EMULSION POLYMERIZATION OF ETHYLENE-VINYL ACETATE-BRANCHED VINYL ESTER USING A PRESSURE REACTOR SYSTEM

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Abstract

A new pressure reactor system was designed to synthesize a novel **b**ranched **e**ster-**e**thylene-**v**inyl **a**cetate (BEEVA) emulsion polymer. The reactor system was capable of handling pressure up to 1350 psig (9.3 MPa) and had a radial or turbine impeller with hollow shaft and blow pipe to provide good mixing of ethylene gas from the headspace to the aqueous charge in the reactor. Research motor valves were used to provide good control of ethylene flow into the reactor through the manipulation of both the temperature and pressure conditions independently. The polymerization was conducted at a fixed agitation rate of 600 rpm which was sufficient for good mixing without causing much foam or coagulum in the reactor. Significant amount of ethylene incorporation of about 14 % by weight was observed even at low pressure of 500 psig (3.4 MPa).

Three series of model BEEVA emulsion polymers were synthesized and their physical properties were characterized. A recipe for the preparation of BEEVA latex was formulated using anionic and non-ionic surfactants and redox initiation process. These model latexes were synthesized by varying the ethylene pressure from atmospheric to 1100 psig or 7.6 MPa at a fixed Neo 10 monomer amount, varying Neo 10 (vinyl neo-decanoate) amount from Neo 10 / vinyl acetate weight ratio of 0 / 100 to 50 / 50 at a fixed ethylene pressure of 500 psig or 3.4 MPa, and varying the types of Neo monomer at fixed ethylene pressure of 500 psig or 3.4 MPa and fixed Neo monomer / vinyl acetate weight ratio of 10 / 90.

Rheological study of these latexes showed that all except the ethylene-vinyl acetate latex without branched vinyl ester, exhibited Newtonian behaviour at low polymer concentrations (5-15 wt%) but significant shear-thinning was observed at higher concentrations (20-30 wt%). The ethylene-vinyl acetate latex showed Newtonian flow behaviour at different concentrations tested. Neo10-10-500 latex (at 500 psig or 3.4 MPa and 10 wt% of Neo monomer to vinyl acetate) had the highest viscosity. This could be due to flocculation of the polymer particles and higher degree of association between the hydrophobic groups on the polymer particles.

Increasing the ethylene pressure contributed significantly to higher level of ethylene incorporation. The amounts of ethylene incorporation by wt% in the BEEVA latexes were determined using the proton Nuclear Magnetic Resonance (NMR) spectrometer. The amount of ethylene was about 14-15 wt% when low ethylene pressure of 500 psig (3.4 MPa) was used. The glass transition temperature (T_g) was lowered by increasing the amount of ethylene incorporation. A qualitative assessment of hydrophobicity of the polymeric films using an indirect method from contact angle measurements showed that BEEVA polymer containing Neo monomer (branched vinyl ester) had higher contact angle than a vinyl acetate-ethylene (VAE) copolymer without Neo monomer. Zeta potential measurements showed higher zeta potential for Neo10-10-500 as compared to Neo10-10-atm with increasing NaOH concentration which probably suggested larger portion of the hydrophobic groups on the particle surface for Neo10-10-500 and higher tendency to adsorb negative ions.

1 INTRODUCTION

1.1 Overview

Vinyl acetate-ethylene (VAE) emulsion copolymers were introduced commercially by the Reduction Company in 1965. VAE copolymers were originally designed to provide improved low-temperature coalescence, long-term stability and binding capacity in adhesive applications, particularly as difficult substrate adhesives. It is internally plasticized by incorporating ethylene co-monomer to provide flexibility to polymeric films without the need of external plasticization, thereby eliminating the problems of plasticizer migration. A typical example of external plasticizer used in vinyl acetate emulsion is dibutyl phthalate (DBP).

The development of VAE latexes derived from ethylene-vinyl acetate (EVA) production was introduced in the 1950s. In contrast to VAE, which typically comprises between 5 – 40% of ethylene by weight, EVA copolymers contains relatively higher levels of ethylene monomer. EVA is more closely related to the polyethylenes and other solid resins used mainly in hot-melt and plastic molding applications. VAE production is usually conducted in batch processes at pressure 1000-2000 psig (6.9 – 13.8 MPa), although continuous systems have been investigated for high productivity. Emulsion polymerization of VAE at low pressure (<1000psig) usually results in low incorporation of ethylene.

The low glass transition temperature of ethylene and its similar reactivity ratio with vinyl acetate provide wide latitude for the formulation of VAE in many different applications, which include adhesive, cement modifier to paint with low odor and volatile organic compounds (VOC). Both ethylene and vinyl acetate are also relatively low cost monomers. However, the disadvantages of using vinyl acetate are poor water resistance and poor hydrolytic stability especially under alkali conditions. These setbacks can be overcome by incorporating hydrophobic branched vinyl esters which have similar reactivity ratio as vinyl acetate. Branched vinyl esters (also known as Neo monomer) enhances the water and alkali resistance in vinyl acetate copolymer latexes with performance better than conventional acrylics. Its long pendent hydrocarbon provides protection against alkali-promoted hydrolysis. This unique and relatively unexplored terpolymer latex comprising of branched vinyl esters, ethylene and vinyl acetate (abbreviated as BEEVA polymer) is being investigated in this research. A completely new pressure reactor system was designed and constructed for handling the emulsion polymerization of the monomers at low to high pressure conditions.

1.2 Motivation and Objectives for This Study

This research is primarily to develop a new pressure reactor system that is able to produce novel ethylene-vinyl acetate-branched vinyl ester emulsion polymer at varying pressure. The synthesis and physical properties of these latexes will be investigated.

CHAPTER 1 INTRODUCTION

Ethylene emulsion copolymers are difficult to be prepared in laboratory scale due to the need of a specially designed pressure reactor system capable of handling emulsion polymerization at high pressure. The emulsion polymerization will be carried out at a fixed temperature. Latexes produced at varying pressure, Neo monomer amount and type will be studied. We will also evaluate the possibility of preparing ethylene emulsion copolymer at low pressure.

The physical properties such as rheological property, contact angle, zeta potential and glass transition temperature of these latexes will be examined.

2 LITERATURE REVIEW

2.1 Relevance and Motivations

Ethylene-based emulsion polymer technology is fast becoming an important and emerging generation of binders for various applications, especially in coatings. This is driven by performance, economic and environmental motivations.

The ethylene-based pressure latex technology is uniquely complemented by the incorporation of vinyl branched esters to produce branched ester-ethylene-vinyl acetate (BEEVA) copolymers that offer the potential for a latex polymer with high performance properties. Essentially, branched vinyl ester provides hydrophobicity and protection against hydrolysis under alkaline condition which is prevalent in cement-based substrates [Slinckx et al., 1997]. High performance for coatings applications is defined as superior scrub resistance, low temperature film formation, very low odor, excellent wet application properties and good weatherability. Durability and washability are two typical attributes of coatings related to scrub resistance. Low temperature film formation relates to good touch-up for paints especially at low temperature. Low odor offers the benefits of paint that can be applied in any settings such as interior office, hospitals or school where people may be irritated by odors in conventional paints. For paint manufacturers, this means a reduced usage of expensive and hazardous flammable solvents used for film formation purposes [Caldwell et al., 1999].

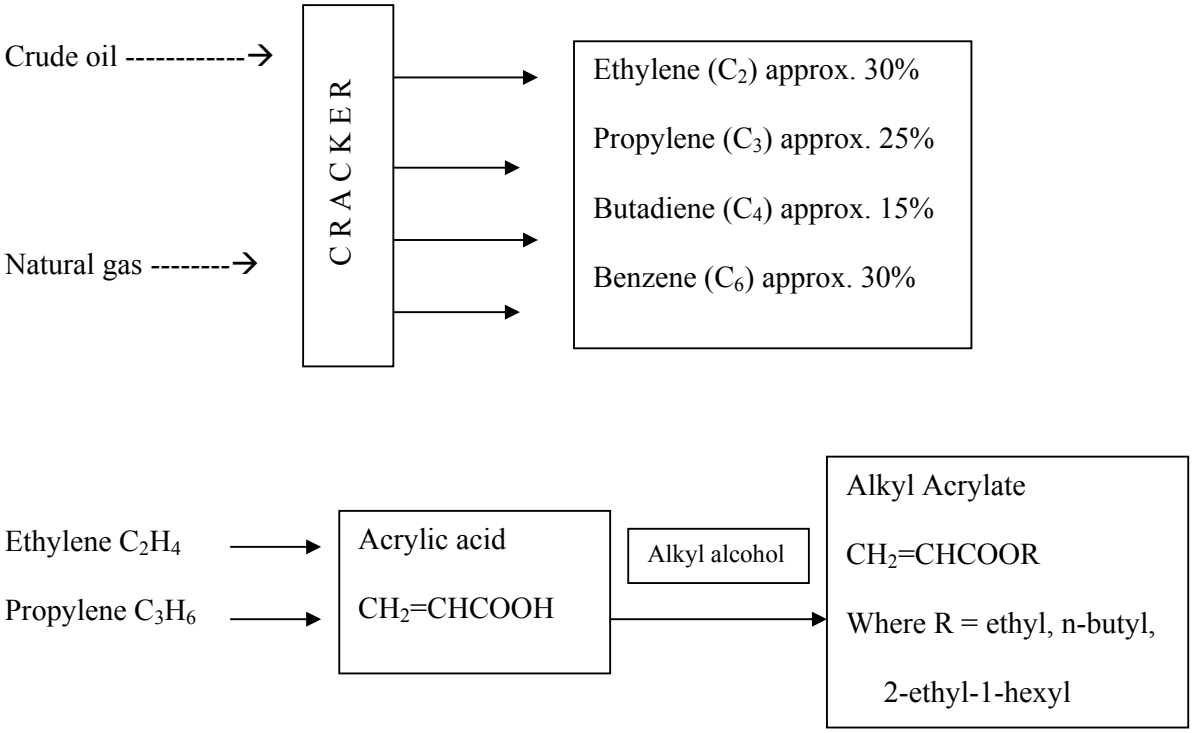
This brings us to the next significant motivation for the development of ethylene-based pressure latex which is zero volatile organic compounds (VOCs) coatings. Zero VOC coatings can be formulated using ethylene-based pressure latex.

Latex paints are increasingly replacing solvent-based paints because they offer several advantages. These, among others, include easy cleanup, environmental friendliness and considerably less health risks. In today's environment, solvent emission is of great concern and there is significant government regulation to decrease and limit the level of VOCs released to the atmosphere as well as to safeguard against overexposure to these organic compounds [Wigglesworth, 1994]. VOC as defined by EPA (Environment Protection Agency, USA) is "any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions." A more practical definition of VOC is any organic compounds detected by EPA Method 24 excluding water and EPA approved exempt solvents. These volatile organic compounds generally contain C_{16} or less and boiling point of less than 250°C. A significant source of residual odor in latex consumer paints is directly related to the coalescing solvents. Coalescing solvents are typically linear (or slightly branched) glycol ethers and esters of about 7 to 12 carbon atoms in length that have boiling points typically above 200°C and solubility parameters appropriate for the latex of interest. The odor associated with the gradual volatilization of coalescing solvents is considered objectionable by consumers. Quite often the odor persists for days or weeks after painting. The ethylene-based pressure latexes are capable of having low film forming temperature (by lowering the glass transition temperature of the

polymer, T_g) which will not require any coalescing solvent to aid in film formation and without significant compromise on dirt pickup. Typically, these latexes such as vinyl acetate-ethylene copolymer have minimum film formation temperature (MFFT) lower than glass transition temperature (T_g) due to hydroplasticization of the film with the incorporation of hydrophilic vinyl acetate into the backbone of the polymer. In Europe where there is more stringent legislation on VOCs, significant amount of vinyl acetate-ethylene (VAE) latexes are used for paints formulated to meet the VOC requirement. The following is a brief summary of the recent legislations related to VOC emission. The European's recent VOC emissions standards are < 500μg/m^3 based on EMICODE EC1 and < 700ppm of boiling point <250°C based on the Blauer Engel standard. In the United States, the regulations for VOC emission of flat coatings are <250g/L (National standard- EPA Clean Air Act). The Southern California's SCAQMD (South Coast Air Quality Management District) requires <100g/l in the year 2001 and <50g/l by 2007. The Ozone Transport Commission (OTC) which covers 12 northeastern and mid-Atlantic states require <100g/l. In China, the government has announced the VOC limit for interior architectural coating to be less than 200g/l under GB 18582-2001 Part A.

Economic motivation is crucial for development of any new polymer. The cost of monomers used normally contribute to the bulk of the cost of the finished polymer. Using low cost monomers to produce high performance polymer has always been the challenge to polymer researchers. The common polymer type produced by emulsion polymerization technology are: polyvinyl acetate (PVAc), vinyl acetate-acrylic copolymer (VA), vinyl acetate-ethylene (VAE), pure acrylics (AA), polystyrene (PS),

styrene-acrylics (SA), vinyl versatate (VV) or vinyl acetate-branched vinyl ester copolymer and styrene butadiene (SB) latex [El-Aasser, 1990]. The monomer with the lowest cost are the olefinic monomers such as ethylene. This is understandable since the cost will increase through the raw material chain from petroleum to monomer (see Figure 2.1). Acrylate monomers are generally more expensive than vinyl acetate and styrene.



C_2H_4 + ½ O_2 + CH_3COOH --------→ $C_2H_3COOCH_3$ + H_2O

Ethylene Oxygen Acetic acid Vinyl Acetate Water

Figure 2.1 : Simplified diagram of the raw material chain from petroleum to monomer

Therefore, the use of ethylene and vinyl acetate in pressure latex will provide one of the lowest raw material cost. As discussed previously, coating manufacturers using ethylene-based pressure latex such as VAE or BEEVA will also benefit by reducing the usage of expensive coalescing solvents when formulating using these pressure latexes. However, one needs to know that the capital investment is high due to the need to have expensive pressurized reactor with safety features to handle such flammable gaseous monomer like ethylene.

2.2 Historical background of VAE pressure latex

The development of vinyl acetate – ethylene (VAE) latexes grew out of ethylene-vinyl acetate (EVA) production during the 1950's. EVA copolymers contain low levels of vinyl acetate monomer and are more related to the polyethylenes and other solids resins used in hot melt and plastic molding applications. On the other hand, vinyl acetate-ethylene (VAE) copolymers contain low levels of ethylene and are used in the coatings and adhesives applications. They were developed and produced commercially for the first time in the United States by The Air Reduction Company (Airco) in 1965 [Lindemann, 1968]. They were designed to fill the need for internally plasticized and flexible resins in the adhesives industry. The copolymers of vinyl acrylics and vinyl acetate-dibutyl maleate or vinyl acetate- dioctyl maleate were the other commonly used adhesives for difficult substrates.

