s]$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Relaxation time</td>
<td>$[s]$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>$[g/cm^3]$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Surface tension</td>
<td>$[N/m]$</td>
</tr>
<tr>
<td>$\tau_{21}$ or $\tau_{yx}$</td>
<td>Shear stress</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$\tau_w$</td>
<td>Wall shear stress</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$\tau_{rr}$</td>
<td>Stress is the $r$ direction</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$\tau_{\theta \theta}$</td>
<td>Stress in the $\theta$ direction</td>
<td>$[Pa]$</td>
</tr>
</tbody>
</table>
A Bubble surface area, [m²]

b Extensional flow parameter, [0 < b < 1]

B Width, [m]; used in various contexts

c Gas concentration, [g/cm³ or g/g]

C₀ Initial dissolved gas concentration, [mol/cm³ or mol/g]

D Diffusivity, or diffusion coefficient [m²/s]

g Gravitational constant, 9.8 m/s²

G Elastic modulus, [Pa]

G' Storage modulus, [Pa]

G'' Loss modulus, [Pa]

H or h Height, [m]; used in various contexts

J Nucleation rate per unit volume of polymer, [#/s·m³]

J₀ Frequency factor

k Thermal conductivity, [W/m · K]

k_B Boltzmann constant, 1.38 × 10⁻²³ J/K

k_H Henry’s Law constant

L Length, [m]; used in various contexts

Mₜ Ratio of gas dissolved over polymer at time t, [g/g, mol/mol]

M∞ Ratio of gas dissolved over polymer after infinite time, [g/g, mol/mol]

Mₙ Number-averaged molecular weight, [g/mol]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_w$</td>
<td>Weight-averaged molecular weight, [g/mol]</td>
</tr>
<tr>
<td>$m$</td>
<td>Power Law parameter</td>
</tr>
<tr>
<td>$n$</td>
<td>Non-Newtonian index in Power Law</td>
</tr>
<tr>
<td>$N_{hom}$</td>
<td>Cell nucleation rate during homogeneous nucleation [cells/s]</td>
</tr>
<tr>
<td>$N_{het}$</td>
<td>Cell nucleation rate during heterogeneous nucleation [cells/s]</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure, [Pa]</td>
</tr>
<tr>
<td>$P_g$</td>
<td>Gas pressure inside a cell, [Pa]</td>
</tr>
<tr>
<td>$P_s$</td>
<td>System pressure, [Pa]</td>
</tr>
<tr>
<td>$phr$</td>
<td>Parts per hundred resin</td>
</tr>
<tr>
<td>$Q$</td>
<td>Volumetric flow rate, [m$^3$/s]</td>
</tr>
<tr>
<td>$r, \theta, \text{and } z$</td>
<td>Cylindrical coordinates</td>
</tr>
<tr>
<td>$R$ or $r$</td>
<td>Radius, [m]</td>
</tr>
<tr>
<td>$r^*$</td>
<td>Critical radius, [m]</td>
</tr>
<tr>
<td>$R_g$</td>
<td>Molar gas constant, 8.314 J · K$^{-1}$ · mol$^{-1}$</td>
</tr>
<tr>
<td>$t$</td>
<td>Time, [s]</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature, [K]</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature, [K]</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature, [K]</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Crystallization temperature, [K]</td>
</tr>
<tr>
<td>$v$</td>
<td>Velocity, [m/s]</td>
</tr>
</tbody>
</table>
\( V_b \)  
Initial volume of bubble, [\( m^3 \)]

\( V \)  
Volume, [\( cm^3 \)]

\( W \)  
Free energy barrier for cell nucleation, [J]

\( X_{apparent} \)  
Apparent solubility, [\( g/g, mol/mol \)]

\( x, y, \text{ and } z \)  
Cartesian coordinates
Chapter 1

Introduction

1.1 Crosslinked Polyolefin Foams and their Processing Technology

Polymer has been one of the most important materials in human society, with its synthesis technology that had been developed since the early 19th century. Polymers are used in many applications, which influence every aspect of our lives. These edge advantages are due to polymers’ properties, such as light weight, easy processability, isolation and other unique properties. To pursue lower density, better isolation and other related properties, foaming technology has been applied into polymers since the 1930s [1,2].

Foam is a substance that entraps on the inside, well-dispersed bubbles/cells. Polymer foams are composed of two phases, in which a blowing agent is used to generate stabilized bubble structures inside the polymer matrix. The foaming technology has been developed, and has been applied with an increasing number of different types of polymers [2,3]. The polymer foam industry is a major part of the U. S. polymer industry, accounting for about 10% of total commodity consumption [4,5]. Polyolefin foams are fourth ranked, after polyurethane (PU), polystyrene (PS), and poly (vinyl chloride) (PVC) foams. The increasing demand for crosslinked polyolefin foams makes polyolefin foams have one of the highest growth rates [5,6]. Polyolefin foam is one of the most important categories within polymer foams. It had first been marketed in the early 1960s and the areas of application include packaging, sports and leisure, toys, insulation, automotive, buoyancy, cushioning and others [7,8].
In terms of final foam properties, the wide range of polyolefin foams can be divided into hard foams, which are obtained using polypropylene (PP) or other high strength basic polyolefin, and softer foams, which are obtained using co-polymer, such as ethylene vinyl acetate (EVA) [7]. Soft polyolefin foam from EVA comes with the property of elasticity, which is due to the ability of the long chains to reshape them back to the original configuration after the applied stress is released. Soft foams made of polyolefin have a wide application, such as cushioned packaging materials, floatation materials, padding in various sports equipment, shock absorbers, and sports shoe soles/slippers/sandals. [3,5,6,7].

In terms of production process and final shape, polyolefin foams can be divided into three groups. The Dow Chemical Company introduced extruded polyolefin foams in 1958. Crosslinked PE foams emerged in the Japanese market in the mid 1960s. BASF AG introduced polyolefin foam moldings in the early 1970s [3,5,7]. Based on the technology, the final foams can also be divided into noncrosslinked foams and crosslinked foams [5].

Crosslinking technology is applied to polyolefin foaming. Crosslinking is a chemical bond between adjacent polymer chains, which can stabilize bubbles during foam expansion, enhance the resistance of the cellular product to thermal collapse, and also improve the mechanical properties (such as anti-creep ability, weatherability, impact absorption, etc) of the final foamed products [3]. Soft EVA foams are usually crosslinked during the manufacturing process, and other related polymer resins, which include LLDPE, LDPE, HDPE, PP, TPE, and other blends[5].

There are several representative processes which are used to manufacture crosslinked polyolefin foams: irradiation crosslinked foam process, chemically crosslinked polyolefin foam
process, chemically crosslinked polyolefin foamed BUN process, grafted resin crosslinked polyolefin foam process, injection molded foam process, and nitrogen autoclave process [3,7,9,10]. In the irradiation crosslinked foam process, an irradiation-unit, which generates electron beams, is used to crosslink foamable solid matrix, after the completion of the extrusion. In the chemically crosslinked polyolefin foam process, the crosslinking agent is used to strengthen polymer resin under a lower heat, that is between the end of an extruder and a hot air oven. In the chemically crosslinked polyolefin foamed BUN process, a press, other than an extrusion system, is used to make foam with a chemical crosslinking agent. In the grafted resin crosslinked polyolefin foam process, a grafted polyolefin resin is used for crosslinking under the condition of heat and moisture [9,10]. In the injection molded foam process, polyolefin with high melt fluidity is cured inside the press, and its foam densities are in the range of 100 – 300 kg/m³ [10]. Zotefoams plc commercialized the nitrogen autoclave process in the early 1960s. High-pressure gas will be injected into the crosslinked polyolefin, and foams (commercially 15 – 120 kg/m³) will be produced during various pressure expansions [7,11,12].

All of the above crosslinked foaming process can be composed of three major steps: mixture formation, crosslinking, and foaming (See Figure1.1). The foam morphology and the properties of the cellular polyolefin will be affected by the crosslinking [3]. For example, crosslinking extends the rubbery plateau of the polymer melt, and widens the temperature range in which stable foams can be produced [13]. In order to improve foam morphology and properties, and to obtain optimum foam using optimum crosslinking, it is important to fully understand the mechanism on how crosslinking affects foaming. Therefore, in this thesis, techniques will be presented to produce chemically crosslinked EVA foams and to characterize the influences of crosslinking and optimize the expansion ratio of chemically crosslinked foams.
These results will help with understanding and the production of other cellular crosslinked polyolefin foams.

1.2 Research Motivation

Academically, the foaming of polymer is a complicated process that involves a delicate thermodynamic phenomenon and a kinetic material transport. The plastic foaming procedure generally has four basic steps: 1) polymer and blowing agent mixing; 2) polymer/blowing agent solution formation; 3) bubble nucleation; 4) cell growth and stabilization (See Figure 1.2) [14].

There is extensive research which helps understand the basic mechanism of plastic foaming. Fundamentally, the production of polymer foams involves preparing a single-phase polymer/blowing agent (BA) solution and then generating bubbles by introducing thermal instability [15,16,17]. Most advanced foaming technologies subject the polymer/blowing agent mixtures to a series of well-defined kinematic events. One of the key issues is to know the amount of the blowing agent dissolved into the polymer, which determines the amount of
blowing agent used to generate cells [18]. Diffusivity of the blowing agent inside the polymer helps the speed of the cell expansion and the speed of the blowing agent that leaks outside of the cells [18]. Thermal instability, which is introduced by either a temperature increase or pressure drop, has a close relation with the cell nucleation, which has a major impact on the final foam cell density and foam morphology [19]. Another key is to control the cell growth and help the bubbles stabilize by controlling rheological properties [20]. Although the crosslinked polyolefin/EVA foaming technology has been used successfully by industries, the development of foaming technologies requires accurate knowledge of the aforementioned areas and especially how crosslinking influences the kinematic subjects.

There are two critical areas that require investigation; 1) to understand the influences of crosslinking on the foaming-related parameters, and the mechanism of crosslinked EVA foaming; 2) to apply the knowledge in order to optimize the crosslinked foaming process, and improve cell morphology.

1.3 General Objectives

The current investigation is targeted at understanding the mechanism on the foaming of chemically crosslinked EVA, and applying the knowledge to optimize the related foaming technology. Cell density and expansion ratio of foams are key parameters in foaming product properties; a better understanding of the crosslinking’s influences on foaming is critical for product development. Furthermore, gaining such insight will allow for the creation of a model that can then serve a predictive purpose in other foaming processes.
1.4 Thesis Format and Outline

This section provides a brief overview of the present thesis.

Chapter 2 introduces the background of polymer foaming and the mechanism of cell nucleation and growth in foam processing. This chapter also reviews relevant work on crosslinked foaming, which leads to the challenges and detailed objectives of this thesis.

Chapter 3 presents the measurement of related rheological properties and its role in foaming. The methods and systems to measure the rheological properties are reviewed. Shear viscosity and extensional viscosity of EVA and crosslinked EVA are presented. Also a tandem extrusion on-line system is used to measure the shear/extensional viscosities of crosslinked EVA with the blowing agent being dissolved. Furthermore, this chapter introduces the methods to characterize the solubility and diffusivity of the blowing agent, and presents the measurements of the solubility data and diffusivity data of a blowing agent in crosslinked EVA. A comparison is made between the data with crosslinking and without crosslinking, and the crosslinking effects are analyzed.

Chapter 4 presents the effects of crosslinking on cell nucleation and early stage of bubble growth of EVA foam. An in-situ visualization batch foaming system is used to monitor the cell growth in the crosslinked EVA. From the video data, it is investigated how crosslinking affects the cell nucleation and bubble growth. At the end of this chapter, a fundamental analysis is presented on the crosslinking’s influences on foaming.

Chapter 5 introduces the batch foaming methodology of crosslinked EVA. The characterization method of foam morphology (foam density, cell density, void fraction, and
expansion ratio), material analysis (chemical blowing agent) and crosslinking degree is presented. A Taguchi design is used to analyze the effects of parameter factors, and a preliminary investigation is conducted on the parameters’ influences on final foam morphology, which includes: processing temperature, chemical blowing agent amount, crosslinking agent amount, and nucleating agent. Furthermore, crosslinked EVA foams are optimized to obtain a desirable foaming expansion ratio and cell density.

Chapter 6 summarizes the contribution of this thesis, and concludes with future work recommendations.
Chapter 2

Background and Literature Review

Plastic foaming is a delicate and involved process, which is to introduce a blowing agent into the polymer matrix and to generate cellular structures. It is a complicated phenomenon, which involves thermodynamics, reaction kinetics, melt/gas rheology, gas diffusion and permeation, and others. In order to design the detailed research methodology for crosslinked EVA foaming studies, this chapter starts with a plastic foaming review. This is followed by a background of blowing agents used in plastic foaming. Then another review is presented on some key issues involved in plastic foaming: cell nucleation and growth, gas solubility and diffusivity, polymer rheological property. In Section 2.3, the research work on the crosslinking involved in plastic foaming is reviewed. Finally, following the literature review, a detailed methodology is presented.