Lindemann spearheaded the technical development of the VAE technology at Airco, which commissioned its first VAE production operation in 1966. A patent application for the process began in 1967 and was eventually accepted in 1973. In 1967, Airco

established a cross-licensing agreement with Du Pont for Airco's 400 Grade VAE technology and Du Pont began commercial production of VAE in 1969. In 1970, Air Products and Chemicals purchased Airco's VAE business and soon thereafter Lindemann left Air Products for a position with Mobil before joining C.S.Tanner in 1974.

C.S.Tanner began commercial VAE production in 1976 and was acquired by Ciba-Geigy in 1978. In 1980, Ciba-Geigy sold C.S.Tanner to National Starch - and in 1983, Du Pont sold its VAE business to Reichhold. Aircoflex 400, which later became Airflex 400 when Air Products acquired the VAE business from Airco, remains the workhorse of the adhesive industry after 35 years since its original market introduction. There are three major VAE producers in the United States, i.e., Air Products and Chemicals, National Starch and Reichhold. These three producers of VAEs use similar technologies based on high pressure batch polymerization. The basic process based on several patents review such as US 6,329,447 B1 and EP0295727 A2 consists of the following steps:

1. Vinyl acetate, colloid stabilizers and deionized water are first added to the reactor and stirred continuously to form an emulsion.
2. Ethylene is then introduced with continuous stirring until an equilibrium pressure is reached.
3. Redox catalyst is introduced to begin polymerization. The reaction rate is controlled with a redox catalyst system which is added incrementally. The pressure is either allowed to decrease as polymerization proceeds or it is kept constant by feeding ethylene during the polymerization.

The applications for VAE as mentioned in patent literatures are wide and also similar to applications of other type of latexes. The end uses include adhesives (particularly difficult substrate adhesive which Airflex 400 is the most common), pressure sensitive adhesives (though currently dominated by acrylics), coatings (particularly for low odor and VOC and high solids latex), textile (especially for non-woven where the N-methylol acrylamide is added for cross-linking), and construction (as cement modifier in polymer modified mortar and waterproofing cementitious membrane).

2.3 Review of patent literature on ethylene-based pressure latex

The review of literature covers mainly patent as there are limited journals publications on preparation and applications of ethylene-based pressure latex system. A summary of the patents reviewed is shown in Table 2.1.

Patents	**Composition**	**Process**	**Application**
US 3,380,851	Vinyl acetate-ethylene-n-methylol acrylamide	Batch process; 600 psig; 50°C and feed time of 4.5 hours	Non-woven binder
US 3,844,990	Vinyl acetate-ethylene	Batch process; 50°C; redox initiation	Paint binder
US 3,404,112	Vinyl-acetate-ethylene-triallyl cyanurate		Paper coating
US 3,644,262		Enhanced ethylene incorporation when free vinyl acetate during polymerization is less than 3.5% of aqueous charge	
US 5,371,137	Vinyl acetate-ethylene-vinyl 2-ethyl hexanoate		Packaging adhesive and pressure sensitive adhesive

WO 97/41163	Polyvinyl alcohol stabilized vinyl acetate-ethylene	Semi-continuous process; 60°C; 50% vinyl acetate added initially while the rest was fed over 45 mins.	
US 3,883,489	Dispersible vinyl acetate polymer powder		Cement modifier
US 5,254,652	Ethylene-vinyl acetate-vinyl neo-nonanoate or vinyl neo-decanoate	7300 to 44,000 psig and 120 to 325°C	Additives for mineral oil distillates
US 5,665,816	Ethylene-vinyl acetate-vinyl branched ester		Polyethylene adhesive, low VOC paint
US 4,322,516	Ethylene-acrylic ester- vinyl acetate-methacrylamide	Batch process; 700 psig and at 50°C	Pressure sensitive adhesive
US 3,440,199	Vinyl acetate-ethylene-glycidyl acrylate	50 psig, 50°C	Wood coating
EP 0381379A1	Vinyl acetate-ethylene-vinyl neo-nonaoate	450 psig and 76°C	Paper coating
EP 0373866 A2	Vinyl acetate-ethylene-epoxy silane		Paint with improved scrub and water resistance
EP 0530013 A1	Ethylene-vinyl acetate-vinyl 2-ethylhexanoate	800 psig	Pressure sensitive adhesive
US 4,164,489	Vinyl acetate-ethylene	Continuous polymerization process at 700-1000 psig	
US 4,331,577	Vinyl acetate-ethylene	Ethylene dissolved in vinyl acetate or vinyl chloride and fed as a liquid	
US 5,633,334	Polyvinyl alcohol stabilized vinyl acetate-ethylene	300 psig and 80°C	
US 4,332,850 US 4,449,978	Vinyl acetate-ethylene-N-methylol acrylamide	“cold initiation” process	Non-woven binder
US 5,084,503	Polyvinyl alcohol/non-ionic surfactant		

	stabilizing system		
US 4,692,366	Ethylene-vinyl acetate-di-2-ethylhexyl maleate-N-methylol acrylamde-acrylic acid		
US 4,963,422	Ethylene-butyl acrylate-vinyl acetate-N-methylol acrylamide	750 psig and 55-60°C	
US 4,762,866	Vinyl acetate-ethylene-dioctyl maleate-acrylic acid		Adhesive for polyether urethane foam
EP 0295727 A2	Vinyl acetate-ethylene-Veova 9		Paint with alkali resistance and non-tacky
EP 0795591 A2	Vinyl acetate-ethylene		Paint
US 6,329,447 B1	Vinyl acetate-ethylene-branched vinyl ester	Enhanced ethylene incorporation at low pressure using inner particulate material	

Table 2.1 Summary of patents reviewed as categorized by invention claims of composition, process and application.

Salient points from the review of patents are as follow:

1. Additional monomer other than vinyl acetate and ethylene is quite commonly used to improve properties relating to its applications. For examples, N-methylol acrylamide is used as crosslinker for non-woven binder application. Epoxy silane is used to improve scrub in paint application while Veova 9 (a branched vinyl ester) is used to improve alkali resistance in paint application.
2. Generally the polymerization pressure is from a few hundreds psig to more than a thousand psig. Pressure range between 700-1200 psig is most common. Redox initiation is usually used. The polymerization temperature can be as

low as 50°C to obtain high molecular weight polymer to high temperature of about 80°C. Batch, semi-continuous and continuous process can be utilized successfully to produce ethylene-based pressure latex.

3. The low Tg ethylene-based latexes are useful in applications such as paint, paper coatings, non-woven binder, adhesives and cement modifier.

US 3,380,851 [Lindemann et al., 1968a]

The first US patent application for ethylene-vinyl acetate latex copolymers was first filed on March 31, 1965. The inventors were Martin K. Lindemann and Rocco P. Volpe of the Air Reduction Company. The work covered vinyl acetate-ethylene copolymers and 5 patents were granted, each in different application areas: paint (US 3,844,990); non-woven fabrics (US 3,380,851); woven fabrics (US 3,345,318) and paper coatings (US 3,404,112 and US 3,645,952). US 3,380,851 disclosed vinyl acetate-ethylene-n-methylol acrylamide interpolymers used as binders for non-woven fabric. Vinyl acetate and ethylene were copolymerized in the presence of n-methylol acrylamide by a batch process. All the vinyl acetate was charged in the initial charge (batch process) and the reactor was pressurized with ethylene to a pressure of about 600 psig. The polymerization temperature was 50 °C and the feed time 4.5 hours. The ethylene content was 17%. The inventors also filed a British patent 1,117,711, which disclosed that the process for making ethylene-vinyl acetate copolymers, which was a batch process that took place in two stages. The first stage was a homogenization and equilibration period in which the vinyl acetate, suspended in water, is thoroughly agitated in the presence of ethylene under the working pressure to effect solution of the ethylene mainly in the vinyl acetate and to a lesser extent in the aqueous phase.

Ethylene will dissolve in the vinyl acetate and aqueous phase to an extent which at its maximum corresponds to the solubility limit of ethylene in vinyl acetate and water at the temperature and pressure of the system. The homogenization stage was followed by a polymerization stage during which the catalyst was added in increments and the constant reactor pressure was maintained by application of constant ethylene pressure. The inventors also suggested that hydrogen peroxide was preferred over t-butyl hydroperoxide because of its higher water solubility.

US 3,844,990 [Lindemann et al., 1974]

US 3,844,990 discloses aqueous paint compositions of ethylene-vinyl acetate copolymers. The inventors are Martin K. Lindemann and Rocco P. Volpe. The polymerization process is a batch process, which involves first a homogenization period where the vinyl acetate suspended in water is thoroughly agitated in the presence of ethylene under pressure to effect solution of the ethylene in the vinyl acetate up to its solubility value at the prevailing conditions in the reactor, while the vinyl acetate is heated to polymerization temperature. The homogenization period is followed by a polymerization period during which the catalyst is added incrementally at a constant pressure by feeding ethylene to the reactor. The inventors stated that it is advantageous to utilize the more water-soluble peroxides, such as hydrogen peroxide, rather than the more oil-soluble peroxides such as t-butyl hydroperoxide. In the examples, potassium persulfate was used in two cases and in the third case t-butyl hydroperoxide was used. The polymerization pressure was 530 psig in two cases and 700 psig for the example in which t-butyl hydroperoxide was used. The

polymerization temperature was 50 °C. The reducer was sodium formaldehyde sulfoxylate in all the examples listed.

US 3,404,112 [Lindemann et al., 1968b]

US 3,404,112 discloses paper coating compositions containing vinyl acetate-ethylene-triallyl cyanurate terpolymers. The level of triallyl cyanurate was in the 0.03 to 0.1 wt% based on vinyl acetate. The polymerization pressure was very similar to the one disclosed in US 3,380,851 and US 3,844,990.

US 3,644,262 [Sthle et al., 1972]

US 3,644,262 claims enhanced ethylene incorporation when the amount of free vinyl acetate during the polymerization is less than 3.5 wt% of the aqueous charge. This would require extensive feed times, but the authors claim an ethylene content of 11% when the polymerization was carried out at 150 psig, 30 °C and an 11 hours feed time.

US 5,371,137 [Blincow et al., 1994]

US 5,371,137 claims an adhesive emulsion composition having a T_g of about 10 °C to about – 65 °C consisting of vinyl acetate, ethylene and vinyl 2-ethyl hexanoate. The composition contains about 54 - 61% by weight of copolymer solids. This composition can be used as packaging adhesive and pressure sensitive adhesive by selecting appropriate T_g.

WO97/41163 [Freidzon et al., 1997]

WO97/41163 claims a vinyl acetate-ethylene copolymer having solids content of at least 65% and preferably a viscosity of less than 4000 cps. The copolymer includes a

fully or partially hydrolyzed polyvinyl alcohol having a molecular weight ranging from 150 to 300 g/mol. In the process, 50 % of the vinyl acetate monomer was added in the initial charge and the reactor was adjusted to the polymerization temperature of 60°C. With the reactor temperature at 60 °C, ethylene was added to the reactor up to a pressure of 651 psig. Following the addition of the ethylene, the initiator, hydrogen peroxide, was added to the reactor over 1 hour. After 10 minutes from the start of the initiator, the remaining 50% of vinyl acetate was added to the reactor over 45 minutes. After all feeds were completely added into the reactor, the reactor pressure was reduced to 175 psig and more hydrogen peroxide was added over 5 minutes. The resulting emulsion had a solids content of 67%, viscosity of 2000 cps and ethylene content of 19%.

US 3,883,489 [Matschke et al., 1975]

US 3,883,489 relates to a process for the preparation of an easily dispersible vinyl acetate/ethylene polymer powder which is used as binding agent in plastics containing mortars. The aqueous vinyl acetate/ethylene dispersions can be prepared in various ways at ethylene pressures of up to approximately 1500 psig, preferably from 145 to 900 psig. The copolymers were claimed to be especially suitable as binding agents in plastics mortars. Mortars of this type are prepared by intensive mixing of mineral aggregates of different grain sizes with the vinyl acetate/ethylene polymer powders with final addition of water. Plasterings prepared with plastics mortars containing these powders are surprisingly free from cracks and are extremely water

resistant. The authors claimed a process for the preparation of copolymer of vinyl acetate and ethylene and optionally at least one further olefinically unsaturated monomer. The olefinically unsaturated monomer is a vinyl ester of a linear or branched saturated aliphatic monocarboxylic acid having 3 to 18 carbon atoms, an acrylic, methacrylic, maleic or fumaric acid ester of a linear or branched saturated aliphatic monohydric alcohol, having 1 to 18 carbon atoms, vinyl chloride, isobutylene or a higher alpha-monoolefin having 4 to 12 carbon atoms, the sodium salt of vinyl sulfonic acid, acrylic, methacrylic, crotonic or itaconic acid, a maleic acid monoester of a linear or branched saturated aliphatic monohydric alcohol having 1 to 18 carbon atoms, diallyl maleate, diallyl phthalate, triallyl cyanurate.

US 5,254,652 [Reimann et al., 1993]

US 5,254,652 claims terpolymers of ethylene, vinyl acetate and vinyl neo-nonanoate or vinyl neo-decanoate and a method for their use as additives for mineral oil distillates. The terpolymers were found to be outstandingly suitable for improving the flow properties of crude oil, mineral oils and mineral oil distillates. The reaction was carried out at pressures from 7300 to 44,000 psig and at temperatures from 120 to 325°C.

US 5,665,816 [Gerharz et al., 1997]

US 5,665,816 claims ethylene-vinyl acetate-vinyl branched ester copolymers suitable as adhesives for gluing polyethylene. The ethylene pressure was in the 450 – 1500 psig range, the polymerization temperature in the 45-90°C range and the feed time 9-11 hours. An example using vinyl neo-endecanoate was also presented. The

copolymer dispersion was partly grafted with cellulose ether. The aqueous dispersion had T_g between -20 to -5°C. This dispersion could be used to formulate low volatile organic constituents (VOC) paint and adhesive.

US 4,322,516 [Wiest et al., 1982]

US 4,322,516 claims a pressure sensitive adhesive composed of ethylene, acrylic ester, vinyl acetate, methacrylamide and other olefinically unsaturated monomers. A batch process was described. The initiator system was either potassium persulfate/sodium formaldehyde sulfoxylate or ammonium persulfate/sodium formaldehyde sulfoxylate. The polymerization pressure was about 700 psig, the polymerization temperature 50°C and the feed time 5 hours.