2.1 Plastic Foams, Blowing Agents and EVA

2.1.1 Categories of Foams

Plastic foams are polymers that contain cells dispersed throughout the polymer matrix. Polymer foam can be viewed from different perspectives, such as product dimension, foam density, cell size, cell density, foam morphology, and foam property [2].

Foamed plastics have a wide density range from about 1.6 kg/m\(^3\) to over 960 kg/m\(^3\). Based on the average cell size and cell density, they can be divided into three main categories: conventional foams (<10\(^6\)cells/cm\(^3\)), fine-celled foams (10\(^6\) to 10\(^9\)cells/cm\(^3\)), and microcellular
foams (>10^9 cells/cm³). In terms of the foam expansion ratio, plastic foams can also be classified into high density foam (<4 folds), medium density foam (4-10 folds), low density foam (10-40 folds), and very low density foam (>40 folds) [8].

Because of less material cost, plastic foams are more environmentally friendly compared with unfoamed ones. Furthermore, plastic foams also have many advantages, such as: light weight, insulating abilities (sound and heat), energy absorption (shock, impact, and vibration), buoyancy, and elastic properties in certain cases. Because of the desirable range of densities and application requirements, plastic foams can be used in products such as: packaging, sports, construction, automotive/transportation, insulation, wires/cables, etc. Generally speaking, higher density foams are used in construction, automotive/transportation applications; while lower density foams are used in insulation, and packaging applications [3,8,21,22].

Plastic foams can also be divided into thermoset foams and thermoplastic foams depending on the polymer matrix. In terms of foam morphology, plastic foams can also be classified as open-cell foams and closed-cell foams. Open-cell foams are widely used in sound insulation and water purification technology [2,23].

### 2.1.2 Blowing Agents in Plastic Foaming

Most plastic foams are manufactured by dispersing a gaseous phase throughout the polymer matrix. The substance that produces a cellular structure in the polymer is defined as a blowing agent (BA) [7]. The gas used for foaming can be classified into two categories based on the mechanism: physical blowing agent (PBA) and chemical blowing agent (CBA).
2.1.2.1 Physical Blowing Agent in Foaming

PBAs provide gas for the expansion of polymers by undergoing a physical state change, which means no chemical transformation happens during the foaming process. Most PBAs are liquids or supercritical fluids. Common liquid physical blowing agents are low boiling liquids and include short-chain (C₅ to C₇) aliphatic hydrocarbons and halogenated (C₁ to C₄) aliphatic hydrocarbons. Common gaseous blowing agent include: CO₂, N₂, short-chain (C₂ to C₄) aliphatic hydrocarbons and halogenated (C₁ to C₄) aliphatic hydrocarbons [7].

It is important to select a suitable PBA for the plastic foaming, by taking into account health concerns, global warming potential (GWP) concerns and ozone depletion potential (ODP) concerns. Chlorofluorocarbons (CFC) were widely used for rigid thermal insulation foam, using both thermoset and thermoplastic (PU and PS), due to its low diffusion coefficient and lower thermal conductivity. However, it phased out due to global ODP concerns in 2010 [24]. Hydrochlorofluorocarbons (HCFC) acted as a transitional alternative to CFC, and is also restricted according to the Montreal Protocol. The use of HCFC will be entirely terminated in 2040 [25]. Hydrofluorocarbons (HFC) have zero ODP, but have GWP issues. HFC are not widely used in polymer foaming, but HFC-134a is used in certain applications such as PU foams and extruded PS sheets [26, 27]. The application of Hydrocarbons (HC) had been limited in earlier times because of its flammability, but this situation has changed a lot recently due to regulation updates and plant modifications. Within the category of HC, pentanes are used in PU foam insulation, and expanded polystyrene (EPS) foams; butanes and propane are used to make polyolefin wrapping and cushioning foams [7].
Insert gases such as CO$_2$ and N$_2$ have been widely used as a blowing agent nowadays due to their low cost, environmentally friendly nature, and relatively moderate critical temperature and pressure [28]. Insert gases have a relatively higher diffusion coefficient compared with other blowing agents described previously. The solubility of N$_2$ in most common polymers is lower than that of CO$_2$, which means higher pressure is required for N$_2$ under similar circumstances. The diffusivities of them are at the same order in most common polymers. Currently they have been widely used to produce fine-celled and microcellular foams [3,18,29-31].

2.1.2.2 Chemical Blowing Agent in Foaming

CBAs are compounds that generate gas under the foaming process, as a result of chemical reactions (either thermal decomposition or components reaction). The gases that are generated are mostly N$_2$ and CO$_2$, and they behave much like a PBA, but with some residues from the decomposition [32]. CBAs can be classified mainly into two categories: exothermic CBA and endothermic CBA. Exothermic CBAs generate heat in the decomposition, and its main decomposition gas is N$_2$; endothermic CBAs absorb heat in the decomposition, and its main decomposition gas is CO$_2$.

It is important to choose the appropriate CBA for the plastic foaming. Generally, there are two critical issues that are required to be considered at first. One issue is that the decomposition temperature of the CBA is close to the processing temperature of the polymer. If the decomposition temperature is too high, the polymer melt strength is low at the foaming temperature, and is not strong enough to maintain the bubble structure or prevent cell coalescence. If the decomposition temperature is too low, the polymer melt is too rigid, which
constrains foam expansion. The other issue is the residence of the CBA decomposition and the generated gases are compatible with the polymer and processing system [7].

Azodicarbonamide (AZC) is one of the widely used exothermic CBA. It generates 65% N2, 32% CO2, CO and NH3. About 200 ml gas under standard temperature and pressure can be generated by 1 gram AZC at 205-215°C. The residues include biurea, cyanuric acid, urazole, urea, cyamelide. In conclusion, its breakdown comprises of 32% gas, 41% solid residues, and 27% sublimate. The solid and sublimate residues are 57% urazole, 38% cyanuric acid, 2% cyamelide [33]. Its decomposition involves many steps of reactions, and here the first major reaction is listed in equation (2-1):

$$\text{azodicarbonamide} \xrightarrow{\Delta} \text{urea} + \text{N}_2 + \text{CO}$$

4, 4’-oxybis benzene sulfonyl hydrazide (OBSH) is another exothermic CBA widely used in a lower temperature range, about 155-160°C. It generates 95% N2 and 5% H2O vapor, 125ml gas under standard temperature and pressure can be generated by 1 gram OT, and its decomposition residue is white, which is called polythiosulfonate[3,34]. The reaction is described in equation (2-2):
2.1.3 Ethylene Vinyl Acetate

Ethylene vinyl acetate (EVA) is a polyolefin copolymer of ethylene and vinyl acetate with 10-36 wt% vinyl acetate [35]. It was derived from “modified polyethylene” technology in the 1930s. Figure 2.1 illustrates the molecular formula of EVA. Figure 2.2 presents the relationship between maximum molecular weight and vinyl acetate content for EVA [36].

EVA has a relatively low softening temperature, which ranges around 60-100°C. EVA approaches elastomeric materials with rubberlike properties of softness and flexibility, and has the processability of other thermoplastics. EVA parts have good clarity and gloss, stress-crack resistance, adhesive properties, and resistance to UV radiation. The main limitation of EVA
copolymers is their comparatively low resistance to heat and solvents [36].

![Graph showing relationship between maximum molecular weight and vinyl acetate content for EVA](image)

Figure 2.2 Relationship between maximum molecular weight and vinyl acetate content for EVA [36]

EVA copolymers are used principally in specialty applications, competing with plasticized PVC and rubber. The applications for EVA copolymers include wire/cable insulation, drug delivery device, packaging film, adhesives/coatings, carpet backing, sandals, sports shoe soles, sports leisure, sound damping sheets [35,36].

### 2.2 Plastic Foaming

Plastic foaming technology has been developing ever since the blowing agent was introduced into the polymer industry since the 1930s. Extensive research is conducted on almost all aspects of plastic foaming technology. The scientific and engineering progress lead to more advanced technologies such as the microcellular foaming and more fundamental mechanism approaches [15,16,37,38]. A review of microcellular foam processing and fundamental foaming mechanisms will benefit the understanding of both technology and science, the combination of which is the driving source for foaming development in both industry and academia.
2.2.1 Microcellular Foam Processing

Microcellular foams are thermoplastic foams with cell sizes in the order of 10µm [14]. The processing methods of microcellular foams can be divided into two categories: batch foaming process, and continuous foaming process. In the batch foaming process, an autoclave is usually used to place the polymer sample, which is saturated with a blowing agent. Foams can be produced by steam heating or by fast pressure drop. Compression molding can also be used in a batch foaming process, especially for chemical blowing agent cases. Alternatively, injection molding and extrusion are two typical methods used for continuous foaming, which makes foam manufacturing easier and more economic.

Since the first patent of microcellular foam was granted in 1984 [39], there have been a lot of researchers working on its development. People make microcellular foams using amorphous and semi-crystalline polymers in their solid state in the batching foaming system. The samples include: PS [40,41], PC [42], PET [43], PVC [44,45], POE [46], PLA [47], etc. Park and his co-workers have done a lot of research on the development of the extrusion foaming processes using insert gases [30,37,38,48]. Trexel has developed the technology to produce microcellular foams in an injection molding machine [49].

Figure 1.2 presents the major mechanism for microcellular foaming [14,15,16,38]. Four basic steps are illustrated: 1) polymer and blowing agent mixing; 2) polymer/blowing agent solution formation; 3) bubble nucleation; 4) cell growth and stabilization. Firstly, the blowing agent is injected into the polymer. Then the blowing agent diffuses into the polymer, which makes a polymer/blowing agent solution. The solubility of the blowing agent inside the polymer determines the viscosity reduction of the polymer because of the plasticizing effect, and also
determines the maximum expansion ratio of the foams that can be obtained theoretically. Next, a thermal instability is required to trigger the cell nucleation, either by increasing the temperature or drop the pressure fast. The cell nucleated is one of the dominant factors to determine the cell density of the foams. Once nucleated, cells start to grow and stabilize. During this process, the blowing agent diffuses from the polymer into the cells to support the bubble continuous expansion. At the same time, the blowing agent will also leak out of the foam, which does not contribute to the foam expansion. In this case, a blowing agent with a lower diffusion coefficient benefits the production of foams with larger expansion ratio. When bubbles continue to grow, adjacent cells squeeze the polymer walls between each other, and make the polymer wall thinner and thinner. During this process, the polymer wall is applied with an extensional stress from expanding bubbles on the side. The melt strength of the polymer/blowing agent is essential to maintain the foam structure by preventing the rupture of the bubble walls under stress and for adjacent bubble coalescence.

2.2.2 Rheology

Rheology is the study of viscosity, which is a measure of the resistance of a fluid to flow. The rheological properties of polymer are determined by many variables, such as polymer molecular structure/weight, temperature, pressure, processing history, strain, strain rate, etc. Unlike those of pure solid and Newtonian fluid, the rheological properties of polymers combine both viscous and elastic characteristics. The viscous behavior means the stress that is applied is related to the strain rate, and the elastic behavior means the stress that is applied is related to the strain [50]. Viscosity is a measure of the rheological properties of the fluid, which deforms when applied with stress. Shear viscosity is a viscosity coefficient when shear stress is applied. Whereas, extensional viscosity is a viscosity parameter when extensional stress is applied.
Rheological properties have an important influence on the foaming process. In the foam extrusion and injection molding processes, the addition and dissolution of blowing agent gases into the polymer melt have an impact on its rheological behaviors and viscosities, even with a low gas concentration [51]. Because the melt experiences stresses by both shear and extension, the rheological behavior of the polymer melt has a significant influence on pressure distributions inside the extrusion barrel [52], through the extrusion die [53], through the injection gate [54], and inside the mold [54]. The pressure distribution will have impacts on the polymer/gas distribution, and the polymer melt flow. What is more, the viscosity of the melt has an impact on the pressure drop of the melt through the die, thereby influencing the nucleation and growth of the bubbles down the line, because the nucleation density is mostly determined by the depressure rate in a die or a mold compared to the solubility pressure of the supersaturated polymer [55].

Rheological properties have an important influence on bubble growth. A bubble model in foaming is presented in Figure 2.3 to describe the diffusion-induced growth of a gas bubble surrounded by a thin film of Newtonian liquid [56,57]. The bubble growth is related to both the pressure difference and the rheological properties of the liquid/gas matrix. Models have been applied to develop models for bubble growth in viscoelastic, power law and Maxwell melts, with the mass and momentum transfer coupled [58,59,60,61]. Leung has applied these equations (momentum equation (Equation 2-3); constitutive equations (Equation 2-4, 2-5)) in the foaming model to describe the bubble growth procedure, which has a reasonable match with the experimental results [19]. In Equation (2-3, 2-4, 2-5), $P_g$ is the bubble pressure; $\sigma$ is the surface tension; $R$ is the bubble radius; $R_{\text{shell}}$ is the radius of the outer volume; $\tau_{rr} - \tau_{\theta\theta}$ is the normal stress difference in the melt; $\lambda$ is the relaxation time; $\eta$ is the viscosity.
Furthermore, the foaming behavior subjected to extensional stress affects the growth of the bubbles as the cell walls of the foam experience biaxial stretching during the bubbles’ expansion (Figure 2.4). If the melt strength is not high enough to avoid wall rupture and cell coalescence, the final foam morphology quality and cell density will be jeopardized [62].
Various methods have been used to increase the melt strength and eventually improve the foamability of polymers, such as temperature cooling [63,64], additives input [65,66,67], polymer blending [68], long chain branching [64], strain hardening [69,70,71], crystallization generation [72,73], and crosslinking [5,74,75]. Section 2.3 will present a detailed review about polymer foaming research involving crosslinking.

Since the rheological property is closely related to polymer foaming, it is important to measure the viscoelastic properties of polymers, so as to provide a quantity guide to help control polymer foaming. Commercial rheometers, such as an oscillating rheometer, elongation rheometer, capillary rheometer, etc., are widely used to measure the polymer viscosity data. In polymer foaming, the melt flow properties are also influenced by the blowing agent, because the blowing agent can increase the polymer free volume and chain mobility [76]. Customized rheometers [77] and dies/channels attached in the extruder end [78,79,80], and where high pressure has to be held, have been used to investigate the reduction of the polymer viscosity due to the gas solution.
2.2.3 Solubility and Diffusivity

2.2.3.1 Solubility

Fundamentally, the foam production involves preparing a single-phase polymer/blowing agent (BA) solution, followed by generating bubbles (also called cells) triggered by the thermodynamic instability, and stabilizing the bubble structure in common surroundings, as illustrated in Figure 1.2. The solubility defines the maximum amount of gas that can be dissolved in the polymer under a given pressure. In order to generate thermodynamic instability to trigger the foaming, the surrounding pressure has to be lowered beyond the solubility pressure. Therefore, solubility and related information are quite important for the foaming process.

A magnetic suspension balance (MSB) system is generally used in the solubility measurement [81]. The weight gain from the dissolved gas in the polymer, $W_g$, was calculated as follows:

$$W_g = W(P,T) - W(0,T) + \rho_{gas}(V_B + V_P + V_S)$$

where $W(0,T)$ is the weight readout of the polymer sample from the balance without gas input; $W(P,T)$ is the weight readout from the balance with gas dissolved; $\rho_{gas}$ is the density of the gas inside the chamber at temperature $T$ and pressure $P$, which can be measured in situ by the MSB; $V_B$, $V_P$, and $V_S$ are the volumes of the sample holder (i.e., the sample container and all measuring load coupling devices), the volume of pure polymer at temperature $T$ and pressure $P$, and the swollen volume of the polymer due to gas dissolution, respectively. $V_B$ is usually determined in advance with a blank experiment. $V_p(P,T)$ can typically be determined by using the Tait equation
for each individual polymer [82]. The value of \( V_s \) has been approached by both theoretical calculation and experimental study.

The Sanchez-Lacombe (SL) equation of state (EOS) and the Simha-Somcynsky (SS) EOS have been used to calculate the swollen volume. Sato et al. extensively measured the solubility of \( \text{CO}_2 \) and \( \text{N}_2 \) in PS, PVC by using the pressure decay method or the gravimetric method with the assistance of SL-EOS [83,84]. Li et al. have conducted solubility measurements of \( \text{CO}_2 \), \( \text{N}_2 \) in PP, PLA and PS by using MSB, SS-EOS and SL-EOS [18,81]. They found that the swelling effect is more significant at higher pressures and lower temperatures.

\( Li \) contributed to the solubility measurement by designing a PVT system, which provides a more accurate method to approximate the swelling data of polymer in high pressure gas \( V_s \), compared with the SL EOS/SS EOS calculation results [85,86].

### 2.2.3.2 Diffusivity

As presented in Figures 1.2; 2.3, and Section 2.2.1, cell growth is driven by the pressure difference between the cell and its surroundings with BA diffusion into the cell [56]. Generally, blowing agent with a low diffusivity has an edge advantage to produce large expansion foams [26,27].

Diffusivity is coupled in numerical equations to theoretically approximate the bubble growth in foaming. As shown in Figure 2.3, the mass balanced equation (Equation 2-7) and the diffusion equation (Equation 2-8) are applied to describe the mass transportation of the gas molecular [19,56,57]. In Equation (2-7, 2-7), \( P_g \) is the bubble pressure; \( R \) is the bubble radius; \( c \) is the gas concentration; \( D \) is the gas diffusivity inside the polymer.
\[
\frac{d}{dt}\left(\frac{4\pi P R^3}{3 RT}\right) = 4\pi R^2 D \frac{\partial c}{\partial r} \bigg|_{r=R} 
\]

\[
\frac{\partial c}{\partial t} + u(r) \frac{\partial c}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D r^2 \frac{\partial c}{\partial r}\right) 
\]

The value of diffusivity can be determined by analyzing the weight curve of the polymer sample, which absorbs BA along with time in MSB. Equation (2-8) can be used to calculate the BA concentration distribution, which is presented in Equation (2-9).

\[
\frac{C - C_0}{C_m - C_0} = -\sum_{n=1}^{\infty} \frac{\cos(n\pi)}{2n-1} e^{-(2n-1)\pi^2/2L} \cos\frac{(2n-1)\pi x}{2L} 
\]

\[
\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{4L^2}\right] 
\]

where \(L\) is half of the sample thickness; \(M_t\) is the BA ratio at time \(t\); \(M_\infty\) is the BA ratio at infinite time. Thus, Equation (2-10) can be used to calculate the diffusivity from the weight data.

### 2.2.4 Homogeneous Nucleation and Heterogeneous Nucleation

Nucleation is the formation of nuclei into a new phase. As presented in Figure 1.2, nucleation is triggered by thermodynamically instability and also tiny bubbles are nucleated in a one-phase polymer/BA solution. When bubbles are formed in a homogeneous/uniform phase, this process is called \textit{homogeneous nucleation}; whereas \textit{heterogeneous nucleation} is generated when bubbles are oriented on a particle surface or in a dirt cavity.

According to thermodynamics and nucleation theory, an excess Gibbs free energy is required for creating a bulk/bubble in a low-molecular-weight liquid, the radius of which has to
exceed the critical bubble radius. The excess free energy can be expressed as Equation 2-11. Larger bubbles will grow further, while smaller ones will dissolve, compared with the critical-radius bubbles [87].

\[
\Delta G = -V_b \cdot \Delta G_v + A \cdot \sigma
\]  

(2-11)

where \(V_b\) is the volume of the bubble nucleus, \(\Delta G_v\) is the difference between the gas phase and the polymer phase per unit volume, \(A\) is the interfacial area, and \(\sigma\) is the surface tension.

The nucleation rate can be calculated according to the classical nucleation theory.

\[
J = J_0 \exp\left(-\frac{W}{k_BT}\right)
\]

(2-12)

where \(J_0\) is the frequency factor, \(W\) is the free energy barrier to initiate bubble nucleation, \(k_B\) is the Boltzmann constant, and \(T\) is the absolute temperature.

In homogenous nucleation, the excess energy is required for the creations of certain volumes and new surfaces (Figure 2.5). Equation 2-11 can be written as Equation 2-13.

\[
\Delta G = -\frac{4}{3}\pi r^3 \cdot \Delta P + 4\pi r^2 \sigma
\]  

(2-13)

where \(\Delta P\) is the supersaturated pressure, \(r\) is the initial bubble radius.
And the free energy barrier for homogeneous nucleation can be written as:

$$\Delta G_{homo} = W_{min} = \frac{16\pi \sigma^3}{3\Delta P^2}$$

(2-14)

The nucleation rate, the number of bubbles formed per unit time, can also be calculated [40]:

$$N_{hom} = C_{hom} f_{hom} \cdot \exp\left(-\frac{\Delta G_{homo}}{k_B T}\right)$$

(2-15)

where $C_{hom}$ is the concentration of gas molecules, and $f_{hom}$ is a frequency factor the rate at which the gas molecules join a critical nucleus.

However, the homogeneous theory does not apply to polymer foaming, as impurities are ubiquitous in commercial resins, and nucleating agents are commonly added to promote nucleation in the foaming process. Calculations have shown that when applied to polymers under typical foaming conditions, the rate of heterogeneous nucleation is dominant [88]. Furthermore, it is found that the free energy barrier may be reduced if the bubble is formed at a solid surface,
as illustrated in Figure 2-6. The free energy barrier (Equation 2-16) and the nucleation rate (Equation 2-17) are now a function of $\theta$, in which case takes on a similar form to that of homogeneous nucleation [89,90].

\[
\Delta G_{het} = \Delta G_{hom} \cdot f(\theta) = \frac{16\pi\sigma^3}{3\Delta P^2} \cdot \left(\frac{1}{4}\right) (2 + \cos\theta)(1 - \cos\theta)^2
\] (2-16)

\[
N_{het} = C_{het} f_{het} \cdot \exp\left(-\Delta G_{het}/k_B T\right)
\] (2-17)

Figure 2.6 Heterogeneously nucleated bubble, where $\theta$ is the wetting angle

There have been many adaptations of the classical theory proposed to better describe the heterogeneous nucleation. The free energy calculation has been modified to account for changes in the polymer free-volume [40], the presence of solid surfaces [40], supersaturation of the blowing agent [88], polymer-solvent interactions in foaming a solution [88], the surface tension reduction due to dissolved gas [91], the shear increase [92], and the elastic and non-ideal solution effects [93]. A simple heterogeneous nucleation model for liquids was proposed in 1975 [94]. Shimoda et al. simulated the cell nucleating phenomena by assuming that the nucleating site surfaces are smooth and planar [95]. Leung et al. incorporated the random surface geometries of
the nucleating agents in the heterogeneous nucleation model and compared the simulation results with the experimentally observed data from a batch foaming process [96].

2.2.5 Cell Growth in Foaming

As presented in Figure 1.2, cells continue to grow once nucleated, until they stabilize with a firm cell wall or collapse/coalescence. Cell growth is an important foaming stage to determine the foam morphology and surface quality of the foamed products. Cell growth is a dynamic process which is driven by the pressure difference between the cell and its surroundings with the BA diffusion into the cell. This process is complicated with many variables that are involved, including the viscosity of the polymer, the gas concentration, the temperature, and the nucleating agent amount. Furthermore, when cells grow, gas concentration decreases, which results in gas diffusivity change and an increasing polymer matrix viscosity. All these make it difficult to establish a cell growth model to well describe the polymer foaming.

Since the properties of cellular materials directly depend on the shape and structure of the cells, it is necessary to be able to predict and control the cell size during the bubble growth. Investigations on the bubble growth and collapse in fluid and polymers can go back as early as the 1910s. The first period models focused on the growth of a single bubble inside infinite fluid surroundings with infinite amounts of gas, which make a great difference with real life foaming processes [48]. Amon et al. introduced a cell model to study the diffusion-induced growth of a gas bubble surrounded by a thin film of Newtonian liquid to simulate the cases where a large number of bubbles grow in close proximity during foaming [56,57]. Arefmanesh et al.[58], Ramesh [59], and Venerus et al. [60,61] developed models for bubble growth in viscoelastic, power law, Maxwell melts, with the mass and momentum transfer coupled. Sharfi, Joshi et al. in
Texas A&M Univ. modeled simultaneously identical initial nucleation and bubble growth for freely expanded polymer foams [97,98]. Ramesh et al. studied a non-isothermal model, and considered the influence of a blowing agent concentration on polymer viscosity and gas diffusivity in thermoplastic foam extrusion; they also tried to approach real processes with the consideration of gas loss in the atmosphere [99,100]. New opportunities have been made for nucleation and bubble growth investigations since Taki et al. [101] and Guo et al. [102] set up a system to capture a nucleation and foam growth event. Leung et al. studied a polystyrene/carbon dioxide system based on a constant-diffusivity, isothermal cell model, and verified the simulation result with the visualization of the beginning period of bubble growth [96,103].