US 3,440,199 [Lindemann et al., 1969]

US 3,440,199 claims a vinyl acetate-ethylene-glycidyl acrylate terpolymer for wood coating applications. The latex particle size was in the 0.1 to 0.2 micron range. The polymerization pressure was 50 psig, the polymerization temperature 50°C and the ethylene content 28%.

EP 0381379A1 [Boodaghians et al., 1990]

EP 0381379A1 relates to aqueous emulsions containing copolymers of vinyl acetate-

ethylene-vinyl neo-nonanoate, which are used as paper coatings. The polymerization pressure was 450 psig, the polymerization temperature, 76°C and feed time, 6.5 hours. The ethylene content was 14%.

EP 0373866 A2 [Allen et al., 1990]

EP 0373866 A2 relates to improved scrub and water resistance of paints and plasters made of emulsions of ethylene/vinyl acetate, which are post-reacted with epoxy silanes. The emulsion is formed in the absence of acid monomer but in the presence of a stabilizing surfactant including a C14 to C20 alkylene moiety such as Emcol K-8300.

EP 0530013 A1 [Blincow et al., 1992]

EP 0530013A1 discloses ethylene-vinyl acetate-vinyl 2-ethylhexanoate copolymers used as pressure sensitive adhesives. Bonding to the surface of lower polarity, i.e., polypropylene, was improved by including vinyl esters of C_4 to C_{18} primary or secondary carboxylic acids. The polymerization pressure was 800 psig and the polymerization temperature was initially 30 °C and subsequently raised to 50°C at 1 hour into feeds. The feed time was 6 hours. The polymer composition was ethylene/vinyl acetate/vinyl 2-ethylhexanoate = 30/45/25.

US 4,164,489 [Daniels et al., 1979]

US 4,164,489 relates to a continuous process for producing vinyl acetate-ethylene copolymer emulsions. The improvement for continuous polymerization of vinyl acetate and ethylene comprises continuously charging a reaction mixture containing

vinyl acetate and ethylene to a polymerization vessel, conducting an initial polymerization of the vinyl acetate and ethylene in the presence of seed latexes under ethylene pressure and continuously removing the latex from the initial polymerization vessel. The polymerization pressures can be in the range of 250 – 1200 psig with preferred pressures in the 700-1000 psig. The polymerization temperature was in the range of 40 to 75°C. The initiator system was hydrogen peroxide/sodium formaldehyde sulfoxylate, once again a redox system instead of a thermal initiator as has been the case in many Air Products' patent.

US 4,331,577 [Hanna, 1982]

US 4,331,577 claims a polymerization process in which ethylene is dissolved in the other monomers, such as vinyl acetate or vinyl chloride, to form a single monomer feed which is then added to the reactor under starved conditions to maintain a pre-selected reactor pressure. Under these conditions, the monomers exist in the aqueous phase at levels below their solubility limits. The process differs significantly from other VAE processes, which either operate under monomer flooded conditions, i.e., the monomers exist in the aqueous phase at levels above their solubility values at the prevailing temperature, or processes which may be starved but in which the liquid monomers are separated from the gaseous ethylene. In this patent, the ethylene enters the reactor as a liquid and in a desired ratio with the other monomers.

US 5,633,334 [Walker et al., 1997]

This patent claims a process for polymerization of ethylene and vinyl acetate in the presence of partially and fully hydrolyzed polyvinyl alcohol. The polymerization

pressure was 300 psig and the temperature at 80°C. However, the glass transition temperature was in the 17 – 23°C, suggesting rather small ethylene incorporation in the copolymer.

US 4,332,850 [Iacoviello, 1982] and US 4,449,978 [Iacoviello, 1984]

These patents disclose the so-called "cold initiation" process for producing vinyl acetate-ethylene-n-methylol acrylamide terpolymers for use in the non-woven goods. The initiation was affected at 35°C and the heat generated by the exotherm was used to bring the reactor contents to the polymerization temperature, which is usually in the 55-60°C range. Again, the catalyst used was a hydrogen peroxide/sodium formaldehyde sulfoxylate redox system.

US 5,084,503 [Iacoviello, 1992]

This patent discloses the simultaneous use of a polyvinyl alcohol/non-ionic surfactant stabilizing system. The author claims that the use of such a stabilizing system does not contribute to increased viscosity especially at high solids.

US 4,692,366 [Mudge, 1987]

US 4,692,366 discloses ethylene / vinyl acetate / di-2-ethylhexyl maleate / n-methyol acrylamide / acrylic acid compositions. The pressure was 750 psig and the polymerization temperature was in the 80-82 °C range. Ethylene contents of 20% were reported.

US 4,963,422 [Katz et al., 1990]

This patent discloses ethylene / butyl acrylate / vinyl acetate / n-methylol acrylamide and ethylene / 2-ethylhexyl acrylate / vinyl acetate / n-methylol acrylamide compositions prepared at pressures of 750 psig, temperatures in the 55-60°C and feed time of 5.25 hours. The initiator system was a redox combination of t-butyl hydroperoxide and sodium formaldehyde sulfoxylate. The mode of addition of vinyl acetate was either batch, i.e., all vinyl acetate added in the initial charge, or delayed feeds. Ethylene contents of 15% were reported.

US 4,762,866 [Shih et al., 1988]

This patent discloses a polymer composition consisting of vinyl acetate / ethylene / dioctyl maleate / acrylic acid for use as an adhesive for bonding a polyether urethane foam to a rigid substrate. The process is a batch polymerization with all the vinyl acetate and dioctyl maleate added in the initial reactor charge followed by the addition of ethylene to a pressure of 750 psig.

EP 0295727 A2 [Scholten et al., 1988]

EP 0295727A2 describes polymer emulsions containing vinyl acetate, ethylene and versatates (Veova 9) for use in paint compositions to give non-tacky surfaces which are alkali resistant. These benefits were demonstrated in comparison to Veova-10. The patent describes polymerizations conducted under pressures in 10-40 bar or 145 – 600 psig range and at temperatures of either 55°C (redox initiation) or 80°C (thermal initiation). The vinyl acetate – vinyl neo nonanoate – acrylic acid monomer mixture

was pre-emulsified and fed to the reactor over 3 hours. Ethylene was supplied to the reactor at the desired pressure and was maintained throughout the polymerization until the monomer pre-emulsion feed was complete. It was claimed that the branched vinyl ester facilitated ethylene incorporation and the higher the level of the branched ester the higher the ethylene incorporation into the terpolymer at the same pressure. However, the dependence of ethylene uptake on the vinyl neo-decanoate level is not monotonic. For example, although, at 10 bars, there is a plateau on the ethylene uptake at different vinyl neo-decanoate levels; at 20 bars, the dependence is very erratic.

EP 0795591A2 [Daniels et al., 1997]

This patent claims vinyl acetate-ethylene emulsions for use in formulating high performance paints without the need for coalescing solvents. The authors believe that the significant factor for providing for the overall combination of properties in the latex paint formulation is attributable to the small particle size distribution. It is stated that when the portion of large particles is high, scrub resistance of the resulting paint is reduced.

US 6,329,447 B1 [Avramidis et al., 2001]

This patent discloses copolymer composition comprising of ethylene, vinyl acetate and branched vinyl ester. Processes for producing enhanced incorporation of ethylene into the copolymer composition at low reaction pressure such as the use of inner particulate material are also mentioned.

My study in the preparation of pressure latex is based on the recipe as disclosed in this patent excluding the protective colloids.

Most of the patents described above consist of ethylene based copolymerization at high pressure (>1000 psig) to achieve sufficiently high ethylene incorporation. It is more difficult to achieve sufficient ethylene incorporation at lower pressure. Studies on polymerization of vinyl acetate-ethylene-branched vinyl ester (BEEVA) latex as described in these patents such as US 6,329.447 B1 are also limited and fairly recent. The possible role of branched vinyl ester in helping transport ethylene molecules to the polymerization sites on the polymer particles is not disclosed in these patents. In this study, we will polymerize BEEVA latexes at low to medium pressure and determine if branched vinyl ester monomer could enhance the incorporation of ethylene.

2.4 Typical Monomer Compositions Used in Pressure Latexes

The two most commonly used pressure monomers in emulsion polymerization are ethylene and butadiene. Typically, ethylene will copolymerize with vinyl acetate, while butadiene will copolymer with styrene mainly due to compatibility of reactivity ratios. Vinyl acetate can also copolymerize with acrylate or dibutyl maleate or dioctyl maleate and vinyl chloride though it may not be in random fashion.

2.5 Plasticization of vinyl acetate

Polyvinyl acetate has a glass transition temperature, T_g of 32°C which is above the T_g required in most coatings applications. Therefore, polyvinyl acetate needs to be plasticized in order to lower its T_g to within a range suitable for use as film former and pigment binder in coating applications. Table 2.2 lists the glass transition

temperatures of different monomers [Brandrup et al., 1989]. This transition temperature can be lowered by adding an external plasticizer such as dibutyl phthalate or by copolymerizing the vinyl acetate with another monomer, which acts as a so-called internal plasticizer. This is a monomer with a much lower T_g than polyvinyl acetate. Internal plasticizers are not subjected to migration or exudation as are external plasticizers, because they are chemically bonded into the polymer molecule and remain in place for the life of the surface coating film.

Monomer	**T_g , °C**
Vinyl Acetate	32
Vinyl neo-decanoate	-2
Vinyl Chloride	81
Butadiene	-85
Styrene	100
Ethylene	-125
Butyl Acrylate	-54
2-Ethyl Hexyl Acrylate	-50

Table 2.2. Glass Transition Temperatures of Selective Monomers

A number of co-monomers are used commercially to plasticize polyvinyl acetate by copolymerization with another monomer with a lower T_g. The most common are butyl acrylate, 2-ethylhexyl acrylate, dibutyl maleate, dioctyl maleate, dibutyl fumarate, and ethylene. For most applications it has been found that it is not critical which one of these comonomers is used for internal plasticization as long as the T_g and the

molecular weight of the final copolymer are similar in each case. Generally, the amount of the co-monomer will determine the T_g of the copolymer, the minimum film-forming temperature (MFFT) and low temperature performance such as coalescence of the paint. However, because of the different copolymerization behaviors of vinyl acetate with these co-monomers, different polymerization techniques have to be used in each case to arrive at identical physical properties in the final polymer. Special techniques are required for each comonomer to obtain comparable molecular weights. This requires a specific polymerization process because the rate of polymerization of different monomers with vinyl acetate is dependent on the co-monomer.

The reaction parameter describing the extent of the copolymerization of two monomers is the reactivity ratio of each of the monomers with the other monomer in the copolymerization process. Accordingly, there are two reactivity ratios in the copolymerization of two monomers since there are four possible propagation reactions. Each reactivity ratio reflects the tendency or preference of one monomer to react with itself, i.e., homopolymerize or copolymerize with the other monomer. The two reactivity ratios have practical importance in the synthesis of copolymers and they make possible the calculation of the instantaneous polymer compositions when the comonomer feed composition is known [Rosen, 1982]. In free radical emulsion copolymerization, the copolymerization equation (as shown below) makes it possible to calculate the monomer ratio or composition entering the polymerization loci, i.e., the particles. When the vinyl monomer is copolymerized with a second monomer

through free radical copolymerization, the relationship between the composition of the initially formed copolymer and the initial monomer mixture is given by:

$$\frac{dm_1}{dm_2} = \frac{M_1(r_1M_1 + M_2)}{M_2(r_2M_2 + M_1)}$$

where m_1 = the moles of monomer 1 entering the copolymer, m_2 = the moles of monomer 2 entering the copolymer, M_1 = the moles of monomer 1 in the monomer mixture, M_2 = the moles of monomer 2 in the monomer mixture, and r_1 and r_2 are the monomer reactivity ratios [Brandrup, 1989].

The composition of the monomer entering the particles will be the same as the composition of the monomer in the feeds (or more precise - in the reactor), only if the reactivity ratio of each co-monomer is equaled to 1. This is uniquely satisfied by both the branched ester and ethylene in their copolymerization with vinyl acetate. The values of these monomers' reactivity ratios for copolymerization with vinyl acetate are listed in Table 2.5. Indeed, this is the most significant contribution of vinyl neo-decanoate and ethylene in the production of BEEVA polymers. However, it is worth mentioning that in emulsion polymerization, there is a possibility that there will be populations of both random and block copolymers in the latex. This deviation can arise as a result of changes in the composition of comonomer mixture assuming that the comonomer reactivity ratio was constant. When the copolymerization proceeds in two or more phases, the composition of the feed has to be different in these phases. Changes in composition can also occur when the concentration of one of the comonomers is kept constant during the copolymerization. Gospodinova et al.

suggested that ethylene-vinyl acetate copolymers obtained by emulsion copolymerization at low and medium pressure (1-6 MPa) had two parts in the copolymer chains [Gospodinova et al., 1992; Gospodinova et al., 1998]. The comonomer units in one part showed a tendency to alternate while the ethylene units in the other part show an enhanced tendency to form block. Investigation of branching EVA emulsion copolymers showed that both long-chain and short-chain alkyl branches were present irrespective of composition and molecular weight, through the analysis of ^{1}H- and ^{13}C- NMR.

Therefore, two properties are important in any copolymerization of vinyl acetate; the T_g and the reactivity ratio of the comonomer. The first relates to the plasticization efficiency and the second to the characteristic, namely, whether random or block copolymer, which, in turn, affects such properties as flexibility, alkali and water resistance and the binding efficiency of the copolymer film. In this regard, the reactivity ratio does affect plasticization efficiency, albeit indirectly.

Ethylene has the lowest T_g of any monomer and therefore it is the most efficient plasticizer for vinyl acetate copolymers and it is at least 50% more efficient on a weight basis than di-butyl phthalate [Edser, 1972]. This is partly due to the fact that ethylene possesses a very low molecular weight, which causes its molar ratio to increase and also because the vinyl acetate chains are more frequently interrupted in the polymer by the non-hydrolyzable ethylene. Vinyl neo-decanoate is not as efficient as an internal plasticizer compared to other co-monomers such as butyl acrylate and 2-ethylhexyl acrylate but it imparts alkali and water resistance to polyvinyl acetate

copolymers of equal or better characteristics than acrylics. Ethylene is also the cheapest raw material of all monomers used in conventional emulsion polymerization and hence an ethylene-vinyl acetate copolymer is cheaper than a vinyl acetate homopolymer. As discussed before, ethylene satisfies another critical requirement; the reactivity ratio of ethylene with vinyl acetate and vinyl neo-decanoate is 1, therefore a random copolymer results when ethylene, vinyl neo-decanoate and vinyl acetate inter-polymerize. The growing chain radicals cannot distinguish between the monomers, and so the addition depends only in the ratio of monomers in the neighborhood of the chain ends. Reactivity ratios dictate the monomer sequence distribution of polymeric chain when batch polymerization is employed. For examples, blocked chain occurs when r_1 (reactivity ratio of vinyl acetate) >> 1 and r_2 (reactivity ratio of comonomer) <<1 or r_1 <<1 and r_2 >>1. Alternating chain occurs when r_1 and r_2 <<1. Random chain occurs when r_1 is close to $1/r_2$. Monomer sequence distribution can also be controlled irrespective of monomer reactivity ratios through monomer addition strategy such as semi-continuous polymerization. In the subsequent section, we will discuss the attributes and unique performance contributions of branched esters in branched ester – ethylene-vinyl acetate (BEEVA) latexes.