### 2.3 Crosslinking in Polyolefin Foam Processing

#### 2.3.1 Crosslinking

Crosslinking is a chemical bond between adjacent polymer chains (Figure 2.7). The bond may be a group of sulfur atoms in a short chain, a single sulfur atom, a carbon-to-carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion [104]. When polymer chains are crosslinked, they lose some of their ability to move as an individual chain; the retractile force increases upon imposed deformation of the polymer material, and the amount of permanent deformation decreases after the removal of an applied force. In general, low-density crosslinking raises polymer viscosity; intermediate-density crosslinking makes polymer have some elastomeric properties; and high-density crosslinking causes polymer to be rigid or glassy.
Figure 2.7 Polymer chains and crosslinking

The first commercial method of crosslinking was developed for natural rubber with sulfur in Springfield, Massachusetts, in 1841, in order to make rubber strong enough and maintain its shape after a large deformation [104]. Nowadays, various techniques have been applied in the crosslinking of plastic and rubber materials. For polyolefin elastomers, there exist three main types of crosslinking procedures: (a) physical crosslinking by electron or gamma radiation; (b) chemical crosslinking by agents such as peroxide; and (c) silane crosslinking.

In radiation crosslinking, the most common method is the application of $\beta$ ray. The radiation generates radicals by breaking the hydrogen from weak carbon-hydrogen bonds. The radicals either bond to each other and form a crosslink, or cleave [105].

\begin{equation}
PH \rightarrow P \cdot + H \cdot 
\end{equation} \hfill (2-18)

\begin{equation}
2H \cdot \rightarrow H_2 
\end{equation} \hfill (2-19)

\begin{equation}
2P \cdot \rightarrow P - P 
\end{equation} \hfill (2-20)

In peroxide crosslinking, free radicals are generated by peroxides, which cleave thermally to produce two oxy radicals (Figure 2.8) [106]. Generally, the reaction of peroxide decomposition is first-order. Furthermore, the rate parameter is called half-life time, which
describes the time needed for the decomposition of 50% peroxide. The selection of proper peroxide is based on its decomposition temperature relative to the polymer melting temperature, its decomposition rate, polymer type, etc.

\[ ROOR \rightarrow 2 RO \cdot \]  
(2-21)

\[ PH + RO \cdot \rightarrow P \cdot +ROH \]  
(2-22)

\[ 2P \cdot \rightarrow P - P \]  
(2-23)

Figure 2.8 Crosslinking using peroxide [106]

Silane crosslinking technology makes the bond through a Si-O-Si moiety instead of the C-C bond created via peroxide or radiation cure. Silane is firstly incorporated into the polymer, either by the grafting of vinyl silane onto the polymer backbone or by the copolymerization of vinyl silane with ethylene. Crosslinking is generated with the aid of suitable catalysts [107].

The method of chemical crosslinking is applied in this research. The curing degree can be easily controlled by the amount of chemical crosslinking agent mixed with the polymer.
decomposition temperature of a proper crosslinking agent is higher than the melting temperature and extrusion processing temperature of the polymer. And its decomposition temperature also needs to be lower than the foaming temperature. It is required to generate crosslinking at a fast cycle time. Excessive crosslinking will not degrade the resins.

2.3.2 Characterization of Crosslinking

It is important to characterize the degree of crosslinking, in order to investigate the impact of crosslinking. There are several methods to characterize the degree of crosslinking in the polymer. A common method is to measure the amount of the remaining gel according to ASTM D2765-90, using the reflux extraction method [108]. A sample of about 0.3g is placed in a pouch made of a 120-mesh stainless steel cloth and immersed in boiling butane for 6h. The gel percentage can be calculated by comparing the remaining weight after extraction with the weight of the original specimen.

The impact of crosslinking on the mechanical properties of polymer has also been used to approximate the degree of crosslinking. One example is the stress-strain behavior of the crosslinked polymer. As the crosslinking degree increases, the stress level increases, but the melt extensibility deteriorates. The stress-strain test, either the uniaxial or biaxial test, helps find the optimized crosslink level [109]. Another similar approach is to measure the shear viscosity using an oscillating rheometer. Because the polymer modulus and viscosity is sensitive to the mutation of the polymer network, the chemical degree of transformation during crosslinking reactions can be monitored by time sweep tests, and the crosslinking effects on polymer viscosity can be investigated by doing frequency sweep tests [110]. Cure meters are one kind of oscillating
rheometers which are specially designed to measure the melt torque, in order to control the quality and uniformity of the vulcanization in the rubber stocks.

Differential scanning calorimetry DSC can also be used to study the crosslinking degree of the polymer by measuring the residual curing enthalpy [112,113]. The heat of the partially cured resin is compared with the heat when the uncured resin is fully cured. As such, this ratio is used to describe the percentage of uncrosslinked polymer (Figure 2.9).

![DSC Heat Flow](image)

**Figure 2.9 Crosslinking using peroxide [113]**

### 2.3.3 Crosslinking in Polyolefin Foam Processing

Crosslinking has been used in the plastic/rubber industry because of its improvement on the physical properties of the polymer. Its applied areas include: tire wheels, various hoses, sport gear, wire/cable, and et al. [114]. The edge advantages of crosslinking have also been used in the development of polyolefin foams. Crosslinking increases the viscosity of the polymer, and extends the rubbery plateau of the melt, widening the temperature range in which stable foams can be produced (Figure 2.10) [13].
There are several representative processes which are used to manufacture crosslinked polyolefin foams: irradiation crosslinked foam process, chemically crosslinked polyolefin foam process, chemically crosslinked polyolefin foamed BUN process, grafted resin crosslinked polyolefin foam process, injection molded foam process, and nitrogen autoclave process [3,7,9,10]. Irradiation crosslinked extrusion foaming process was originally developed by Sekisui Electrical Co., using LDPE, EVA or blends, which involves three stages: sheet extrusion, irradiation crosslinking, and expansion. The chemically crosslinked extrusion foaming process was developed independently in Japan by Furukawa Electric Co. and Hitachi Chemical Co.. The chemical crosslinking agent that is used in this foaming process was developed by both companies. However, there are some difference between their methods: in the Furukawa process, the crosslinking and foaming reactions go on concurrently when the extruded sheet goes through the heated oven at around 230°C; while in the Hitachi process, the crosslinking reaction is accomplished at a relatively lower temperature, prior to subsequent foaming at a higher temperature. The press molded crosslinked foam process is a semi-continuous process, which
can be used to produce foams with a larger thickness, compared with the extruded foam process described above. The press molded crosslinked foam process can also be divided into a one-stage process and two-stage process depending on the relative timing of the crosslinking reaction and blowing agent decomposition reaction. The injection molded foam process can be used to produce crosslinked foams when polymers have high melt fluidity, combining the technology of the press molded crosslinked foam process and injection molding. In the late 1950s, the nitrogen autoclave process was originally developed, and this technology was commercialized in the early 1960s by Zotefoams. This process is comprised of three stages: crosslinking, high pressure gassing and low pressure expansion.

All of the above crosslinked foaming processes can be composed of three major steps: mixture formation, crosslinking, and foaming. The foam morphology and the properties of the cellular polyolefin will be affected by the crosslinking [3]. There have been some studies on the effects of crosslinking on the polyolefin foaming, which have been providing some insights to help further understand and develop the technology of crosslinked polyolefin foams.

Yamaguchi et al. investigated the light crosslinking of PE, and its blending effects on the rheological properties and foaming processability of PE. They found that a small addition of crosslinked PE increased the strain-hardening behavior in the elongational viscosity. This enhancement prevented foam deformation and helped PE foams with a higher expansion ratio and better cell distribution [69,70,71].

Some studies have been conducted on the foaming of low density poly (ethylene-co-octene) resins by injection molding. The quantity of the crosslinking agents needed to be chosen properly according to the MFI of the polymer resin, in order to provide sufficient melt strength to
stabilize the bubble growth; meanwhile, excessive crosslinking prohibited the cell growth in the injection molding foaming [115]. The effects of the crosslinking agent content on the viscosity of poly (ethylene-co-octene) were investigated, and the results were linked to the morphology and density of the corresponding foams. Moreover, they found the optimal crosslinking agent content with 5.2% of AZDC at 160°C [116]. Later, an off-line ultrasonic characterization technique was used to further investigate the foaming system in the injection molding foaming [117]. This study illustrated the complexity of the CBA decomposition, the effects of crosslinking on the degassing pressure and the dependence of gas molecule diffusion on the crosslinking [117].

Hong-Jer Tai studied the molecular structure evolution in peroxide-initiated crosslinking of EVA and POEs. His earlier research investigated the crosslinking efficiencies, gel content, conversion degree, and average molecular weight at varying curing conditions. There is a close linear increase in the crosslink density for POEs with a DCP concentration increase of up to 5 phr (parts per hundred resin) [118]. He continued to design a batch foaming system, and used it for the foaming of crosslinked Metallocene polyolefin elastomer, using a chemical blowing agent and organic peroxide. He found that the crosslink density is the most important factor for controlling the cell size, and claimed that the foam cell size could be roughly scaled by the ratio of gas pressure to crosslink density [119]. There is a general trend that the cell size increases with increasing CBA content (within 6 phr) and with decreasing DCP content (within 5phr); the cell size increases by increasing the ratio of gas pressure to crosslinking density [119]. However, the effect of nucleation and its relation with crosslinking were not discussed in this research.

Shih et al. studied the effects of crosslinking on the structure and mechanical properties for SBS/PS/SBR foams. Their results showed that the cell density of the foams increased as the crosslinking agent amount increased. They explained its reason is that the melting strength and
the viscosity of the blends were enhanced enough to prevent the diffusion and the combination of gas bubbles from increasing the content of the crosslinking agent [120]. However, they did not pursue the rheological properties of the polymer and gas diffusion properties, nor did they study the crosslinking effects on them.

Excessive crosslinking restricts foam expansion, while insufficient crosslinking results in bubble rupture and gas loss [121]. More effects have been made to investigate the optimum crosslinking for large foam expansion. An optimum crosslinking prevents bubble rupture and enhances the efficiency of blowing agent. Furthermore, it does not restrain the expansion of the cells.

Early investigations have been conducted on the optimum expansion of crosslinked polyethylene [122,123,124]. Lasman studied the expansion characteristics of peroxide-crosslinked polyethylene along with gel fraction of the polymer, and found that the gel level at the inception of foam expansion needs to be around 30-40%, in order to get the maximum expansion ratio of PE foams. It was also found that the average cell size decreases with the increase of gel level [122]. Radiation technology has also been used to modify polymer viscoelasticity to produce foams [125,126,127]. Similar “mountain shape” trends were observed on the foaming results of radiation crosslinking experiments [127]. Crosslinking over 45% caused a foam split phenomenon, which restricted the foam expansion. Crosslinking below 20% caused cell rupture. With a given amount of blowing agent in the experiments, crosslinking between 30%-40% leads to the highest expansion ratio of POE/LDPE bends [127]. Marcilla et al. studied the crosslinked foaming of PE at atmospheric pressure, and found there was an optimum crosslinking agent amount to produce PE foams with lowest density [124].
Recently, Riahinezhad et al. investigated the influence of nanocomposite on the foaming of LDPE, EVA, and their blends, and found that 3 phr nanoclay content is the optimum amount to produce foams with minimum cell size [128].

When the degree of crosslinking keeps increasing, the molecular mobility of the polymer chains is reduced, which will influence the thermal transitions of the polyolefins, such as glass transition temperature, melting temperature and crystallization [114]. Babu et al. Found that $T_g$ of PP and PP/EOC (ethylene octene copolymer) marginally increases as the peroxide dosage increases from 0 to 4phr [129]. Legranda and Bellengerb found that $T_g$ of amine-crosslinked epoxy increases from -20°C to around 140°C when the cure time keeps increasing [130]. Abe and Yamaguchi found that during the expansion stage, the crosslinked PE foam with lower $T_c$ shrinks to a great degree prior to the crystallization, which is attributed to the volume reduction of the gas in the cells, and therefore the expansion ratio decreases. And the degree of the shrinkage decreases with increasing $T_c$, because of the effects of the crystallization [131].

### 2.4 Objectives and Methodology of the Thesis

The reviews presented in the previous sections show that little have been done to pursue the fundamental mechanisms about how crosslinking affects polymer foaming. The measurement of the fundamental properties is important for the understanding of the cell nucleation and bubble growth in the crosslinked EVA. The solubility determines the amount of blowing agent that can be dissolved inside the EVA, which will be used to generate bubbles. To start the bubble nucleation, the system pressure needs to drop below the solubility pressure. The diffusivity of the blowing agent in the polymer has influence on the gas concentration profile in the matrix during the foaming. It also indicates the speed of the blowing agent leaking out of the polymer. PVT
The viscosity property of the polymer is closely related to the heat generation during the polymer processing. It also has impacts on the bubble growth rate, the stress applied on the bubbles, and the stabilization of the bubble structures. The knowledge of all these fundamental properties can help better understanding of the foaming behavior of crosslinked EVA, and the further development of its foaming technology.

The objectives of this thesis are:

1. To determine experimentally the foaming-related properties of chemically crosslinked EVA polymers, such as the rheological properties, the blowing agent solubility, the blowing agent diffusivity, etc.

2. To investigate the relationship between crosslinking and cell morphology of EVA foams. The impacts of processing and material parameters on the chemically crosslinked EVA foams will be investigated. And the processing parameters will be optimized to maximize the expansion of crosslinked EVA using chemical blowing agent.

However, the final target to know the mechanism and to optimize the foaming is a comprehensive task requiring processing and performance analysis, which are required to be supported by polymer analysis (EVA resin), as well as, chemical characterization (chemical blowing agent, crosslinking agent), rheological investigation (shear viscosity, extensional viscosity), gas solubility measurement, gas diffusivity measurement, cell nucleation and growth study. So the work of this thesis was conducted in the following sub-projects specifically:

- To investigate the effects of the crosslinking on the foam processing
  - Study of rheological properties of crosslinked EVA
- Study of rheological properties of EVA/blowing agent flow with crosslinking
- Measurement of the solubility of the blowing agent in crosslinked EVA
- Measurement of the diffusivity of the blowing agent in crosslinked EVA
- Visualization monitor of cell nucleation and bubble growth in crosslinked EVA in a batch foaming system
- Theoretical analysis of crosslinking’s effects on polymer foaming
  - To investigate the foaming feasibility of the crosslinked EVA foams
  - Set-up of a lab-scale experimental system for crosslinked EVA processing
  - Characterization of foam morphology of crosslinked EVA foams
  - Set-up of a facility to characterize the crosslinking content of the products
  - To investigate the influences of processing parameters on crosslinked EVA foams
    - Effects of the mold temperature on the foaming morphology
    - Effects of the blowing agent content on the foaming morphology
    - Effects of the crosslinking agent content on the foaming morphology
    - Effects of the nucleating agent on the foaming morphology
  - To optimize the foaming of chemically crosslinked EVA
    - Optimization of crosslinked EVA foaming using a chemical blowing agent
Chapter 3
Effects of Crosslinking on Fundamental Properties of EVA/Gas Mixtures

3.1 Introduction

As discussed in Chapters 1 and 2, it is critical to approximate the fundamental properties of the crosslinked EVA in order to better understand the influences of crosslinking on the EVA foaming. This chapter describes the measurements of the rheological properties of the crosslinked EVA/Gas mixtures, the BA solubility in the crosslinked EVA, and the BA diffusivity in the crosslinked EVA.

The rheological behavior of the polymer plays a significant role in the foaming process. At the early stage of bubble formation and growth, excessive melt strength will restrain the bubble growth, resulting in a low foam density. As the bubble continues to grow, the bubble walls stretch. The tensile stresses applied on the walls cause extensional deformation so that this segment of the foaming process is influenced by the extensional viscosity, and melt elasticity of the polymer. In the subsequent stage when the bubbles stabilize, sufficient melt strength is needed to prevent cell coarsening or cell coalescence.

The solubility and diffusivity of the blowing agent (gases) in the polymer melts are also critical parameters, especially when they are at foaming conditions. For effective optimization of the foaming process, accurate solubility data of the blowing agent in the polymer melt is vital. During the diffusion-controlled bubble growing period, the expanding rates of the cells are influenced by the diffusivity of the blowing agent. A low diffusivity is preferable to reduce the
gas loss into open air through the foamed product surface, which enhances the efficiency of the blowing agent used for bubble generation and growth.

In order to fully understand the foaming characteristics of crosslinked EVA, this chapter presents the measurement systems used to experimentally determine the fundamental properties and measurement procedures. Furthermore, the influences of crosslinking on these properties are discussed.

3.2 Methods for Characterizing Rheological Properties

3.2.1 Commercial Rheometers

In this study, several commercial rheometers have been used to measure the shear and extensional viscosities of EVA. An ARES rheometer (TA Instruments Inc.) was used to measure the oscillatory shear viscosity at low-shear-rate range. The ARES rheometer is equipped with two 25-mm parallel disks with a 0.8-mm gap (Figure 3.1).

![Figure 3.1 Oscillatory shear](image)

A twin-bore capillary rheometer (RH2000, Malvern Inc.) was used to measure the shear viscosity at high-shear-rate range. In the experiments, melts were extruded through a 1-mm diameter, zero length capillary die and a 1-mm diameter, 20-mm long capillary die at the same
time. The shear viscosity is calculated from the pressure difference between the zero-length die and long die.

The extensional viscosity was also measured using the ARES rheometer (TA Instruments Inc.) with an Extensional Viscosity Fixture (EVF) attached. EVF uses two cylinders to wind up the sample: one cylinder rotates, while the other measures the force. In order to wind up the sample equally on both sides, the rotating cylinder moves on a circular orbit around the force measuring cylinder while rotating around its own axis at the same time (Figure 3.2).

![Figure 3.2 Schematic of the Extensional Viscosity Fixture](image)

### 3.2.2 The Hele-Shaw Channels and the Processing System

To determine the planar extensional viscosities of polymer melts and polymer/blowing agent solutions, Wang et al. proposed a technique that is based on pressure drop measurements in a thin Hele-Shaw die channel [80]. The die channel has a hyperbolic converging geometry. With this geometry, extensional rates are nearly constant in the core of the flow as compared to the abrupt contraction in conventional filamentary channels. This technique also accounts for the dependence of extensional viscosity on strain, as well as the strain rate experienced by the
polymer melt in the flow [80]. The extensional and shear viscosity measurements in this study were conducted using the technique and the thin Hele-Shaw die channel developed by Wang et al..

The geometry of the Hele-Shaw die channel is presented in Figure 3.3. The geometric parameter H and B is referred as the height and depth of the die channel, respectively. The inlet section of the channel is a three-dimensional wedge-shaped diffuser. After flowing through the diffuser, the flow of the polymer will be re-directed to a rectangular flow. The subsequent Hele-Shaw section is comprised of a high-aspect-ratio straight channel followed by a hyperbolic channel. As illustrated in Figure 3.3, pressure readings along the die will be sampled from three points along the centerline of the straight channel. The drop in pressure from the first to the second transducer ($\Delta P_{\text{shear}}$) is mainly due to the shear the melt experiences. In the convergent region of the die, the pressure drop across the second and third transducer ($\Delta P_{\text{convergent}}$) will be a result of both shear and extension [80]. Based on the obtained pressure drop profile, the shear and extensional rate the melt experiences as well as the shear and extensional viscosity of the melt can be evaluated.

The Hele-Shaw die channel was equipped on a tandem line extrusion system. The system is a laboratory-scale, single-screw tandem extrusion foaming system. The system is comprised of: (i) a 0.75-inch primary extruder for polymer plasticizing and blowing agent dissolution, (ii) a 1.5-inch secondary extruder for melt cooling, and (iii) a positive-displacement pump for blowing agent injection. Figure 3.4 shows a schematic of the tandem extrusion foaming system.
Figure 3.3 Schematic of the Hele-Shaw die (the circles indicate the diaphragms of the pressure transducers) [80]

Figure 3.4 Schematic of the tandem extrusion system
3.3 Study of Shear Rheological Properties of Crosslinked EVA and EVA/Gas Flow

Ethylene-Vinyl Acetate (Elvax 360, 25% Vinyl Acetate by weight, MFI=2g/10min, 0.948g/cm³), supplied by DuPont Inc., and dicumyl peroxide (DCP), 99% purity, supplied by R. T. Vanderbilt Inc., were used in this study.

Elvax 360 resin was compounded with a certain amount of DCP content. This process was carefully conducted to avoid any premature reaction, and to achieve homogenous distribution. A disk-shaped sample was made from the compounded melt using a hot press, and was ready for the ARES rheometer test. In the tests, samples were put between the parallel-plates in the ARES rheometer. Firstly, the dynamic time sweep test was applied to the samples to investigate the cross-linking behaviors of EVA. Dynamic time sweep applies a sinusoidal deformation at constant frequency while taking successive measurements at a user-selected time interval. Dynamic Time Sweep provides a means of monitoring the buildup or breakdown of network structure.

Figure 3.5 and Figure 3.6 show the rheological property of an EVA sample with 0.16phr DCP, which was heated from 100°C to 190°C at the rate of 0.7°C/s. 100°C is selected as the initial point because sample is melted at that temperature without any crosslinking reaction taking place. Sample is heated to 190°C because it is within the proper foaming process window, and it is above the crosslinking temperature and the decomposition temperature of blowing agent which will be selected. The strain control was set at 1%, the stress was 6000Pa.s and the shear rate was 1rad/s, during when the modulus and viscosity were recorded, to monitor the increment of the crosslinking degree as the test time (or the temperature) increased.
Figure 3.5 Time sweep curve for crosslinking

Figure 3.6 Loss tangent with time

From the curve (Figure 3.5), it is evident where the reaction started. The viscosity $\eta$ had some drop because of the temperature-increase effect, but began to increase after the crosslinking took effect when the temperature reached around $120^\circ$C. In the final stage, the viscosity $\eta$
reached a stabilized value. This effect is termed as “plateau”, which showed that chemical peroxide is the effective crosslinking agent for Elvax, rather than “marching” nor “reversion”. “Marching” means the viscosity value keeps increase, and “reversion” means the value will decrease eventually. In the tests, crosslinking enhanced the storage modulus $G'$ to a much greater extent compared with the loss modulus $G''$. As known, the storage modulus is largely a measure of only the elastic component of rheological behavior, whereas the loss modulus is generally measured with the imposition of a sinusoidal and small strain at a certain frequency. We can say crosslinking increases the elasticity ratio against plasticity, and the EVA sample has more rubberlike properties (Figure 3.6).

Dynamic time sweep tests have been applied to samples with varying amounts of crosslinking agent, in order to investigate the influence of crosslinking on the final plateau value of complex viscosity (Figure 3.7). Elvax 360 were compounded with varying DCP contents (0.08phr, 0.16phr, 0.4phr, 0.8phr, 1.2phr), and the samples were tested using time sweep with temperature increasing to 170°C at 0.7°C/s. The test shear rate is 1rad/s, the stress is 6000Pa.s. EVA samples have a higher plateau viscosity with a higher crosslinking agent compounded.
In this test, Elvax 360 were compounded with varying DCP contents (0phr, 0.08phr, 0.1phr, 0.16phr, 0.2phr, 0.5phr, 1phr, 2phr), and the samples were tested using time sweep with temperature increasing to 170°C at 0.7°C/s. We can use time sweep tests to monitor the
crosslinking reaction progress from the time sweep results. As the crosslinking agent content increases, more crosslinking points will be established between the polymer chains. Crosslinking density continues increasing until it reaches a saturation point, when all the potential points along the polymer chains have been used up. This process is called the fully crosslinked stage (Figure 3.8).

The gel content of the specimen was measured using the reflux extraction method. The gel content is the insoluble fraction in the crosslinked polymer which cannot be extracted with solvents such as decahydronaphthalene or xylenes. A sample of about 0.3g was placed in a pouch made of 120-mesh stainless steel cloth and immersed in boiling butane for 6h. The amount of remaining gel is calculated according to ASTM D2765-90. The gel content for crosslinked EVA can be determined by the solvent extraction test method (ASTM D2765). Under 190°C, 0phr DCP results in 0% gel content, 0.08phr DCP results in 18.3% gel content, 0.16phr DCP results in 38.1% gel content. The higher DCP leads to a saturated gel content when the sample is fully crosslinked with the reaction time being long enough.
Figure 3.9 Rheological behavior of EVA: (a) shear viscosity; (b) relaxation time

Shear viscosity and relaxation time are quite important parameters for numerical simulation of bubble growth. Viscosity values of low shear rates were measured using the oscillating rheometer. The effect of shear rate on the rheological properties of EVA 360 can be indicated in Figure 3.9, which was obtained from dynamic frequency sweep tests. Dynamic
frequency sweep tests applies a sinusoidal deformation of constant peak amplitude over a range of frequencies, and by using the dynamic frequency sweep test, we can investigate the effect of varying the frequency of deformation on the storage modulus, $G'$, loss modulus, $G''$, and complex viscosity, $\eta^*$. The dynamic properties, $G'$ and $G''$ were evaluated from these viscosity data at two temperatures, 170°C and 190°C, and a relaxation time was determined for each temperature from the crossover point. As shown in the Figure, the relaxation time, $\lambda$, of 0.063s and 0.019s was determined for pure Elvax 360 for temperatures 170°C and 190°C, respectively.