Ethylene is a small symmetrical molecule. Since it does not contain any oxygen atom, it tends to be hydrophobic. However, ethylene is more soluble in water than most hydrophobic monomers, such as styrene, 2-ethylhexyl acrylate and vinyl neo-decanoate, probably because of its small size. At 4500 psig and 85°C, the solubility of ethylene monomer in the aqueous phase is 0.3 – 0.6 moles/liter (8.4 – 16.8 grams/liter), depending on the emulsifier concentration [Stryker et al., 1969]. For

comparison, the reported solubility of vinyl acetate in aqueous phase for a polyvinyl acetate emulsion polymerization is 0.33 mol/liter (28.4g/liter). Therefore, ethylene is considered to be a water-soluble monomer [Stryker et al., 1969]. Undoubtedly, at high pressures the solubility of ethylene in water increases, however, during the polymerization process ethylene is gaseous because the polymerization temperature is above the boiling point of ethylene.

Both ethylene and vinyl acetate are stable molecules, but their radicals are very unstable, which make them very reactive. The reactivity of radicals is quantified by studying its rate of polymerization. The ethylene radical is more reactive than the vinyl acetate radical or most substituted vinyl radicals, which are to various degrees resonance stabilized [Stryker et al., 1965; Stryker et al., 1966; Stryker et al., 1967; Stryker et al., 1969; Rosenblum, 1972] and the formation of ethylene and vinyl acetate radicals is the rate determining step in ethylene-vinyl acetate polymerizations. As a result, the initiator system is of immense importance for VAE polymerizations. In addition, the high reactivity of ethylene radicals give rise to chain transfer leading to short chain branching. Chain transfer also occurs with emulsifier adsorbed on the particle surface which retards the rate of polymer formation [Stryker et al., 1969]. The molecular weight of the polymer is proportional to the particle diameter and the rate of polymer formation is inversely proportional to the emulsifier concentration. This chain transfer of ethylene radicals is the main reason for the low molecular weights encountered in VAE polymers.

The interplay between the monomer concentration and the concentration of radicals is significantly more in high pressure VAE polymerizations than in atmospheric pressure polymerizations. Accordingly, the reaction rate and the polymer molecular weight in VAE polymerizations rely heavily on the interplay between these two variables. Higher initiator levels are needed if the same number of radicals is to be formed in an ethylene-based emulsion polymerization as in the corresponding atmospheric emulsion polymerization, i.e., the emulsion polymerization of the same monomers in the absence of ethylene. At the same conditions, formation of ethylene radicals is less favored than formation of radicals of other monomers. At initiator levels similar to those used in atmospheric polymerizations, ethylene lowers the reaction rate in the VAE polymerization and yet it leads to higher molecular weights (kinetic chain length) because the number of radicals is smaller. At initiator levels considerably higher than those of atmospheric experiments, the number of radicals formed is high resulting in higher reaction rates but lower molecular weights because of pronounced chain transfer. Finally, the number of ethylene radicals compared to vinyl acetate radicals is also important. Provided there is a sufficient level of initiator, starved polymerizations, in terms of vinyl acetate, will lead to higher ethylene contents because of the larger number of ethylene radicals relative to vinyl acetate radicals. This, in turn, will lead to lower molecular weights due to the enhanced chain transfer.

In the coating industry, ethylene copolymers have attracted greater interest partly because of the low price of ethylene, which has led to expectations of a substantial cost savings in latex costs. However, ethylene is a gas at normal temperatures and

pressures. Emulsion polymerizations of ethylene-based are done at elevated pressures. This requires special high pressured reactors with thick walls, pressure resistant seals and valves, and similar items not required in conventional (atmospheric pressure) latex production. Furthermore, handling and storage of ethylene requires special equipment and ethylene is most conveniently stored as a liquid under cryogenic conditions at moderate pressure. Initial plant costs are considerably higher than for conventional latex production [Edser, 1972]. Therefore, if ethylene copolymerizations can be made at low pressure, significant cost savings due to the lower cost of the raw materials can be realized. This has been demonstrated to be possible with the use of branched vinyl esters as disclosed in a recent patent [Avramidis et al., 2001].

2.6 Comparison of ethylene vs. acrylates as co-monomer for vinyl acetate

Polyvinyl acetate is a hard and brittle polymer (T_g of 30°C) which has to be plasticized to be useful as a film former and pigment binder in coating applications. Therefore, different low glass transition temperature (T_g) monomers, referred to as soft comonomers, are used in the polymerization of vinyl acetate. It is the co-monomer that provides flexibility and softness that differentiates VAEs (vinyl acetate ethylene) and conventional vinyl acrylics. Ethylene is a two carbon, i.e., a very small hydrocarbon molecule with no oxygen atom, thus it contains no hydrophilic moiety.

The soft monomer in conventional vinyl acrylics, usually butyl acrylate, is an acrylic ester which is more hydrophobic than vinyl acetate. The structures of a VAE and a vinyl acetate-butyl acrylate copolymer containing 25 mole % ethylene and acrylate, respectively, are shown in Figure 2.2.

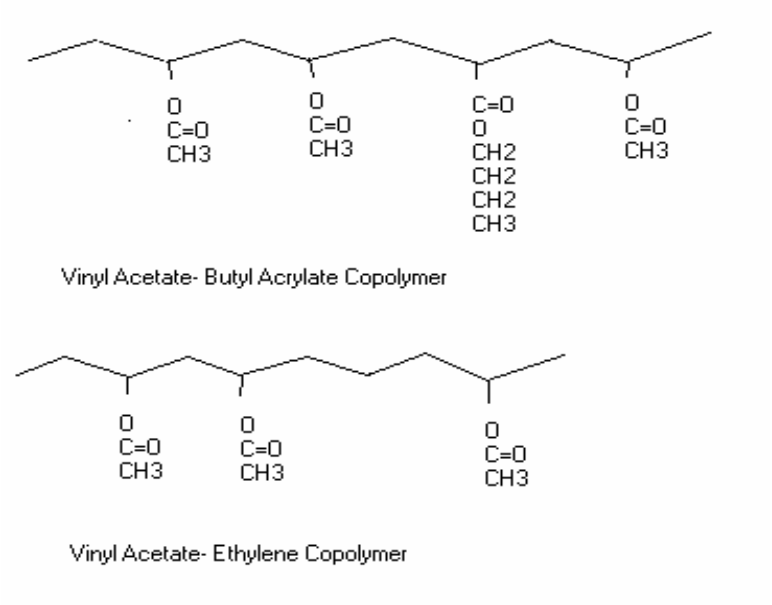


Figure 2.2 . Vinyl Acetate-Butyl Acrylate and Vinyl Acetate-Ethylene Copolymers containing 25 mole % Acrylate and Ethylene, respectively.

Currently, the conventional binder system for architectural coatings is the poly(vinyl acetate-co-butyl acrylate) copolymer latex. The high scrub vinyl acrylic technology, embraced by the industry about 10-15 years ago, has been the standard for superior scrub resistance. To develop better scrub resistance and acceptable low temperature

film formation, these systems rely on higher levels of coalescents, usually 9-12% based on polymer solids contents [Caldwell et al., 1999]. Two to six gallons of ethylene or propylene glycol per 100 gallons of paint are usually required for surface wetting and system compatibility and freeze-thaw stability. Besides their costs, these solvents contribute to odor.

Polyvinyl acetate-ethylene (VAE) latexes developed for coatings provide even higher scrubs than their high scrub vinyl acrylic predecessors. What makes these new resins so impressive is that they surpass the current high scrub resistance standard in the absence of coalescents and the glycols required by the high scrub vinyl acrylic latexes. They also show excellent stability and low temperature coalescence, all at VOC's of less than 10grams/liter compared to 120-200grams/liter for the high scrub vinyl acrylics [Caldwell et al., 1999].

Another important aspect is adhesion to different substrates [Edser, 1972; Rosenblum, 1972]. In VAE copolymers the polarity is conferred totally by pendant acetate groups. The only difference between the VAE molecule and vinyl acetate is the frequency at which the acetate group occurs in the chain. The polarity contributor in VAE polymers is the same as that of polyvinyl acetate and adhesives properties would be expected to be roughly the same. Since there is a large abundance of acetates in polyvinyl acetate, the effects of copolymerization with ethylene would not be expected to significantly reduce polarity at the contacting surfaces [Edser, 1972; Rosenblum, 1972]. On the other hand, there is greater flexibility in the backbone chain so that with any change in the dimensions of the substrate such change would be

absorbed by the flexing of the backbone and in the absence of any displacement of the bonded sites on the substrate. Therefore, adhesion is preserved with vinyl acetate-ethylene polymers over wider temperature range than with conventional vinyl acetate-alkyl acrylate copolymers. As a result, VAE copolymers find extensive use in the caulk and sealant industries. The flexibility of the vinyl acetate-ethylene copolymers is directly dependent on the amount of ethylene in the copolymer. This flexibility by itself will promote adhesion to a wider variety of surfaces.

Other ingredient such as surfactant, functional monomer, etc. is also important in influencing the performance the latex. Heldmann et al. showed that some of the most important properties of a paint such as pigment binding capacity, gloss and blocking resistance using vinyl acetate-branched vinyl ester and vinyl acetate-ethylene emulsions depended very much on a proper choice of the nonionic surfactant [Heldmann et al., 1999].

2.7 Pressure Emulsion Polymerization Techniques

Similar to atmospheric emulsion polymerization, pressure emulsion polymerization can be made either by batch, semi-continuous or continuous process. Conventional emulsion polymerization techniques used in atmospheric emulsion polymerization are also possible such as homogenous feed, seeded polymerization, staged feed, and power feed to give a variety of particle morphologies. The main difference in pressure emulsion polymerization is the incorporation of gaseous monomers such as ethylene.

The emulsion polymerization of ethylene, vinyl acetate and vinyl neo-decanoate is a gas-liquid polymerization. Gas-liquid polymerizations are more complex than single-phase, i.e., liquid counterparts because one of the monomers is a gas. As a result, the number of phases increases by one compared to conventional polymerizations and therefore, the number of degrees of freedom is reduced by one. For gas-liquid polymerizations in general and for our BEEVA polymerizations in particular, in addition to the polymerization reaction per se, diffusion processes are extremely important since the participation of ethylene in the polymerization reaction requires it to be in the liquid phase. In fact, because of the importance of diffusion processes in gas-liquid polymerizations, the bulk transport of the gas, becomes the rate-determining steps in the polymerization reaction. Accordingly, diffusion, mass transfer and the associated gas-liquid mixing processes are very important in gas-liquid reactions.

When the two phases are brought into contact they are not in equilibrium and the rate at which a species is transferred from one phase to the other depends on the departure of the system from equilibrium and the quantitative treatment of these transfer processes requires knowledge of the equilibrium state of the system. Therefore, Vapor-Liquid Equilibrium (VLE) relationships are needed in order to understand the effect of process variables, such as temperature and pressure for example, on both the diffusion of the components from one phase to the other but also because thermodynamics controls the maximum possible conversion. VLE is the relationship of the composition of the vapour phase and the liquid phase when the phases are in physical equilibrium.

At any time during the emulsion polymerization of a branched ester-ethylene-vinyl acetate monomer composition, the reaction system consists of monomer droplets, latex particles and ethylene gas bubbles. In addition to the bubble-liquid interface, the two phases are also separated by the planar interface between the liquid and gas phases. A schematic is shown in Figure 2.3. Ethylene incorporation in the latex particles is a two-step process: first ethylene molecules must be transported from the gas bubbles to the latex particles via the aqueous-monomer (vinyl acetate-branched ester) liquid phase and once at the particles, where the polymerization takes place, the ethylene molecules will react with the other monomers.

It is of benefit to describe here the mass transfer resistances encountered during ethylene copolymerization. These resistances are:

1. the planar gas-liquid interface separating the latex and the vapor space above the latex surface in the reactor,
2. the curved (bubble) gas-liquid interface formed by the ethylene bubbles in the reactor, and the liquid phase resistance to mass transfer.

Increasing pressure can improve ethylene mass transfer and solubility in latex particles. 2500 psig pressure gives a solubility of 0.17g ethylene /g polymer while 3300 psig pressure gives a solubility of 0.21 g ethylene / g polymer [Stryker et al., 1969].

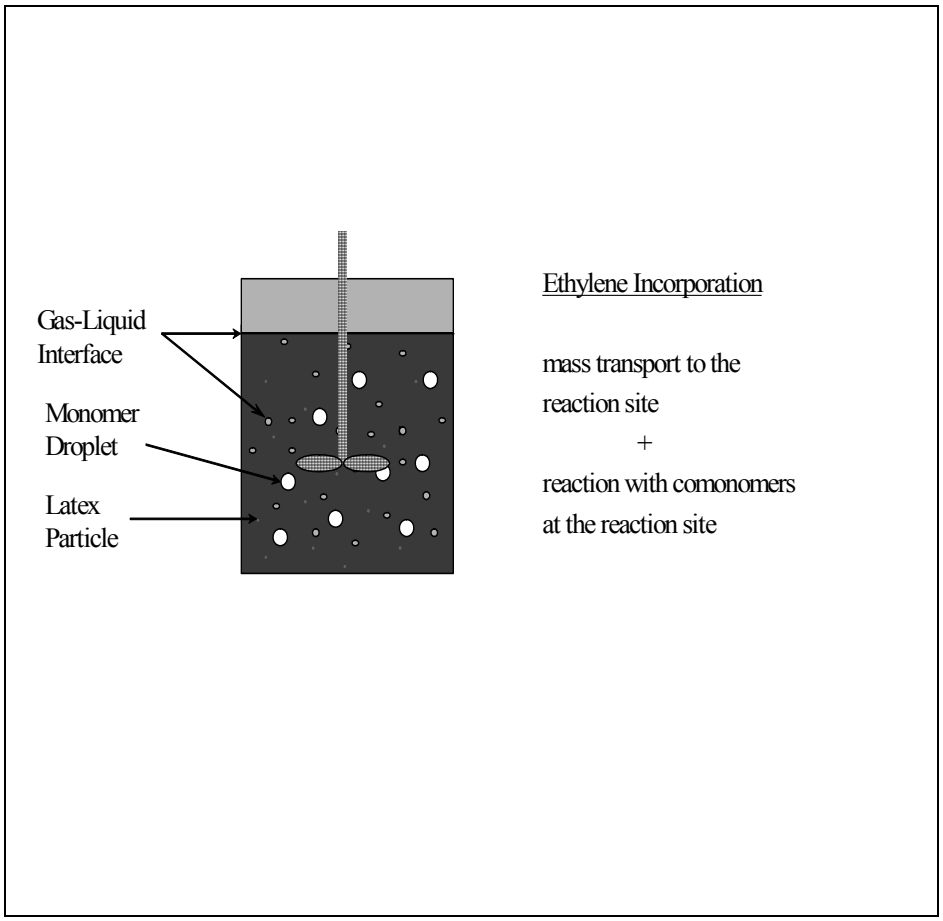


Figure 2.3. Mass Transfer with Chemical Reaction in the BEEVA Reactor

The largest of these resistances is the planar gas-liquid interface separating the latex and the vapor space above the latex surface in the reactor. In the gaseous phase, ethylene transport is only due to diffusion since there is no bulk motion contribution to the total mass flux. The liquid phase resistance to mass transfer refers to the diffusion of dissolved ethylene molecules in the aqueous-monomer phase that reach the reaction loci, i.e., the polymer particles, where the polymerization of the monomers takes place. The diffusion coefficient of ethylene dissolved in the liquid

phase, viz., aqueous and monomer phases, along with the concentration gradient existing in the liquid phase, i.e., the saturation concentration and the concentration at the reaction loci, control the transport of dissolved ethylene to the reaction sites.

The total mass transfer of ethylene is given by Fick's first law (here in Cartesian coordinates and in the z-direction) 

$$N_{Az} = -cD_{AB}\frac{\partial x_A}{\partial z} + x_A(N_{Az} + N_{Bz}) \qquad (1)$$

where N_{Az} is the total molar flux (i.e., total number of moles of ethylene passing through a unit area per unit time) of species A in the z-direction, c is the total molar density of the solution (aqueous and monomer), D_{AB} is the diffusivity of an ethylene monomer molecule through the aqueous phase, x_A is the mole fraction of ethylene in the system (aqueous and monomer) and N_{Bz} is the flux of the aqueous phase in the total system (aqueous and monomer). In the application of this equation to our system, we do not consider the particles but one can assign the value of N_{Bz} to include the flux of the particles plus the aqueous phase in the total system, which is the aqueous – monomer - polymer phases.

The first term in the right hand side of equation (1) is the molar flux of ethylene resulting from diffusion superimposed on the bulk transport of ethylene. The second term in the equation refers to bulk mass transfer of ethylene molecules, such as by

agitation for example. It is therefore evident that ethylene incorporation to the copolymer requires an appropriate flow profile to maximize the bulk contribution to the total flux. Such a profile can be achieved by the appropriate agitation level, reactor configuration (baffles, agitator dimensions and design, etc.). The effect of these variables will be addressed later. The diffusion coefficient is a function of the monomer concentration in the liquid phase, the monomer phase composition as well as the pressure and temperature during polymerization.

Equation (1) in the absence of bulk ethylene transport reduces to the familiar Fick's law

$$N_E = K_L (C_{eq.} - C_{rs}) \qquad (2)$$

In equation (2) N_E is the flux of ethylene, K_L is the mass transfer coefficient, $C_{eq.}$ is the saturation concentration of ethylene at the prevailing reactor conditions and C_{rs} is the concentration of ethylene at the reaction site, i.e., the latex particle.

Based on this model, it is useful to list the different factors that affect the mass transfer of ethylene to the reaction sites. Ethylene mass transfer is controlled by the following factors:

1. reactor pressure
2. reactor temperature
3. agitation
4. total reaction volume, or percent fill

5. liquid monomer level and composition
6. Surfactant type and concentration

   6a. droplet size

   6b. surfaces properties of the droplets

   6c. ethylene-water & ethylene-oil interfaces

   6d. size of ethylene bubbles (gas distributor configuration; sparging)

   6e. surface tension of the ethylene-liquid interface

   6f. surface viscoelastic properties of the ethylene-liquid interface
7. Aqueous phase (water miscible solvents)
8. Viscosity of the liquid phase

Senrui et al. found that during ethylene emulsion polymerization an agitation rate of less than 400 rpm reduced the rate of polymerization [Senrui et al., 1974]. This suggests that gas-liquid mass transfer limitation arise below an agitation rate of 400 rpm affecting the concentration of ethylene monomer in solution. In this study, we fixed the agitation rate at 600 rpm, an arbitrary high speed to ensure excellent mixing without causing too much foaming. Scott et al. suggested that the most effective method of overcoming gas-liquid mass transfer limitations was to increase the agitation rate [Scott et al., 1994]. A second, less effective method of increasing the mass transfer surface area was to reduce the size of the polymer particles. This can be done by changing surfactant type or increasing the amount of surfactant. The

effectiveness of this method is marginal unless the agitation rate is very low as shown by Scott et al [Scott et al., 1993]. In other words, other gas-liquid mass transfer mechanisms dominate over the particle size effect. Scott et al. also showed that axial-flow impellers (characterized by 45° pitch-blades) provided better mixing of the latex with the gas in the headspace of the reactor [Scott et al., 1994]. However, coagulum formation and particle flocculation could be reduced by using radial-flow impellers and a high agitation rate. In our study, we used radial-flow impellers with hollow shaft and at high agitation rate of 600 rpm (which is above 400 rpm).

In order to increase the total mass transport of ethylene across the planar gas-liquid interface separating the latex and the vapor space above the latex surface in the reactor, a specially designed agitator configuration was employed.

The DISPERSIMAX is a turbine-type agitator with a hollow shaft connected to the driving mechanism via a coupling. A schematic of the DISPERSIMAX is shown in Figure 2.4. There is a 0.25'' opening on the surface of the coupling that covers about one-half of the perimeter of the coupling. As the agitator rotates, it displaces the liquid between the blades and as a result gas is drawn from the vapor space through the opening on the coupling and the agitator and through the hollow shaft to the two-circular openings on the lower end of the shaft where the impeller is attached as shown in Figure 2.4. Accordingly, the resistance to mass transfer due to the planar gas-liquid interface separating the latex and the vapor space above the latex surface is eliminated.

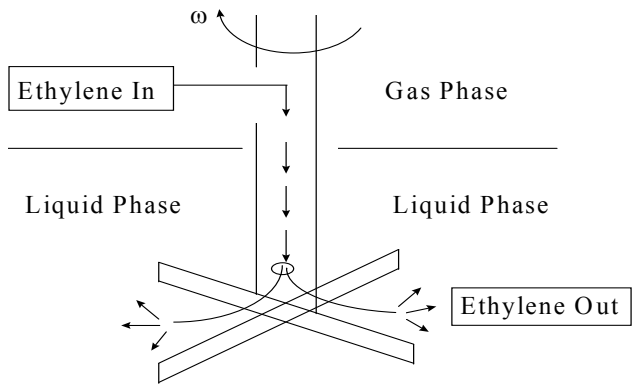


Figure 2.4. Schematic of the DISPERSIMAX Agitator used in BEEVA Polymerizations

The DISPERSIMAX is based on a principle that the centrifugal force due to rotation creates a pressure drop (vacuum) across the hollow agitator shaft. As a consequence, the ethylene gas is drawn to the blades under the free latex surface, thereby eliminating the mass transfer resistance offered by the planar gas-liquid interface. In addition, since the pressure drop across a planar gas-liquid interface is zero, it is immaterial at what pressures the polymerization takes place. Ethylene is transported to the reaction sites by an "externally" applied pressure drop, viz., the vacuum created across the agitator shaft. As a consequence, enhanced incorporation of ethylene in the final inter-polymer can be achieved at low pressure levels.

2.8 Aspects Of Branched Vinyl Esters In Vinyl Latex Polymerization

In Europe, the introduction of vinyl esters of highly branched carboxylic acids containing nine and ten carbon atoms, vinyl neo-nonanoate (Neo-9) and vinyl neo-decanoate (Neo-10), respectively, has enabled the formation of all-vinyl emulsion based coatings, which are more suitable for exterior use and possess better alkali resistance than conventional acrylics. Weathering studies in the Netherlands clearly demonstrated that for asbestos cement panels coated with 40% PVC (pigment volume content) white pigmented 70/30 (weight by weight) Vinyl Acetate / Neo-10 emulsion paints, there was no significant alkaline erosion after 10 years of south vertical exposure.

By comparison, paints based on all-acrylic latex experienced approximately 20% erosion over the same time period, while those formulated from vinyl acrylics had completely eroded away after seven years of exterior weathering [Smith et al., 1993].

There are several factors that contribute to the stability of vinyl acetate copolymers. Given that adjacent hydroxyl groups have been shown to promote hydrolysis of acetate moieties in partially hydrolyzed polyvinyl acetate, one would expect that any comonomer capable of separating the pendant acetate groups on the polymer backbone should effectively decrease the rate of saponification [Smith et al., 1993]. Since vinyl esters possess very similar reactivity ratios, copolymerization of vinyl acetate with a more sterically hindered esters, i.e., one more resistant to hydrolysis, would be expected to decrease the rate of saponification. In other words, the co-monomer would form a random copolymer with vinyl acetate, thereby separating the

vinyl acetate moieties, which, in turn reduced the number and lengths of the vinyl acetate sequences, and thus the extent of hydrolysis. On the basis of this argument, ethylene is the co-monomer of choice because its low molecular weight allows for the maximum introduction of non-hydrolyzable segments on a per weight basis [Smith et al., 1993]. Contributing to ethylene's effectiveness is the fact that hydrocarbon segments tend to reduce water solubility, thus imparting greater hydrolytic stability. More specifically, polymers with a high oxygen content can more easily facilitate attack by water than more hydrophobic polymers comprising little or no oxygen.

Branching and pendant length are also important for vinyl monomers. Accordingly, on a molar basis -: n-butyl acrylate < Neo 5 < vinyl 2-ethyl hexanoate ~ Neo 9 ~ Neo 10 in the resistance against alkali saponification of vinyl acetate/branched ester copolymers and vinyl acetate/branched ester/butyl acrylate terpolymer latexes at 2/1 vinyl acetate/branched ester molar ratios [Smith et al., 1993]. That Neo-5 provides lower protection than either Neo-9 and Neo-10 points to the importance of pendant chain length in enhancing hydrophobicity and alkali resistance (all three possesses di-methyl substituted (tertiary) alpha carbons). It has also been established that pendant chain length takes precedence over a tri-substituted alpha carbon in providing protection against hydrolysis. Therefore, BEEVA copolymers with branched ester consisting of either vinyl 2-ethylhexanoate, vinyl neo-nonanoate (Neo-9), vinyl neo-decanoate (Neo-10) and vinyl neo-endecanoate (Neo-11) possess better alkali resistance than the inter-polymer where the branched ester is vinyl neo-pentanoate (Neo-5).

The vinyl esters of a tertiary carboxylic acids having 5,9,10 and 11 carbon atoms in the acid moiety, known as vinyl pivalate, vinyl neo-nonanoate, vinyl neo-decanoate and vinyl neo-endecanoate readily copolymerize with vinyl acetate and ethylene to form BEEVA latexes which are useful in a variety of applications, particularly in paints and adhesives. Of special importance is the use of the BEEVA polymers in low- and zero- VOC coatings in paint. In addition, branched esters provide unmatched hydrophobicity to BEEVA copolymers.

Vinyl neo-decanoate, which is the most commonly used branched vinyl esters used in the industry, is represented by the following structure.

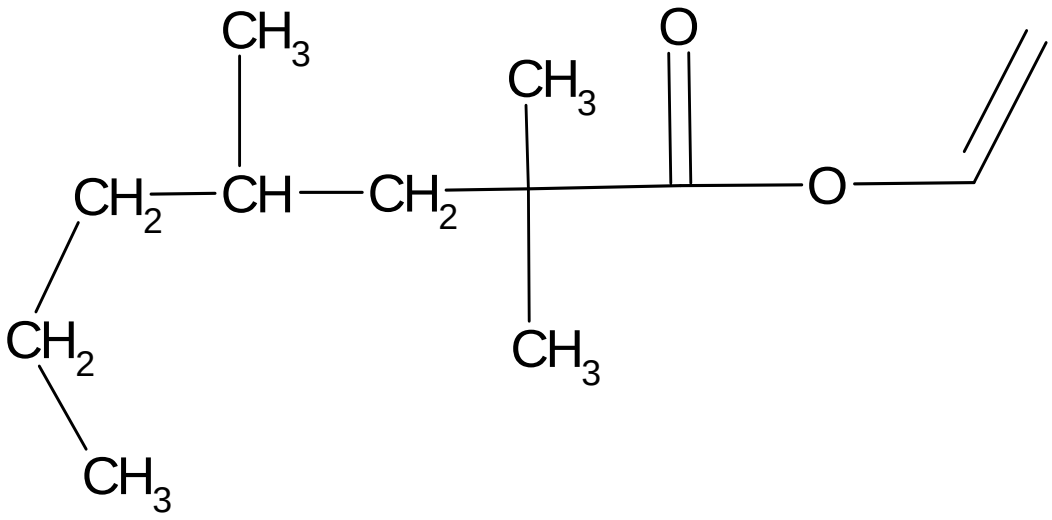
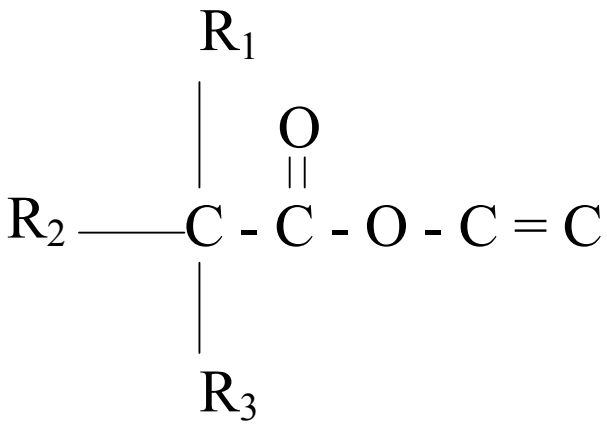


Figure 2.5. Structure of Vinyl neo-Decanoate

The total number of carbons in the acid moiety is 9 for neo-nonanoate, 10 for neo-decanoate and 11 for neo-endecanoate.