![Rheological behavior of EVA obtained from the capillary rheometer](image)

**Figure 3.10** Rheological behavior of EVA obtained from the capillary rheometer

For high shear rates, viscosity values were determined using the capillary rheometer with a 1-mm diameter, and 20-mm long capillary. Measurements from the capillary rheometer are plotted in Figure 3.10. With the increase of the temperature, the shear viscosity of EVA decreases. It is observed that the shear viscosities converge at high shear rate, which is because the effects of shear thinning. There exists molecular alignment in the direction of the flow, which decreases the resistance exhibited by the polymer.
For medium shear rates, the viscosity values were approximated from the pressure drop profile obtained using the Hele-Shaw die channel. As the polymer melt flows into the Hele-Shaw die channel, the pressure experienced by the melt will gradually drop. The pressure loss in the straight section of the channel is determined by the fluid’s viscosity. The viscosity data can be estimated based on channel dimensions and measurements of the pressure drop and flow rate, by following the approaches as suggested by Laun et al.\[132]:

\[
\tau_w = \frac{\Delta P}{L_0} \cdot \frac{H}{(1+H/B)} \quad (3-1)
\]

\[
\dot{\gamma}_w = \frac{6Q}{B_0H^2} \cdot \left(\frac{2+b}{3}\right), \text{where } b = \frac{d[\log(6Q/B_0H^2)]}{d[\log(\tau_w)]} \quad (3-2)
\]

\[
\eta = \tau_w / \dot{\gamma}_w \quad (3-3)
\]

In this approach, \(\Delta P\) is the pressure difference between the first two transducers in Figure 3.3, \(\tau_w\) is the wall shear stress, \(\dot{\gamma}_w\) is the corrected wall shear rate, \(Q\) is the volumetric flow rate, and \(\eta\) is the viscosity. Equation (3-3) in this approach has incorporated the Rabinowitch correction to account for the wall shear rate difference between a Newtonian and a shear-thinning fluid [133].
Figure 3.11 Overall rheological behavior of EVA: (a) 170°C and (b) 190°C
The shear viscosity data obtained from each of the aforementioned methods is plotted in Figure 3.11. It is observed that the data obtained from the three methods correspond well with each other. It is known that the temperature has an impact on the rheological properties of the resin. Results in this study, as shown in Figure 3.12, also reveal that the shear viscosity of the resin drops with an increase in the temperature from 170°C to 190°C. By applying the Carreau-Yasuda model (equation 3-4) on the estimated viscosity curves, the power-law index, $n$ for pure Elvax 360 EVA resin at high shear rates was estimated to be 0.0493, which indicates that the EVA resin experiences a strong shear thinning effect at high shear rate. The best-fitting parameters described by the Carreau-Yasuda model were calculated: $\eta_0 \ 6.32 \times 10^4$ Pa·s (170°C), $\eta_\infty \ 0$ Pa·s, $\lambda \ 0.369$ s, $\alpha \ 0.285$.

\[
\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = [1 + (\lambda \dot{\gamma})^a]^{-\frac{n-1}{a}}
\]

(3-4)

Using the calculation approach described above, EVA viscosity data was obtained under the influences of crosslinking and blowing agent. Figure 3.13 (a) (b) shows the viscosity profile.
of EVA resins with different crosslinking agent contents. It is observed that the shear viscosity increases proportionally as the content of the DCP is raised from 0phr to 0.08phr and 0.16phr. Similar observations were found from the data obtained at both 170°C and 190°C. It is shown that there exists difference between the slopes of the viscosity curves of the uncrosslinked and crosslinked EVA. The viscosity of crosslinked EVA increases to a much higher value compared with the viscosity of uncrosslinked EVA when the shear rate decreases. This is because that EVA has more elasticity characteristics of a solid material with the addition of crosslinking.

As for the plasticizing effect of the blowing agent gas on the polymer melt, it is observed from Figure 3.14 that the shear viscosity for EVA resins decreases when 1wt% of supercritical N₂ was injected into the melt. The decrease amount of the shear viscosity of the pure EVA because of the dissolved gas is slightly higher as compared to the viscosity drop amount of the partially crosslinked EVA. What is more, the viscosity of partially crosslinked EVA is higher than that of pure EVA, even the former is injected with 1wt% of supercritical N₂.
Figure 3.13 Effects of crosslinking on EVA shear viscosity (a) 170°C; (b) 190°C
3.4 Study of Extensional Rheological Properties of Crosslinked EVA and EVA/Gas Flow

The ARES rheometer (TA Instruments Inc.) with an Extensional Viscosity Fixture (EVF) was used to measure the extensional viscosity of the crosslinked EVA. Figure 3.15 shows the curves of the extensional viscosity at (a) 170°C and (b) 190°C.

As seen in the figure, the extensional viscosity of the crosslinked EVA increases with the weight percent of the DCP. This result demonstrates that the high level melt strength is ascribed to the enhanced strain hardening in extensional viscosity as the crosslinking degree increases. The extensional viscosity of uncrosslinked EVA starts at a relatively lower value, and decreases along with the extension and time.
At the initial experiment stage of crosslinked EVA, the extensional viscosity starts at a low value, which means the polymer matrix gives a low resistance to the nucleated bubble and allows it to continue expanding with relative ease and no shrink back. However, as time progresses and the bubble size increases, more extensional strain is exerted on the elastomer in the bubble walls. Eventually, the polymer network chains stretch out completely and start aligning along the bubble walls leading to the observed strain hardening. As seen in Figure 3.15, the extensional viscosity continues to increase with time at both (a) 170°C and (b) 190°C. This is critical to maintain the growing bubble morphology, and to prevent bubbles from rupturing. The relatively low value of the extensional viscosity at initial stage and the high value of the extensional viscosity with strain hardening are beneficial for the early bubble generation and growth, and bubble stabilization.
Figure 3.15 Growth curves of extensional viscosity for crosslinked EVA at (a) 170°C, (b) 190°C with 0.08 phr and 0.16 phr at various strain rates: 0.01 s\(^{-1}\), 0.05 s\(^{-1}\) and 0.10 s\(^{-1}\)
The tandem system with the Hele-Shaw die was used to measure the extensional viscosity of the crosslinked EVA with gas dissolved. As the polymer melt flows into the Hele-Shaw die, $\Delta P_{\text{convergent}}$, the pressure drop at the converging section of the die depends on the elastic normal stresses exerted onto the melt. With reference to the literature [80], the increase in the extensional stress along the channel centerline to its maximum at the exit, $\Delta P_e$, can be estimated through the following equation:

$$\Delta P_e = \Delta P_{\text{convergent}} - \frac{L_1}{L_0} \cdot \Delta P_{\text{shear}} - \int_0^{L_2} \left( \frac{\partial \tau_{yx}}{\partial y} + \frac{\partial \tau_{zx}}{\partial z} \right) dx - \Delta P_{\text{exit}}$$  \hspace{1cm} (3-5)

where $\Delta P_{\text{shear}}$ is the pressure drop at the shear section of the die, $\Delta P_{\text{exit}}$ is the pressure drop at the exit section of the die, and $L_0$ and $L_1$ are the geometrical parameters of the die. If shearing on the hyperbolic walls is neglected, the extensional rate along the centerline, $\dot{\varepsilon}_{\text{HS}}$, will become constant. The value of $\dot{\varepsilon}_{\text{HS}}$ may be estimated from equation:

$$\dot{\varepsilon}_{\text{HS}} = \frac{dv_{\text{HS}}}{dx} = \frac{(2n+1)Q}{(n+1)H} \cdot \frac{1}{\frac{1}{B_1} \cdot \frac{1}{B_0}}$$ \hspace{1cm} (3-6)

where $v_{\text{HS}}$ is the centerline velocity and $n$ is the power-law index obtained from the Carreau-Yasuda estimation. Based on the value of the extensional stress and extensional rate evaluated, the extensional viscosity that the melt experienced can be estimated through:

$$\eta_P = \frac{\tau_{xx} - \tau_{yy}}{\dot{\varepsilon}} \approx \frac{\Delta P_e}{\dot{\varepsilon}}$$ \hspace{1cm} (3-7)

The response of the melt’s extensional viscosity on the temperature, the degree of crosslinking, and the content of blowing agent was summarized in Figure 3.16. It is observed that the extensional viscosity of the melt had dropped as the melt temperature was increased and as the blowing agent was injected into the polymer. As the DCP was compounded to the resin, the
extensional viscosity of the melt had increased due to the partial crosslinking network formed in
the melt.

Figure 3.16 Effect of crosslinking on EVA extensional viscosity

3.5 Methods for Characterizing Solubility and Diffusivity of
Blowing Agent in Polymers

The effects of the crosslinking degree on the diffusivity and solubility of the blowing
agent in the polymer matrix were investigated based on the sorption experiments and by using
MSB (Rubotherm GmbH). The basic theoretical mechanism is based on the experiments with a
disk-shaped specimen pressurized in a pressure vessel with the blowing gas. At various times,
the mass uptake was recorded. The mass will stay steady once the polymer is saturated with the
gas. In the experiments, approximately 0.5 grams of crosslinked polymer without chemical
blowing agents were shaped in the form of a disk with 3mm thickness. A schematic of the MSB
system is shown in Figure 3.17 [18].
Before the sorption experiment, a precisely weighed polymer sample was placed in the sealed absorption chamber, degassed in the vacuum, and preheated to a designated temperature. The balance readout at vacuum \((P=0)\) and temperature \((T)\) for the polymer sample without any dissolved gas was recorded as \(W(0,T)\); this value reflected the weight of the vacuum. The high-pressure gas was subsequently charged into the chamber, and the sorption occurred. When the saturation stage was reached, the sorption stopped and the weight readout from the balance was recorded as \(W(P,T)\) at pressure \((P)\) and temperature \((T)\). Hence, the weight gain from the dissolved gas in the polymer, \(W_g\), was calculated as follows:

\[
W_g = W(P,T) - W(0,T) + \rho_{gas}(V_B + V_P + V_S)
\]

where \(\rho_{gas}\) is the density of the gas inside the chamber at temperature \(T\) and pressure \(P\), which can be measured \textit{in situ} by the MSB; \(V_B\), \(V_P\), and \(V_S\) are the volumes of the sample holder (i.e., the sample container and all measuring load coupling devices), the volume of pure polymer at temperature \(T\) and pressure \(P\), and the swollen volume of the polymer due to gas dissolution,
respectively. \( V_B \) is usually determined in advance with a blank experiment. \( V_P(P,T) \) can be determined by using the Tait equation for each individual polymer.

By ignoring the polymer’s swollen volume \( (V_S) \) in Eq. 1, the measured weight gain \( W_g \) in Eq. 1 can be transformed to the apparent solubility (Eq. 2), \( X_{\text{apparent}} \), which is less than the actual solubility:

\[
X_{\text{apparent}} = \frac{W(P,T) - W(0,T) + \rho_{\text{gas}}(V_P + V_S)}{\text{mass of sample}}
\]  

(3-9)

Li, Y.G. et al. [86] developed a visualization apparatus system (Figure 3.18) to monitor the PVT (pressure-volume-temperature) behavior of the polymer/gas solution. In the experiment, a droplet-shaped polymer sample was placed on the plate inside the chamber. The chamber was then heated to a designated temperature, and injected with gas to a designated pressure. A camera was used to capture the shape of the polymer droplet along with time. Sample volumes were calculated from the sample shapes. Therefore, the value of a swollen volume of polymer \( (V_S) \) was obtained experimentally. The corrected solubility data can be calculated, to be compared with the results from equation 3.9.

![Figure 3.18 Schematic of PVT System [86]](image_url)

Figure 3.18 Schematic of PVT System [86]
Based on the sorption curve from the MSB system, the diffusivity can be calculated utilizing Equations 2-7, 2-8, 2-9, 2-10 as described in Section 2.2.3.2. The diffusivity of the gas can be calculated as:

$$\frac{M_t}{M_{\infty}} = 4\left(\frac{D}{\pi}\right)^{1/2} \left(\frac{t^{0.5}}{L}\right)$$

(3-10)

A plot of \(\frac{M_t}{M_{\infty}}\) versus \(\left(\frac{t^{0.5}}{L}\right)\) can be used to determine the diffusivity D.

### 3.6 Study of the Influence of Crosslinking on the Solubility and Diffusivity of Blowing Agent in Crosslinked EVA

The sorption experiments were conducted under 190°C, with 6.9MPa, 13.8MPa, and 20.7MPa N\(_2\) respectively. Firstly, EVA pellets and dicumyl peroxide (DCP) were compounded together using a batch mixer. The mixing process made the crosslinking agents evenly distributed into the polymer matrix. Four various amounts of DCP were investigated (0 phr, 0.08 phr, 0.16 phr, and 0.5 phr). The samples were kept at 190°C to accomplish the crosslinking reactions. The rotational rheometer was applied to examine the uniformity of the compounding distribution by measuring the melt modulus, which will be enhanced by the crosslinking reaction.
The swollen volumes of pure polymer were determined using the PVT measurement system (Figure 3.19). It is observed that the polymer swelling ratio increases with the applied
pressure. More gas is dissolved at a higher pressure, leading to a greater swelling effect. Figure 3.19 also illustrates the swelling ratio with different amounts of the crosslinking agents. With more crosslinking agents, the swell ratio drops down and goes to a constant value as the crosslinking becomes saturated. It is believed that the induced crosslinked molecular chains generate a higher resistance to the volume expansion.