Shell Chemical Company developed a manufacturing process for producing highly branched tertiary monocarboxylic acids (actually a mixture of isomeric acids) over 30 years ago. The C9 – C11 acid mixture (versatic acid) is prepared via the Koch process, which involves oligomerizing propylene in the presence of water and carbon monoxide with acid catalyst to produce branched acids containing a neo structure on the carbon adjacent to the carbonyl carbon. The acid can then be converted into its vinyl ester by reaction with acetylene [Slinckx et al., 1994]. The generic structure of branched vinyl esters is shown in Figure 2.6.

The neo-esters are named according to the average number of carbons in the neo acid precursor. Union Carbide Company Inc. (now, a subsidiary of The Dow Chemical Company) developed a transvinylation process for preparing a variety of vinyl esters, including vinyl 2-ethylhexanoate (V2EH) and vinyl pivalate (Neo-5) from vinyl acetate but this process is less economical than the traditional acetylene process [Murray, 1991]. Shell (now under Resolution Performance Products) has introduced Neo-9, Neo-10 and Neo-11 under the tradenames of Veova 9, Veova 10 and Veova 11.



where R_1, R_2 and R_3 are alkyl groups

Figure 2.6. The generic structure of branched vinyl ester

The glass transition temperatures, formula and total mass of the vinyl ester monomers is shown in Table 2.3 [Bassett, 2001]. Scholten and van Westrenen illustrated the effect of chain branching by measuring the glass transition temperatures of a series of polymers prepared from Neo 9 isomers [Scholten et al., 1991]. The T_gs were found to range from 10 to 119°C which showed that the T_gs of branched vinyl ester homopolymers are a consequence of the chain lengths and degree of branching with the various isomer mixtures.

Monomer	**Tg, °C**	**Formula**	**Total Mass**
Vinyl Acetate	30	$C_4H_6O_2$	86.1
Vinyl Neo-pentanoate	65	$C_7H_{12}O_2$	128.2
Vinyl 2-Ethylhexanoate	-36	$C_{10}H_{18}O_2$	170.3
Vinyl Neo-nonanoate (Neo-9)	60	$C_{11}H_{20}O_2$	184.3
Vinyl Neo-decanoate (Neo-10)	-3	$C_{12}H_{22}O_2$	198.3
Vinyl Neo-endecanoate (Neo-11)	-40	$C_{13}H_{24}O_2$	212.3

Table 2.3 Glass Transition Temperatures, Formula and Total Mass of Vinyl Ester Monomers

The fundamental basis of the effect of branched esters on ethylene uptake during the polymerization is dependent on two factors:

1. the hydrophobicity of such monomers that help drive the ethylene through the aqueous/monomer phase to the polymerization loci, i.e., minimizing the liquid phase resistance to ethylene transport, and
2. the reactivity ratio of branched esters with ethylene and vinyl acetate which is close to 1, suggesting random copolymerization.

Polymerization of ethylene at low pressures requires overcoming the resistance to mass transfer of ethylene molecules to the reaction sites. The diffusion component of the total mass transfer of ethylene to the polymerization loci, i.e., the polymer particles, becomes increasingly important at low polymerization pressures, and it is more difficult to be enhanced compared to the bulk component of the total mass flux

of ethylene. The later can be enhanced by mechanical means, such as agitator configuration and agitation speed. The diffusional component can be enhanced by the use of hydrophobic monomers, such as the vinyl branched esters, which help transport the ethylene molecules to the polymer particles. Ethylene itself cannot be considered a hydrophobic monomer [Stryker et al., 1969]. On the other hand, vinyl acetate is a water-soluble monomer and as such it promotes the solubilization of ethylene in the aqueous/monomer phase. However, there is a need for a carrier of ethylene molecules to the particles and that role can be facilitated by branched esters. The presence of vinyl acetate or any hydrophilic monomer that has good reactivity with ethylene is also important for achieving maximum ethylene incorporation. On the other hand, the hydrophobic carriers of ethylene to the reaction sites should also be easily polymerizable with vinyl acetate and ethylene in order to help establish and sustain a concentration gradient of ethylene from the aqueous phase to the particles, and therefore, result in ethylene incorporation in the terpolymer. Also, surface active agents that are capable of transporting ethylene to the polymerization sites can be used.

These carriers are especially important because they offer both a hydrophobic and hydrophilic property, and as such can help solubilize and simultaneously, transport ethylene to the particles. In addition to branched esters, system variables such as pressure, temperature and composition also affect ethylene transport to the particles resulting in differences in ethylene incorporation to the polymer.

Since the BEEVA polymerizations are carried out at low pressures, both factors discussed above are critical for the incorporation of ethylene and this can be accomplished by the use of branched esters. The branched esters are the most hydrophobic of the monomers employed in emulsion polymerization and the identical reactivity ratio of both vinyl acetate and ethylene will result in the production of random ethylene-vinyl acetate-vinyl branched ester interpolymers. Table 2.4 lists the water solubility of different monomers and Table 2.5 lists the reactivity ratios of common monomers with vinyl acetate [Bassett., 2001]. Although styrene is the next most hydrophobic monomer to the branched ester, its reactivity with vinyl acetate does not result in random copolymerization, and copolymerization with vinyl acetate is very difficult, if at all possible. Styrene also suffers from poor ultra violet (UV) resistance while branched ester similar to vinyl acetate has excellent UV resistance.

Monomer	Solubility (g/100g)
Acrylonitrile	7.1
Methyl acrylate	5.2
Vinyl acetate	2.5
Ethyl acrylate	1.8
Methyl methacrylate	1.5
Ethylene	1.1
Vinyl chloride	0.60
Butyl acrylate	0.16
Styrene	0.03
2-Ethylhexyl acrylate	0.01

Vinyl neo-pentanoate	0.08
Vinyl 2-ethylhexanoate	<0.01
Vinyl neo-nonanoate	<0.001
Vinyl neo-decanoate	<0.001
Vinyl neo-endecanoate	<0.001

Table 2.4 . Water Solubility of Monomers at 20°C

Monomer 2 (m_2)	r_1	r_2
Vinyl neo-decanoate	0.99	0.92
Vinyl neo-nonanoate	0.93	0.90
Ethylene	1	1
Acrylic acid	0.02	20.64
Butyl acrylate	0.05	5.89
2-Ethylhexyl acrylate	0.04	7.5
Methyl methacrylate	0.03	22.21
Styrene	0.03	24.18
Vinyl chloride	0.60	1.40

Table 2.5 Calculated monomer reactivity ratios for copolymerization with vinyl Acetate (m_1)

Vinyl neo-decanoate is one of the most apolar vinyl monomers commercially available. Its heavily branched alkyl structure with no hydrogen atoms in the alpha position of the ester group confers high hydrophobicity, outstanding hydrolytic stability and excellent UV resistance to latex binders. The vinyl branched ester enhances the water and alkali resistance of conventional vinyl acrylics and provide performance better than those of conventional acrylics. Ethylene plasticizes vinyl acetate, imparts more flexibility to the copolymer, increases the cohesive strength, provides better adhesion to most substrates and bestows good plasticizer resistance to most films.

Branched esters provide outstanding hydrophobicity to VAE copolymer film especially when ethylene and vinyl acetate are not hydrophobic. The use of branched esters opens up an extensive range of polymer properties. The hydrophobicity and alkali resistance of branched esters and the film formation imparted by ethylene are obvious benefits for exterior paint. The more hydrophobic nature of BEEVA copolymers, as well as improved extensibility at low temperatures is an obvious advantage in preventing cracking in mobile substrates, which make these polymers suitable for use in caulk and sealant formulations. The structure of BEEVA polymer is as shown in Figure 2.7.

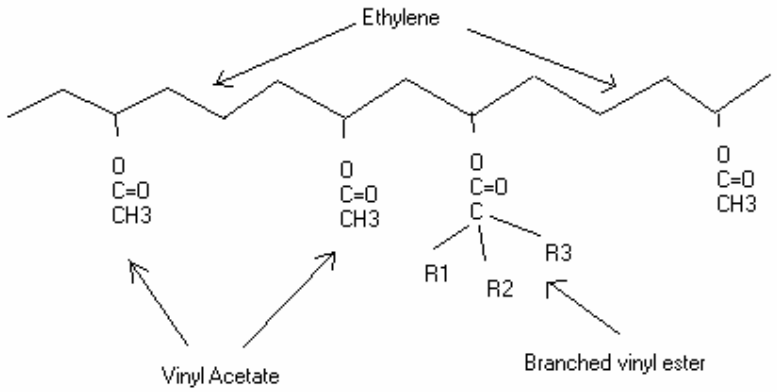


Figure 2.7. Structure of BEEVA polymer

2.9 Physical properties of ethylene-based latex and analytical methods used

Typical physical properties evaluated for ethylene-based latex are glass transition temperature (T_g), rheological behaviour, contact angle and compositional evaluation using high resolution proton Nuclear Magnetic Resonance (NMR).

Ethylene copolymers composition may be analyzed by several instrumental techniques such as infrared spectrometry, high-energy radiolysis, gas chromatographic analysis of copolymer pyrolysates and nuclear magnetic resonance [Lindemann, 1968]. High resolution nuclear magnetic resonance can be used with ease and accuracy for vinyl acetate-ethylene copolymers over a wide range of vinyl acetate contents above 1%, which is the practical accuracy limit of the method [Porter et al., 1963; Chen et al., 1964].

Avramidis et al. showed that the ethylene content was between 10 – 14 wt.% at 435 psig and the ethylene amount increased with increasing pressure as determined by nuclear magnetic resonance (NMR). 17 wt.% of ethylene were incorporated at 785 psig and about 21 wt. % ethylene at 1135 psig were reported. They also showed the effect of agitation speed in improving ethylene incorporation into the latex polymerization. Ethylene uptake was increased by 160% when the agitation was increased from 400 rpm to 600 rpm at low pressure of 435 psig. The effect of using branched vinyl ester (vinyl neo-decanoate) was also investigated. The ethylene incorporation was significantly enhanced in the presence of branched vinyl ester at pressures of 290 psig and 435 psig. At higher pressure such as 1100 psig, the presence of the branched vinyl ester did not appear to have a significant effect on ethylene incorporation [Avramidis et al., 2001].

Lindemann also reported the pressure-ethylene content relationship for vinyl acetate – ethylene copolymers. Ethylene content increased with increasing pressure and higher ethylene content was achieved at lower (50°C compared to 78°C) polymerization temperature. For examples, at 10 atmospheres pressure, the ethylene content was 4.5 wt. % and 5.7 wt. % at 78°C and 50°C, respectively. At 20 atmospheres pressure, the ethylene content was 8.9 wt. % and 11.6 wt. % at 78°C and 50°C, respectively [Lindemann, 1968]. Scott et al. used proton nuclear magnetic resonance to determine composition of vinyl acetate – ethylene copolymer. As pressure was increased from 200 to 500 psig, the solubility of ethylene increased and, consequently, the ethylene content of the copolymer produced increased. Moreover, as the semi-batch feed period was extended from 2 to 4 hours (i.e., the vinyl acetate flow rate reduced), the

ethylene content of the copolymer increased. The explanation for this was the increased reaction time, which allowed for maximum solubilization of ethylene (i.e., effective gas-liquid mass transfer) [Scott et al., 1994a]. Scott et al. also studied the effect of ethylene content on the glass transition temperature, T_g of the vinyl acetate – ethylene copolymers. They showed that as the ethylene content of the copolymer was increased, an almost linear decrease in T_g was observed illustrating the plasticizing effect of ethylene. The introduction of ethylene into poly (vinyl acetate) increases the separation of the acetate groups within the copolymer chain, thereby increasing the flexibility of the polymer chains, which accounts for the observed decrease in T_g. It also showed that a minimum amount of ethylene (approximately 8-10 wt. %) was required before this plasticization effect was evident [Scott et al., 1998a].

Surface free energy or surface tension analysis of polymer films is very important from a practical point of view in order to understand their adhesion, coalescence, wettability, and water repellency properties during application. In general, the surface structure of polymers can be investigated by X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infra-red spectroscopy (a.t.r., FTIR) and more practically by the contact angle measurement [Erbil, 1996]. The indirect determination of the surface free energy of the polymers by the one-liquid contact angle method (the air-liquid-polymer system) had been proposed by Fowkes [Fowkes, 1964], Girifalco et al. [Girifalco et al., 1957] and Owens et al. [Owens et al., 1969].

The elastic and viscous constraints make it difficult to have direct method of measuring the surface energy of solids. However, wettability measurements

employing liquids of different polarity can serve as a convenient indirect method to estimate the surface energy of a solid as well as the nature of the interactions between two materials. In the method of Zisman [Zisman, 1964; Zisman, 1972], contact angles are measured for liquid drops applied to the surface of interest for a series of selected liquids. The cosine of the contact angle (Θ) is plotted against the liquid surface tension, and the intersection of the resulting curve with the coordinate, where Θ = 0 (complete wetting) and cosine Θ = 1, gives the critical surface tension (γ_c) for wetting the surface.

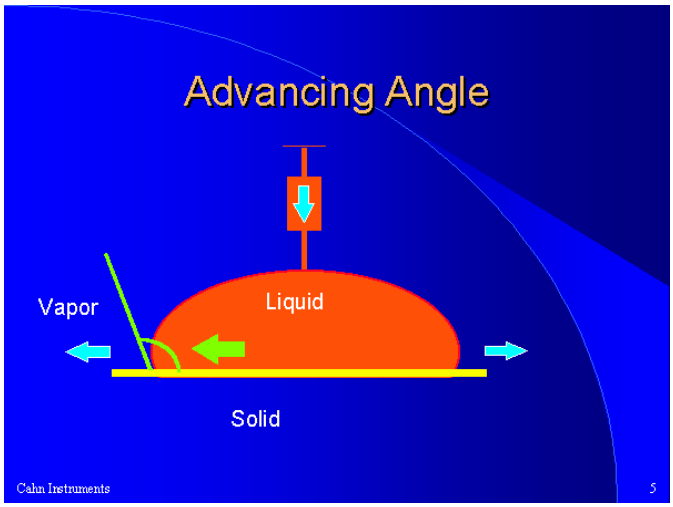


Figure 2.8 Description of contact angle measurement.

The drop of liquid forming an angle with the substrate may be considered as resting in equilibrium by balancing the three forces involved, namely the interfacial tensions between solid and the liquid, between solid and vapor, and between the liquid and vapor. The angle within the liquid phase is known as the contact angle. It is the angle

between the tangent plane to the surface of the liquid and the tangent plane to the surface of the solid at any point along their line of contact [Davies et al., 1961].

Solid surfaces that are not easily wetted by water form liquid beads when water drops contact the surface and therefore exhibit large contact angles (θ). These surfaces are classified as hydrophobic without a standardized reference. Researchers have different criteria to classify hydrophobicity or hydrophilicity of a material. A commonly used cutoff value is $\theta = 90°$. When $\theta > 90°$, the solid surface is named hydrophobic or non-wetting by water. For solids resulting in $0° < \theta < 90°$, the solid surface is said to be "wetted" or "partially wetted". When $\theta = 0°$, the solids surface is said to be "wet out" by water [Dai et al., 2004]. Hydrophobic polymers have low surface energy and are more difficult to wet. The contact angle of a hydrophobic polymer is higher than a hydrophilic polymer. Therefore, contact angles represent an easy way to qualitatively assess the hydrophobicity of polymeric films. In this study, the Neo monomer contributed the most to the polymer's hydrophobicity.

A commonly used technique to study surface charge characteristics of latex is zeta potential. Zeta potential also known as electrokinetic potential measures the potential difference across the diffuse double layer on the polymer particle surfaces. The distribution of ions close to the surface of the particles is usually known as the electrical double layer. A diffuse electrical double layer is the layer of ions close to the surface that stretched out in a spatial domain where the extension depends on salt concentration. In many systems, it is the diffuse layer potential which controls the colloid stability of the system [Ottewill, 1990]. The quantity of diffuse layer potential is a model potential and not easy to determine but a quantity closely approaching it in

sign and magnitude, the so-called zeta-potential, can be determined from electrokinetic experiments. One of the most direct techniques for polymer latex particles as used in this study is to determine the electrophoretic mobility. Zeta potential can then be calculated with known mobility, viscosity of the medium and other numerical factor.

The term "rheology" was invented by Prof. Bingham and it means the study of the deformation and flow of matter. Rheological properties are obtained using a rheometer, capable of shearing a fluid at a known shear rate and producing the value of stress associated with shear rate. The term shear rate is defined as the rate of change of velocity with cross-section and is commonly denoted as $\dot{\gamma}$. Qualitatively, viscosity (η) is the property of a material to resist deformation with increasing rate of deformation. Viscosity is defined as shear stress, τ divided by the velocity gradient or shear rate, $\dot{\gamma}$ in steady simple-shear flow. This relationship is also called Newton's Law, which best describes ideal viscous fluids [Barnes et al., 1989].

$$\eta = \tau / \dot{\gamma} \qquad (3)$$

Any liquid whose viscosity does not change with time of shearing, and obeys the above relationship, is said to be a Newtonian liquid. And for liquid not obeying Newton's relationship, is called non-Newtonian liquid. When a network matrix is formed in the system, resistance to flow is built-up in the system. The system of this type becomes thinner on stirring because the structure is broken down and becomes thicker again on standing because the structure is re-established. The shear thinning

characteristic is called pseudoplasticity. The degree of pseudoplasticity can be determined from the relation between shear stress and shear rate by using the power law [Sato, 1995].

$$\dot{\gamma} = K \tau^n \qquad (4)$$

or

$$\log \dot{\gamma} = \log K + n \log \tau \qquad (5)$$

where K is the consistency index and n is the flow index which is a measure of the degree of deviation from Newtonian behaviour. If n =1, then the system is Newtonian. If n > 1, the system is shear thinning and if n < 1, the system is shear thickening. Although this equation lacks theoretical significance, most experimental data do fit it at least over part of the shear stress-shear rate range.

In this study, the rheological flow behavior and viscosity are investigated with various amount of hydrophobic Neo monomer (branched vinyl ester) used. High viscosity of polymer solutions can be due to increasing association of molecular clusters of hydrophobic polymer chains [Tan et al., 2000].

3 EXPERIMENTAL METHODS AND MATERIALS

3.1 Preparation of BEEVA Latexes

3.1.1 Model BEEVA Latexes

We can vary different parameters of the emulsion polymerization process of ethylene-vinyl acetate-branched vinyl ester to obtain different compositions of BEEVA latexes. Compositional variation can be achieved by:

1) varying the polymerization pressure in the reactor system at fixed branched vinyl ester (Neo monomer) type and amount. Higher pressure is generally contributed through higher ethylene pressure being fed into the pressure reactor.
2) varying the amount of branched vinyl ester such as Neo-10 to vinyl acetate by weight at fixed pressure.
3) Changing the type of Neo monomer at fixed Neo monomer to vinyl acetate monomer by weight and at fixed pressure.

The labeling of the latexes was done according to the (1) Type of Neo monomer, (2) Amount of Neo monomer in relation to vinyl acetate by weight %, and (3) The ethylene pressure (in psig) in the reaction maintained throughout the polymerization.

Neo [Type of Neo monomer] **–** [Amount of Neo monomer by weight % in relation to vinyl acetate monomer] **–** [polymerization pressure in psig].

The three BEEVA model series are:

1) Varying the ethylene pressure (atmospheric, i.e., no ethylene, 200 psig or 1.4 MPa, 350 psig or 2.4 MPa, 500 psig or 3.4 MPa, 750 psig or 5.2 MPa and 1100 psig or 7.6 MPa) at fixed Neo 10 monomer and weight ratio of Neo 10 / vinyl acetate of 10 / 90. The latexes in this series are labeled as Neo10-10-atm, Neo10-10-200, Neo10-10-350, Neo10-10-500, Neo10-10-750 and Neo10-10-1100;
2) Varying the amount of Neo 10 to vinyl acetate by weight % (0, 10, 20, 30, 40 and 50% of Neo 10 monomer) at a fixed pressure of 500 psig or 3.4 MPa. The latexes in this series are labeled as Neo-0-500, Neo10-10-500, Neo10-20-500, Neo10-30-500, Neo10-40-500 and Neo10-50-500;
3) Changing the type of Neo monomer (Neo 9, Neo 10 and Neo 11) at a fixed Neo monomer / vinyl acetate weight ratio of 10 / 90. The latexes in this series are labeled as Neo9-10-500, Neo10-10-500 and Neo11-10-500.

Some labeling examples of the model BEEVA latexes synthesised are:

a) At weight ratio of Neo-10 / vinyl acetate of 10 / 90 and at 500 psig (3.4 MPa) pressure, the latex is labeled as Neo10-10-500.
b) At weight ratio of Neo-10 / vinyl acetate of 20 / 80 and at 500 psig (3.4 MPa) pressure, the latex is labeled as Neo10-20-500.
c) At weight ratio of Neo-10 / vinyl acetate of 10 / 90 and at 750 psig (5.2 MPa) pressure, the latex is labeled as Neo10-10-750
d) At weight ratio of Neo -9 / vinyl acetate of 10 / 90 and at 500 psig (3.4 MPa) pressure, the latex is labeled as Neo9-10-500.

e) When no Neo monomer is used and only vinyl acetate and ethylene copolymerisation at 500 psig (3.4 MPa) pressure, the latex is labeled as Neo-0-500

The amount of Neo monomer by weight ratio converted to mole ratio in relation to vinyl acetate monomer is shown in Table 3.1.

Neo-10 / Vinyl acetate (wt%)	**Neo-10 / Vinyl acetate (mole ratio)**
10 / 90	1 / 20.7
20 / 80	1 / 9.2
30 / 70	1 / 5.4
40 / 60	1 / 3.4
50 / 50	1 / 2.3
Neo-9 / Vinyl acetate (wt%)	**Neo-9 / Vinyl acetate (mole ratio)**
10 / 90	1 / 19.3
Neo-11 / Vinyl acetate (wt%)	**Neo-11 / Vinyl acetate (mole ratio)**
10 / 90	1 / 22.2

Table 3.1 . Ratio of Neo monomer to vinyl acetate in weight % and in mole ratio.

3.1.2 Materials Used For Synthesis of BEEVA Latexes

The monomers used in the polymerization process were used as received without removing any polymerization inhibitors prior to use.

Ethylene was supplied in a 30 lbs (13.6 kg) cylinder from MESSER (Singapore). Vinyl acetate monomer was supplied from The Dow Chemical Company. Branched vinyl esters monomers were supplied from Resolution Performance Products. Rhodacal DS-4, a sodium dodecylbenzene sulfonate anionic surfactant was supplied from Rhodia. Sodium vinyl sulfonate was supplied from Air Products while Tergitol NP-15, a nonyl phenol ethoxylate (15 mole E.O.) non-ionic surfactant was supplied from The Dow Chemical Company.

Sodium acetate and ammonium persulfate were supplied by Goodrich Chemical Entreprise. Sodium formaldehyde sulfoxylate was from Nacalai Tesque, Inc, Japan. Sodium metabisulfite was supplied from Mallinckrodt Chemical while t-butyl hydroperoxide was from Akzo Nobel. Ferrous sulfate was supplied by Merck and the defoamer Nalco 2343 was of a proprietary composition by Nalco Chemical company. The preservative used was Preventol P-840 (combination of 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT), 2-methyl-4-isothiazolin-3-one (MIT) with a formaldehyde condensation product) from Bayer. Deionized water was used for polymerization and dilution.

3.1.3 Recipe For Model BEEVA Latexes

The recipe for the model BEEVA latex Neo10-10-500 is listed in Table 3.2. The other BEEVA latexes will follow the same recipe except for changes in Neo monomer type, ratio of Neo monomer with vinyl acetate and pressure.

Ingredients	**Weight, grams**
In the aqueous charge:	
Deionized water	3984
Sodium acetate	11.48
Rhodacal DS-4	125
Tergitol NP-15	131.8
Ferrous sulfate	0.06 g dissolved in 40 g water
Defoamer Nalco 2343	5.4
Sodium vinyl sulfonate	23.1
In the monomer mixture:	
Vinyl acetate	5140.8
Neo-10 monomer (Veova 10)	571.20
Defoamer Nalco 2343	27.20
Ethylene	Add to reactor up to 500 psig
Initial oxidizer solution:	
Ammonium persulfate	7.3
Deionized water	80

Initial reducer solution:	
Sodium metabisulfite	7.36
Deionized water	60
Delayed oxidizer feed solution:	
Ammonium persulfate	20.54
Deionized water	656
Delayed reducer feed solution:	
Sodium metabisulfite	10.27
Deionized water	666.2
Post oxidizer feed solution for residual monomer treatment:	
Post oxidizer feed solution:	
t-butyl hydroperoxide (70% active)	10.92
Deionized water	217
Post reducer feed solution:	
Sodium formaldehyde sulfoxylate	6
Deionized water	220
Preservative / biocide:	
Preventol P-840	12

Table 3.2 Recipe for BEEVA latex Neo10-10-500

The agitation speed was fixed at 600 rpm. Agitation speed of less than 600 rpm resulted in poorer mixing (by visual observation) for the incorporation of ethylene gas into the aqueous phase while agitation speed of higher than 600 rpm created too much turbulence in the reactor and foaming. The monomer feed time was fixed at 3 hours while the polymerization temperature was maintained at 80 °C for all the model series prepared in this study.

A description of the procedure used is outlined below:

1. The aqueous charge was heated to 80°C
2. Once the temperature was reached, the agitator was turned off, and the reactor was evacuated to –10 psig using the vacuum pump. Ethylene was then introduced to a pressure of 10 psig and was then held for 5 minutes, before the reactor was vented.
3. The reactor agitator was set to 600rpm, and the initial monomer mixture amounting of 445.6g was charged to the reactor.
4. Ethylene was then charged to the desired pressure (such as 500 psig for Neo10-10-500), and the pressure was maintained for 15 minutes to ensure the solubilization of the ethylene gas.
5. An initial amount of oxidizer, followed by the reducer was charged to the reactor.
6. The temperature of the reactor was monitored and cooled to prevent the temperature from exceeding 85°C.
7. The feeds (monomer mix feed, oxidizer feed and reducer feed) was then charged after 30 mins.

8. The polymerization temperature was kept at 80±3°C and feed time was 3 hours. The following conditions were maintained, i.e., monomer feed rate = 29.4g/min; oxidizer feed rate = 3.7g/min; reducer feed rate = 3.7g/min.
9. Once all the reaction mixtures have been introduced to the reactor, the reaction was allowed to continue for another 30 minutes with the temperature kept at 75 – 80 °C.
10. Simultaneously, any unreacted monomer was treated by feeding post oxidizer and post reducer over a period of 60 minutes. The settings were, post oxidizer feed rate = 3.8g/min ; post reducer feed rate = 3.8g/min.
11. The reactor pressure was decreased and cooled to below 30°C over a 30 minutes duration.

3.2 Preparation of samples

The BEEVA latexes at low pH (ca. 3-5) were dialyzed in distilled-deionized water using regenerated cellulose tubular membrane. The dialysis process was carried out over a one-month period where the water was replaced every week. This cleaning process removes all the impurities and un-reacted chemicals.

The concentrations of the samples were checked by gravimetric determination of the moisture loss through drying. A small aluminum tray was weighed and the weight was noted. A gram of latex (the exact weight of latex was noted) was placed in the tray and this was dried in the oven at 80°C for 24 hours. After drying, the dried sample with the tray was weighed and the concentration of the stock polymer can be calculated. After determining the stock concentration of the samples, varying

concentrations of BEEVA polymer solutions were prepared for NMR, glass transition temperature, contact angle and rheological measurements. 5, 10, 15, 20, 25 and 30 wt% polymer solutions were prepared.

3.3 Rheological measurements

Rheological studies of the diluted polymer solutions were carried out using Contraves LS 40 controlled rate rheometer. The Contraves LS40 was fitted with a concentric cylinder measuring system consisting of a cup and bob geometry with a diameter of 12 and 11mm, respectively, to measure high and low viscosity solutions.

All experiments were conducted under the temperature of 25 ± 0.1°C unless otherwise stated. A total of 20 data points were recorded for each experiment. The steady shear viscosity data presented in this study was conducted under equilibrium viscosity condition. This was done by allowing sufficient pre-shear time to avoid collection of data in the transient or start-up flow region. The measuring time must be long enough to ensure that the system has reached equilibrium. The shear rate range for the steady measurements of the solutions was from 0.5 to 100 s^{-1}.

3.4 Contact angle measurements

Dried polymer samples were prepared by casting the latex over glass slide with the aid of a 0.003 inch caster. The sample was dried for 24 hours in a covered desiccator to minimize accumulation of dust on the surface. The dried polymer sample was placed in the First Ten Angstroms FTA 200 dynamic contact angle analyzer. Droplet of deionised water in syringe was introduced by means of mechanical gears onto the

surface of the dried polymer. Snapshots were taken by an attached camera. The resulting water droplet on the polymer surface picture will be measured for the polymer's contact angle.