The solubility of N$_2$ in EVA is shown in Figure 3.20. It was observed that the N$_2$ solubility in the crosslinked EVA increases as the pressure increases. Furthermore, by increasing the amount of the crosslinking agent, the solubility decreases and goes to a constant value. The crosslinking generates high resistance to the volume expansion, which reduces the ratio of the swelling caused by the gas dissolution, and also creates less accommodation of the polymer melt for the small gas molecules. Once the crosslinking is saturated, the gas solubility value goes stable. Figure 3.20 also illustrates that the N$_2$ diffusivity in the EVA decreases as the crosslinking agent amount increases.

3.7 Summary

In this section, the rheological properties of the crosslinked EVA/gas flow, the solubility and the diffusivity of the blowing agent were experimentally characterized using novel systems. An oscillatory rheometer can be used to monitor the procedure of the crosslinking reaction. Crosslinking increases both the shear and extensional viscosities of EVA significantly. It is observed that the shear and extensional viscosities of crosslinked EVA decreases when the nitrogen gas is dissolved into the polymer. Nevertheless, the addition of crosslinking still plays a dominant role in increasing the viscosity of EVA. We can predict that the crosslinking can make
the foaming easier by maintaining the bubble’s structure with increased melt strength. Both the solubility and the diffusivity of N₂ decrease with the increase of the crosslinking agent amount.
Chapter 4
In-Situ Visualization Study on the Effects of Crosslinking on Cell Nucleation and Early Cell Growth of EVA Foam

4.1 Introduction

It is noted that the addition of crosslinking plays an important role in the polyolefin foaming, based on the research review of Section 2.3.3. Previously, people had been studying the influence of crosslinking on the foaming based on the analysis of final cell morphology of foamed products. Owing to the progress of the development of the visualization batch foaming system, we can visually observe the bubble growth in the foaming.

Ohyabu et al. [134] designed a high-pressure visualization device in order to observe the early stages of the foaming process of PP using CO₂. Taki et al. [135] subsequently used a similar high-pressure cell and studied the foaming behaviors of homo PP using CO₂. Guo et al. [102] designed a system to accommodate high-pressure drop rates (up to 2.5GPa/s) and high frame rates (up to 120,000 frames/s) [102] in order to capture the polymer's foaming behaviors.

In this study, the early stage of bubble growth of the crosslinked EVA samples was investigated using a batch simulation system with the visualization capabilities. The experimental results were analyzed to assess the fundamental mechanisms of the cell generation and the early stage of bubble growth for the crosslinked EVA, which have not thus far been clearly identified.
4.2 In-Situ Visualization of Bubble Growth in the Crosslinked EVA Foaming

4.2.1 Materials, Experimental Apparatus and Procedure

Ethylene-vinyl acetate (EVA) (Elvax 360) with a vinyl acetate weight content of 25% was supplied by DuPont Inc. This EVA resin is in a pellet form and has a melt index of 2g/10min. The melting point of this EVA is about 78°C based on the DSC data conducted. N₂ was used as the blowing agent and was supplied by Linde Gas. The crosslinking agent used in this study was di-cumyl peroxide (DCP), 98% purity and its reaction temperature is around 120°C.

Figure 4.1 On-line visualization system
A disk-shaped compounded sample with 0.5mm thickness was placed in a sealed chamber at the desired temperature. The pressure loading was first considered as coming from the decomposed gas. After a certain amount of hold time, the gas valve was opened to trigger foaming. During this process, bubble growth behaviors were recorded and analyzed by image analysis software (Image Pro). During the experiments, bubble size profile was used for further analysis and comparison.

Table 4.1 shows all the experiments that have been conducted in the visualization batch foaming investigation. For each case, three batches have been conducted.

<table>
<thead>
<tr>
<th></th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>CA (phr)</th>
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<tbody>
<tr>
<td>1</td>
<td>6.9</td>
<td>170</td>
<td>0.08</td>
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<tr>
<td>2</td>
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<td>18</td>
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</tbody>
</table>

Table 4.1 Experiment design of visualization batch foaming

Figure 4.2 shows the one case of captured bubble growth pictures along with second going at 6.9MPa 180°C. From the picture series, it is easy to observe that the bubble number
increased significantly at the initial time. During the bubble growth process, the pressure data was recorded. After accounting the cell numbers, the cell density change along with time was graphed (Figure 4.3). Cell density $n$ was calculated as the number of cells per unit volume with respect to the un-foamed polymer (Equation 4-1). $\rho_p$ is the bulk density of pure polymer, $\rho_f$ is the bulk density of foamed sample. What is more, the bubble diameter could be measured, and the average cell size along with time could also be graphed. The data was used to further investigate the crosslinking effects on the bubble growth in the elastomer foaming.

$$n = \left( \frac{n_c}{l^2} \right)^{3/2} \times 10^{12} \times \frac{\rho_p}{\rho_f} \quad (4-1)$$

Figure 4.2 Captured images of bubble growth

Figure 4.3 Cell density calculations
4.2.2 Results and Discussion

4.2.2.1 Effects of Crosslinking Agent Content

Figure 4.4 shows the pictures of the bubble growth at the early stage. Figure 4.5 shows the data calculated from Figure 4.4. It illustrates the cell density increases with the time at varying crosslinking agent amounts. It is observed that the cell density increases with the crosslinking agent content, which is because of the modification of the crosslinking density. Crosslinking causes an increase in the local stress variations around the crosslinked sections, and thereby cell nucleation will be promoted from the sections subject to a tensile stress. On the other hand, the molecules are connected through crosslinking, and therefore, the expansion will be promoted through an increase in the melt strength. There were no significant differences between the times when the first bubble was observed with varying crosslinking agent contents. What is more, the bubble growth speed decreases with the addition of the crosslinking agent.
(a)

(b)
4.2.2.2 Effects of Gas Pressure

Figure 4.6 illustrates the cell density increase along with the time at varying gas pressures. It is observed that with higher pressure, higher cell density is obtained. This is because that with higher pressure, more blowing agent is dissolved into the polymer which can be used for the cell nucleation. Furthermore, higher pressure introduces faster pressure drop rate and more thermodynamical instability during the degassing and higher cell density. Furthermore, bubble nucleation starts earlier in the foaming experiment with higher saturation pressure.
(a)

(b)
Figure 4.6 Cell density increase with time at varying gas pressure (a) 0phr DCP (b) 0.08phr DCP (c) 0.16phr DCP

4.3 Theoretical Analysis

The previous batch foaming study using the visualization system showed how the addition of crosslinking influences the cell generation and early bubble growth of EVA experimentally. The impacts of crosslinking can also be studied through the theoretical analysis based on the knowledge of numerical model of foaming and measurements of fundamental properties in previous sections.

Early growth of single bubble (Figure 2.3) can be described and governed by a group of equations that include: the mass balance equation over the bubble (equation 4-2), the gas
diffusion equation in the polymer around the bubble (equation 4-3), the momentum equation (equation 4-4), and the constitutive equations (equation 4-5, 4-6) [19, 103].

\[
\frac{d}{dt} \left( \frac{4\pi P R^3}{3\eta T} \right) = 4\pi R^2 D \frac{\partial c}{\partial r} \bigg|_{r \to R} \tag{4-2}
\]

\[
\frac{\partial c}{\partial t} + u(r) \frac{\partial c}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( Dr^2 \frac{\partial c}{\partial r} \right) \tag{4-3}
\]

\[
P_g - \frac{2\sigma}{R} - P_f + 2 \int_{r_{\text{shell}}}^{R} (\tau_{rr} - \tau_{\theta\theta}) \frac{dr}{r} = 0 \tag{4-4}
\]

\[
\frac{d\tau_{rr}}{dt} = - \left( \frac{1}{\lambda} + \frac{4R^i \dot{R}}{y + R^i} \right) \tau_{rr} - \frac{4\eta}{\lambda} \frac{R^i \dot{R}}{y + R^i} \tag{4-5}
\]

\[
\frac{d\tau_{\theta\theta}}{dt} = - \left( \frac{1}{\lambda} - \frac{2R^i \dot{R}}{y + R^i} \right) \tau_{\theta\theta} + \frac{2\eta}{\lambda} \frac{R^i \dot{R}}{y + R^i} \tag{4-6}
\]

In the calculation for the partially crosslinked EVA, the relaxation time $\lambda$ and the viscosity $\eta_0$ were obtained from experiment. The diffusivity $D$ was concluded from the solubility profile by MSB. The same calculation strategy was applied with a fourth-order Runge-Kutta method as the research work conducted by Leung [19, 103]. With a lower diffusivity, less gas can be accumulated in the region around bubble, which decreases the average bubble growth rate. The lower diffusivity also leads to a lower gas loss to the surrounds, and slower bubble collapse. The higher viscosity decreases the average bubble growth rate; however it plays a more important role in the bubble stabilization in the final stage of foaming, which could not be observed in our visualization experiments.
4.4 Summary

A batch foaming simulation system with a visualization component can be used effectively to evaluate the foamability of the crosslinked EVA. It is observed clearly that crosslinking has an influence on the bubble generation and early bubble growth in the EVA foaming. The experiments conducted in this study led to the following conclusion, which is that, the cell density of the EVA foam increases as the crosslinking content increases. We also observed that the bubble grow rate decreases with the addition of crosslinking. Furthermore, the gas amount and pressure also have significant effects on cell density.
Chapter 5

Compression Molding of Crosslinked EVA Foams

5.1 Introduction

This chapter presents the foaming experiments of crosslinked EVA using a compression molding machine. According to the previous sections, the addition of crosslinking can be beneficial for the EVA foaming because it helps cell generation, increases melt strength, and reduces the gas loss. It is important to investigate the influences of crosslinking on the final foam morphology of EVA, as the results can provide a better idea to optimize the foam quality and foam expansion ratio.

At high crosslinking level, the motions of polymer molecular chains become restricted, and the "tight" network is incapable of dissipating much energy. Crosslinking levels must be high enough to prevent failure by viscous flow, and low enough to avoid brittle failure upon extension by the growing bubbles during foaming. Thus, EVA has an optimum crosslinking density range for foaming. We can predict that there exists a mountain-shape curve to describe the relationship between the foam expansion ratio and the crosslinking amount.

This chapter will study the influences of the processing parameters on the cellular morphology of crosslinked EVA foams, and the optimization of the foam expansion ratio by controlling the crosslinking agent amount.
5.2 Experimental Design

5.2.1 Processing Strategies

Figure 5.1 shows the procedure of the batch foaming using chemical blowing agent (CBA). Polymer pellets, blowing agents and crosslinking agents were compounded together. The mixing process made the blowing agents and crosslinking agents evenly distribute into the polymer matrix, without any premature decompositions. The rotational rheometer was applied here to examine the compounding distribution uniformity by measuring the complex viscosity, the value of which can be controlled by the degree of crosslinking. Next, the compounded plastic melt was melted and shaped in the cavity of the mold, which was made up of the male and female mold parts clamped shut by the hydraulics. The mold temperature was then increased. After a certain amount of time, the male and female mold parts were separated. A foamed product was obtained and cooled in open air.

Figure 5.1 Schematic of batch foaming process
5.2.2 Material Properties

Ethylene-vinyl acetate (EVA) (Elvax 360) with a vinyl acetate weight content of 25%, supplied by DuPont Inc., was used. This EVA resin is in a pellet form and has a melt index of 2g/10min. The melting point of this EVA is about 78°C based on the DSC experiments conducted. The CBA used was Celogen® OT. The crosslinking agents used in this study were di-cumyl peroxide (DCP) with 98% purity and Di-Cup 40C, both supplied by R. T. Vanderbilt Inc. The latter has a DCP weight content of 40% and a decomposition temperature of 120°C.

5.2.3 Characterizations

A scanning electron microscope (SEM, JEOL JSM-6060) was used to evaluate the morphology. The samples were dipped in liquid nitrogen and then fractured to expose the cellular morphology and then the fractured surface was sputter-coated with gold. The expansion ratio \( \nu_e \) was calculated as the ratio of the bulk density of pure polymer \( \rho_p \) to the bulk density of foamed sample \( \rho_f \) as shown in Equation 5-1. The void fraction \( V_f \) was calculated as shown in Equation 5-2. The number of cells \( n_c \) could be defined in the SEM pictures in an area \( l \times l \). Cell density \( n \) was calculated as the number of cells per unit volume with respect to the un-foamed polymer (Equation 5-3).

\[
\nu_e = \frac{\rho_p}{\rho_f} \tag{5-1}
\]
\[ V_f = 1 - \frac{\rho_f}{\rho_p} \]  
(5-2)

\[ n = \left( \frac{n_e}{T^2} \right)^{3/2} \times 10^{12} \times v_e \]  
(5-3)

5.2.4 Foaming Processing Window

Experiments were designed to approximate the processing window for the crosslinked EVA foaming, which included the crosslinking agent content, the blowing agent content, the mold temperature, the nucleation site content and the molding time. Taguchi method was utilized in this design of experiment. Firstly a proper processing window was found and chosen: temperature (170°C - 190°C); CBA percentage (3phr - 9phr); crosslinking agent amount (1phr – 4phr); nucleating agent amount (0-3phr); curing time (3min – 9min).

Next experiments were conducted to find which factors have more influence on the performance. Design parameters X included x1 temperature (170°C, 190°C); x2 CBA percentage (3phr, 6phr, 9phr); x3 crosslinking agent percentage (1phr, 2phr, 4phr); x4 nucleating agent amount (2.4phr, 4.8phr, 7.2phr); x5 curing time (3min, 6min, 9min). Outputs Y included y1 foam density; y2 expansion ratio. Component parameters (including x2, x3, and x4), processing parameters (including x1, x5) were analyzed by one set of experiments based on Taguchi Method. L54 orthogonal array (1 column of level 2 and 4 columns of level 3) were used to guide the accomplishment of experiments, and Minitab software was used for the data analysis.
Figure 5.2 shows that both the crosslinking agent amount and CBA amount have high influence factors, which means these two factors play the dominant role on the expansion ratio of the final EVA foams. The amounts of CBA and crosslinking agent need to be chosen properly, so as to obtain the crosslinked EVA foams with the maximum expansion ratio. This result helps the study in Section 5.4.

5.3 Preliminary Analysis of Processing Parameters

5.3.1 Effects of Temperature

The effects of the temperature on the foaming of crosslinked EVA were investigated. The temperatures were set to be 170°C, 180°C and 190°C. The other parameters were: 4 phr CBA, 1.6phr crosslinking agent, 2.4phr calcium carbonate as nucleation sites and 6min curing time. Figure 5.3 illustrates the relationship between the cell morphology and the foaming temperature.
The influence of the temperature on the cell density is very slight. The foam density and the expansion ratio remain quite similar.

Figure 5.3 Crosslinked EVA foams with varying temperatures (a) data graph (b) SEM images
5.3.2 Effects of Chemical Blowing Agent Content

The effects of the CBA content on the foaming of crosslinked EVA were investigated. The amounts of the CBA were set to be 1phr, 2phr, 3phr, 4phr, 6phr. The other parameters were: 190°C foaming temperature, 1.6phr crosslinking agent, 2.4phr calcium carbonate as nucleation sites and 6min curing time. Figure 5.4 illustrates the relationship between the cell morphology and the CBA content. The cell density increases with CBA increasing; the foam density decreases, and the expansion ratio increases. CBA content increases, providing more gas used for generating bubbles. With all other parameters remaining constant, the cell density gradually goes to a plateau value when CBA content keeps increasing.
5.3.3 Effects of Crosslinking Agent Content

The effects of the crosslinking agent content on the foaming of crosslinked EVA were investigated. The amounts of the crosslinking agent were set to be 0.08phr, 0.4phr, 0.8phr, 1.2phr, 1.6phr. The other parameters were: 170°C and 190°C foaming temperature, 3phr CBA, 2.4phr calcium carbonate as nucleation sites and 6min curing time. Figure 5.5 illustrates the relationship between the cell morphology and the crosslinking agent content.

Similar trends were observed when the crosslinked EVA were foamed at both temperatures. The cell density increases with crosslinking agent increasing; the foam density
decreases; and the expansion ratio increases. CA content increases, providing higher melt strength, which is vital to get a nice foam.

![Graph showing cell density and expansion ratio](image)

(a)

![SEM images of foam structures](image)

0.08phr 0.4phr 0.8phr 1.2phr 1.6phr

(b)
5.3.4 Effects of Nucleating Agent

The effects of the nucleating agent on the foaming of crosslinked EVA were investigated. The amounts of the nucleating agent were set to be 0phr, 2.4phr calcium carbonate, 2.4phr talc powder. The other parameters were: 190°C foaming temperature, 1.6phr crosslinking agent, 4phr CBA amount and 6min curing time. Figure 5.6 illustrates the relationship between the cell morphology and the nucleating agent. It is observed that with the addition of the nucleating
agents, the cell density increases significantly. Nucleating agents provide more sites for the bubble generation, leading to a higher cell density.

![Graph showing cell density and expansion ratio](image)

(a)

![SEM images of crosslinked EVA foams](image)

(b)

Figure 5.6 Crosslinked EVA foams with different nucleating sites (a) data graph (b) SEM images
5.4 Optimization of the Processing Parameters to Maximize the Expansion of Crosslinked EVA Foam using a Chemical Blowing Agent

It is very important to obtain the foamed products with maximum expansion ratio, which can benefit the industry by saving more material. What is more, the pursuit of the optimization of the processing parameters can motivate academic professionals to better understand the mechanisms of the technology.

Results in Section 5.2.4 show that the crosslinking agent and CBA amounts are most dominant factors in determining final foam expansion ratio. In this set of experiments, the foaming temperature was set to be 170°C, the talc powder was chosen to be the nucleating sites at 2.4phr and the curing time was set to be 6min. All the experiments have been conducted twice at the same condition, and five samples have been characterized for each experiment condition.
We can better understand the influence of the crosslinking on the foaming behavior with the knowledge of the crosslinking percentage. Section 2.3.2 presented several methods to characterize the curing percentage. A DSC was used in this investigation. EVA samples were placed into the DSC, and the residual curing enthalpies were measured for each sample. EVA sample with 9 phr DCP compounded is considered to be fully cured at 170°C for 30min. Therefore the curing percentage was calculated as:

\[
\% \text{ cured relative to 9phr} = \frac{\text{Uncured Enthalpy Change} - \text{Residual Enthalpy Change}}{\text{Uncured Enthalpy Change of 9 phr}} \times 100
\]
Figure 5.8 shows a heat flow graph of a crosslinked EVA sample (cured with 1.2 DCP for 3 min). The residual enthalpy was calculated from the peak to be 4.493 J/g. Figure 5.9 shows the curing percentage of EVA crosslinked with varying DCP contents. The degree of curing increases along with time, until all the crosslinking agent have been used, or all the available points on the polymer main chains that can be crosslinked have been used.

Figure 5.8 Heat flow of partially crosslinked EVA

Figure 5.9 Curing percentage compared with fully crosslinked EVA (9phr DCP, 30min)
Figure 5.10 EVA foams with varying crosslinking percentage (a) expansion ratio; (b) cell density
It is observed that there exists an optimum value of crosslinking agent amount to obtain maximum expanded foams at a fixed amount of CBA. When the crosslinking amount is low, the melt strength is not high enough to hold the bubble structures. This is the reason that foams with low expansion ratios and low cell densities were obtained when the crosslinking agent amounts were low. When the crosslinking agent amount increases, the cell density and expansion ratio increases. With excessive crosslinking agent amounts, the expansion ratio of the foams decreases. This is because too much crosslinking restrains the bubble growth in the foaming. Excessive crosslinking will cause a more elastic deformation, so the elastic component in bubble growth will increase. This means that the expansion ratio will be decreased. What is more, the glass transition and crystallization properties of EVA will change with excessive degree of crosslinking, which will affect the stabilization of the EVA foams during cooling.

A mountain shape curve exists to describe the relationship between the foam expansion ratio and crosslinking agent amount. This is similar to the relationship between the foam expansion ratio and die temperature in the foam extrusion [136]. Furthermore, when the blowing agent used for the foaming increases, the value of the optimum crosslinking agent, which is to obtain foams with maximum expansion ratio, also needs to be increased.

### 5.5 Summary

In this Chapter, experimental studies were carried out to investigate the foaming feasibility of crosslinked EVA and the processing parameters were optimized to maximize the expansion ratio of the crosslinked EVA using a CBA. There exists an optimum value of crosslinking degree to obtain the maximum expansion ratio of EVA foams, when other
processing parameters are fixed. The expansion ratio of the EVA foams is low when the
crosslinking content is in the very low range, because the melt strength is not strong enough to
maintain the cell structure. When the crosslinking content is excessive, the expansion ratio of the
EVA foams is also low because the cell growth is restrained by the high melt strength. A
mountain-shape curve can be used to describe the relationship between the expansion ratio of the
EVA foams and the crosslinking content.
Chapter 6

Conclusions

6.1 Concluding Remarks

A comprehensive research has been conducted to understand the foaming behaviors of crosslinked EVA with chemical blowing agents and chemical crosslinking agents. The research aims to address the gaps in our knowledge of crosslinked EVA foaming by proposing a fundamental mechanism to correlate the crosslinking content and the foamability of EVA. Firstly, some fundamental properties of crosslinked EVA/gas have been measured experimentally. Then an in-situ visualization system is used to monitor the early stage of the foaming of crosslinked EVA. Based on the video and image data, a thorough analysis is therefore conducted to describe the influence of crosslinking on the early stage of cell growth, with the understanding of the results of fundamental properties. Finally, experimental studies are carried out to investigate the foaming feasibility of crosslinked EVA and the processing parameters have been optimized to maximize the expansion ratio of the crosslinked EVA using a chemical blowing agent.

The work conducted in this research leads to the following conclusions:

1. Both shear and extensional viscosities of crosslinked EVA have been experimentally measured. Crosslinking increases the viscosity of the EVA matrix, under both circumstances, with and without the blowing agent being dissolved. The strain hardening and viscosity enhancement, especially the extensional viscosity enhancement caused by crosslinking, helps maintain the bubble structures with fewer bubbles that can collapse or coalesce.
2. **Measurements** have been conducted to approximate the solubility and diffusivity of the nitrogen inside the crosslinked EVA. Both the solubility and diffusivity of the nitrogen in the crosslinked EVA decreases with the crosslinking degree. The lower diffusivity makes less blowing agent to leak outside, which helps with bubble generation.

3. The swelling ratios of crosslinked EVA with dissolved gas are determined experimentally using a PVT visualization system. The swelling ratio of crosslinked EVA increases with the increase of the gas pressure, and decreases with the increase of the crosslinking content.

4. In this study, compression molding foaming experiments are carried out using EVA, chemical blowing agents, and chemical crosslinking agents. It is critical to have additives distributed evenly inside the polymer melt during compounding, without any chemical premature decomposition. The foaming experiments aimed to clarify how the expansion ratio and cell density can change in response to the variations in the temperature, the blowing agent content and the crosslinking agent content. When the crosslinking is not excessive, the cell density increases with the crosslinking agent content.

5. A visualization batch foaming system is used to study the early stage of the bubble growth in the crosslinked EVA. With the help of a high-speed, charge-coupled device (CCD) camera, the early stages of bubble growth are visually observed. The effects of the blowing agent pressure and the crosslinking content are investigated based on the recorded video and image data. Cell nucleation density increases with the crosslinking agent content; bubble growth rate decreases with the crosslinking agent content.
degree increase, which makes fewer bubbles coalescence, and also leads to a larger unfoamed area and more gas to nucleate bubbles.

6. There exists an optimum value of crosslinking degree to obtain the maximum expansion ratio of EVA foams, while other processing parameters are fixed. The expansion ratio of the EVA foam is low when the crosslinking content is in the very low range, because the melt strength is not strong enough to maintain the cell structures. When the crosslinking content is excessive, the expansion ratio of the EVA foams is also low because the cell growth is restrained by high melt strength. A mountain-shape curve can be used to describe the relationship between the expansion ratio of the EVA foams and the crosslinking content. Furthermore, with more blowing agent used in the foaming, the value of the optimum crosslinking content at the maximum expansion ratio increases.

6.2 Recommendations for Future Work

Many questions remain while continuing this project and the following suggestions are made for the direction of future research, which involves the foaming with crosslinking.

1. Further research on the crosslinked foaming using injection molding is suggested. Other than chemical blowing agents, a physical blowing agent can be used in the injection molding system under high-range pressure, so as to obtain foamed samples with higher expansion ratio.

2. Further study can be conducted on other relatively new polyolefin elastomers, which are emerging on the present polyolefin market. Polymer resins with different MFI's and modifiers can be studied.
3. The deformation of the crosslinked foams is not fully understood. Crosslinked foams shrink to a certain degree and stabilize while being cooled in the open air. More comprehensive investigations on the impacts of crosslinking on the foam shrinkage are suggested. The final shapes of the foams can be more consistent if this deformation mechanism is better understood.

4. More comprehensive investigations on the impacts of additives on the crosslinked foaming are suggested, such as zinc oxide, nano particles, etc.

5. Further study can be proposed on the effects of crosslinking on the thermal transition of EVA, including melting temperature, glass transition temperature and crystallization properties. This is important for analyzing the deformation of the crosslinked foams during the cooling stage, and especially for the foaming of EVA with excessive amount of crosslinking degree.
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