3.5 Glass transition temperature measurements

Perkin-Elmer Thermal Analysis DSC 7 Sub-ambient Differential Scanning Calorimeter (DSC) was used to determine the glass transition temperature (T_g) of the polymer. About 10-20 mg of dried BEEVA polymer was placed in the aluminum sample pan and crimped. The sample placed in the DSC cell (in a nitrogen environment) was heated from -40 to 200°C to heat condition the cell at a controlled rate of 50°C/min. It was then cooled to -40°C and reheated at 10°C/min. A plot of heat flow versus temperature can be analyzed to determine the glass transition temperature. The middle point of incline in the plot was taken as the mid-point of the T_g.

3.6 Nuclear Magnetic Resonance (NMR) spectra measurements

Nuclear magnetic resonance (NMR) is useful for the chemical analysis of materials, usually organic containing magnetic nuclei such as proton (^1H). In this study, we used a high resolution proton NMR to analyze the amount of ethylene in the synthesized BEEVA polymers. NMR spectra of these polymers were recorded using Bruker Spectrospin ACF-400 (400MHz) Fourier Transform spectrometer. The spectrum is described in terms of a) chemical shifts, b) spin-spin coupling of the magnetic nuclei, and c) number of nuclei in each chemically shifted group present. Sample solutions were prepared by dissolving about 0.5mg of the solid BEEVA polymer in about 0.5ml of $CDCl_3$ solvent (Aldrich) with tetramethyl silane (TMS) as internal reference.

3.7 Zeta potential and particle size measurements

Brookhaven Zeta Potential analyzer and Zeta Plus Particle size analyzer were used to determine zeta potential and particle diameter, respectively. These are part of the Brookhaven laser light scattering system.

The electrodes used for mobility and zeta potential measurements, consisted of a noble metal, usually palladium and was mounted on a machined support. The support also had a temperature sensor to measure the temperature near the sample. A small amount of sample was placed in the cuvette and this was positioned in the laser light scattering instrument. The temperature was set at 25°C. Using the same instrument setup without the electrodes, particle size measurements can be determined using the Zeta Plus software.

4 DESIGN OF PRESSURE REACTOR SYSTEM

4.1 Design of Pressure Polymerization Hardware

The design of the pressure polymerization hardware has many components of a standard atmospheric polymerization reactor system but is capable of handling gaseous monomer in addition to liquid monomers. The reactor vessel should be able to withstand pressure up to a maximum working pressure of 1500 psig (10.3 MPa). The agitator should be designed for good mixing and enable sufficient introduction of gaseous monomer into the aqueous mixture. Moreover, coagulum formation should be minimized with the use of appropriate impeller. As mentioned previously, Scott el al. showed that radial (turbine) impeller gives lower amount of coagulum formation as compared to axial impeller [Scott et al., 1994]. Agitation rate should be at least 400 rpm to provide sufficient mixing. The ethylene monomer addition into the reactor should be able to be controlled through valves as actuated on temperature and pressure. Safety aspects taken into the design should be of high priority as we are dealing with ethylene which is a highly flammable chemical and at high pressure.

The overall process flow sheet of the pressure reactor system is shown in Figure 4.1.

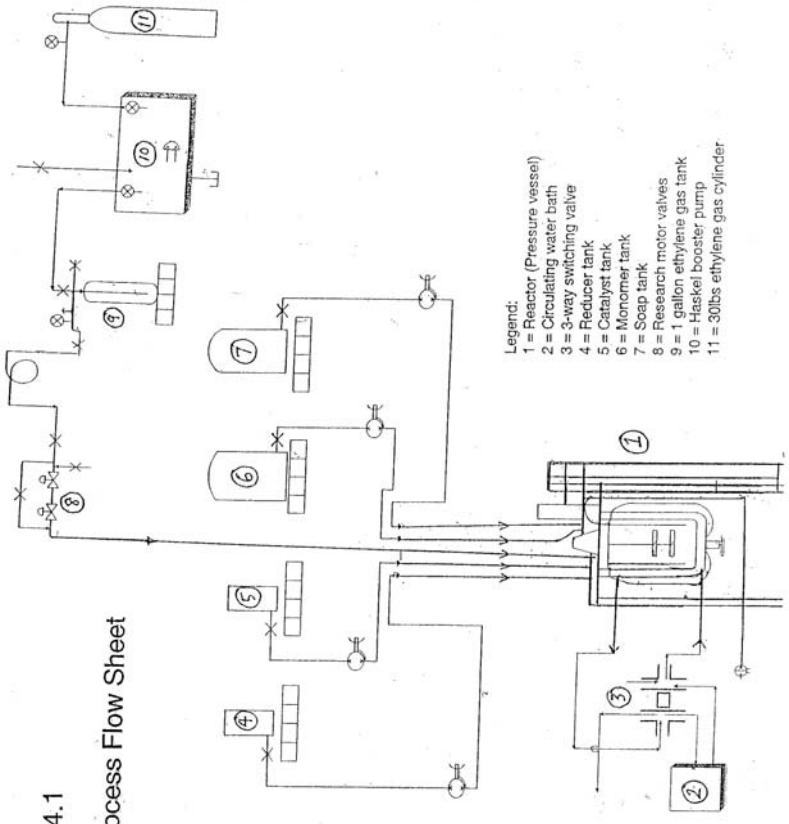


Figure 4.1 Overall Process Flow Sheet

4.1.1 Pressure vessel

The pressure vessel was designed and built by Autoclave Engineers, a division of Snap-tite, Inc., Erie, Pennsylvania, U.S.A. (Refer to Figure 4.2). Its specifications are tabulated below.

Specifications	
Capacity	5 U.S. gallons
9.56 Inch I.D.	16 inch Straight Length
Design criteria	ASME Code, Section VIII, Division 1
MAWP* Vessel	1500 psig at 500°F
MAWP* Jacket	150 psig at 500°F
Vessel body	316 SS
Vessel cover	316 SS
Vessel jacket	304 SS
Studs and nuts	SA193-B7 and SA194-2H
Baffles	Full length, Qty (4), 90° apart

*MAWP = Maximum Allowable Working Pressure

Table 4.1 Specifications of pressure vessel

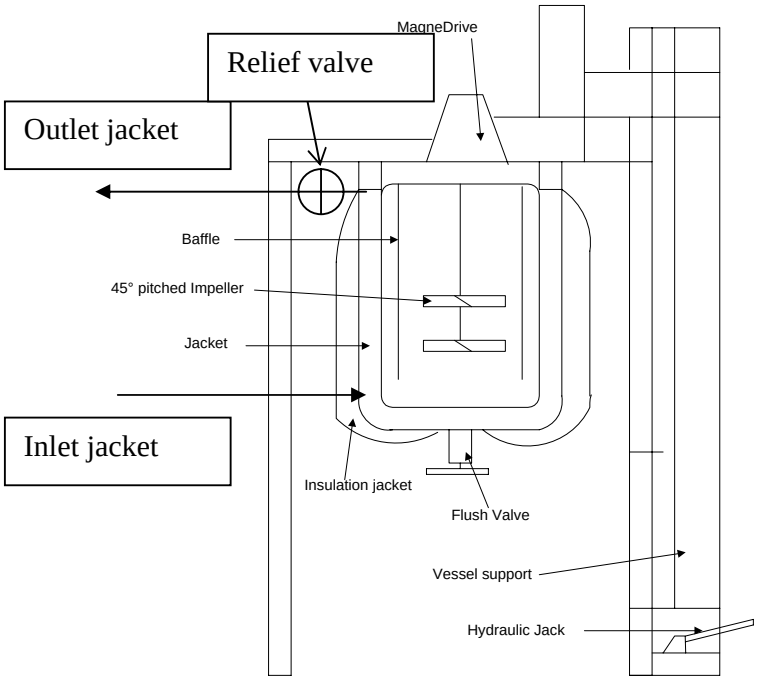


Figure 4.2 The 5-gallon reactor assembly

Both the inlet and outlet jackets are connected to a pneumatic actuator by Swagelok Quick-Connects (QC series - 1/2”). This actuator which is a 3-way switching valve controls the feed from the water bath and city water supply to the jacket (refer to Figure 4.1). There is a relief valve Nupro SS-8CPA2 (50-150 psi) at the jacket outlet which is calibrated to a cracking pressure of 130 psi. The vessel body can be hydraulically lowered and swung out for ease of cleaning.

The cover of the reactor is attached to the vessel support stand and is sealed to the vessel body via studs and 40mm nuts (12 each) and a face seal (Teflon O-ring) (see

Figure 4.3 for top view of reactor cover). A Teflon coated Viton O-ring (located around the lid of the reactor cover) is longer lasting as it has more resiliency. The 40mm cover nuts need to be torqued to 165 ft-lbs_f (or 224 Nm) using a adjustable torque wrench.

The body can be removed and can be pushed around by attaching the legs with wheels on it which can be connect below the insulation jacket, if needed.

Flow directions for all the lines are clearly indicated by the “arrow” sign and the different feed lines are differentiated by color code -i.e., blue color for monomer line, green color for catalyst line, yellow color for reducer line and red color for ethylene line. All the valves have pressure rating higher than the maximum operating pressure.

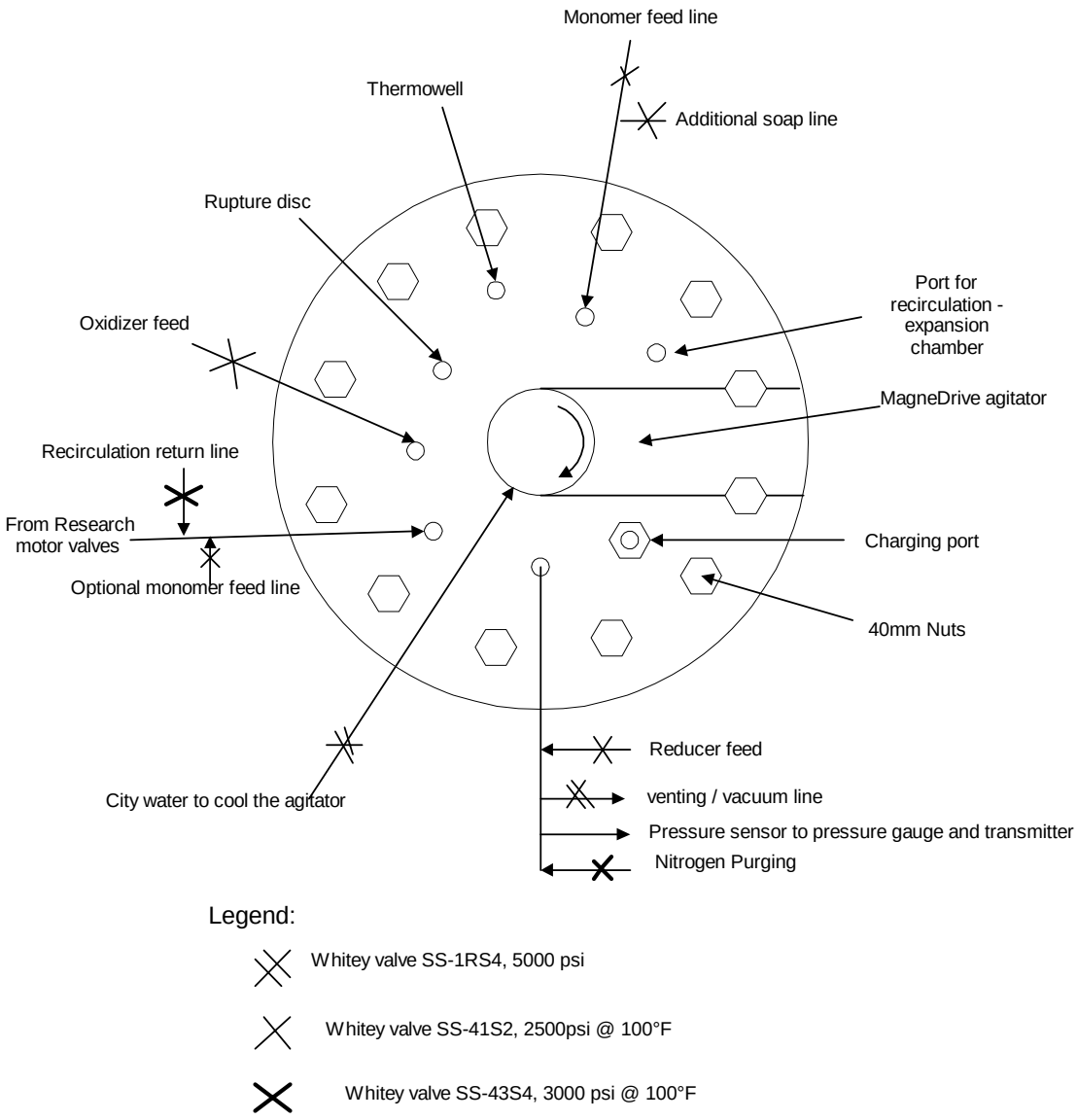


Figure 4.3 Top view of reactor cover

The stainless steel tubings used are:-

1/4” O.D. and 0.035” thickness SS316 with MAWP of 5100 psi and

1/8” O.D. and 0.028” thickness SS316 with MAWP of 8600 psi.

These tubings are used to connect between the tanks, pumps, valves, reactor, gas cylinder and water bath as shown in Figure 4.1.

The weakest point in the reactor is the rupture disc. This rupture disc is an ASME certified 1/2" STD inconel rupture disc. It is set to burst at 1530 psi at 72°F or 1438 psi at 500°F.

4.1.2 Agitator

The reactor is agitated via an Autoclave MagneDrive (3/4 HP variable speed motor) and overhung shaft which utilizes adjustable impellers. Mixing vortices are broken up by four removable baffles. The number of baffles could be reduced due to the many existing feed lines and thermowells in the reactor. In the MagneDrive, high speed rotary agitation is effected by the rotation of external magnets which actuate internal magnets attached to the shaft. A tachometer pick-up is located on top of the MagneDrive housing and converted to an indicated speed electronically on the Model MSC20R2311000 Speed Controller. MAWP of MagneDrive is equal to the MAWP of the reactor. Maximum speed is slightly more 600 rpm but can be extended by increasing the drive pulley at a 1/2" O.D. increment. However, this modification increases wear on the bearings.

For pressure polymerization, we use a DISPERSIMAX double disk turbine impeller for enhanced gas liquid mixing and is used with a blow pipe (see Figure 4.4). DISPERSIMAX is the manufacturer of impeller. This shaft is hollow to pull ethylene gas from the head space through and out from the turbine impeller. The blow pipe is

connected to the ethylene line and supply the gas right next to the impeller for good mixing. Impeller for atmospheric polymerization is shown for comparison purpose. This impeller is located inside the reactor (pressure vessel).

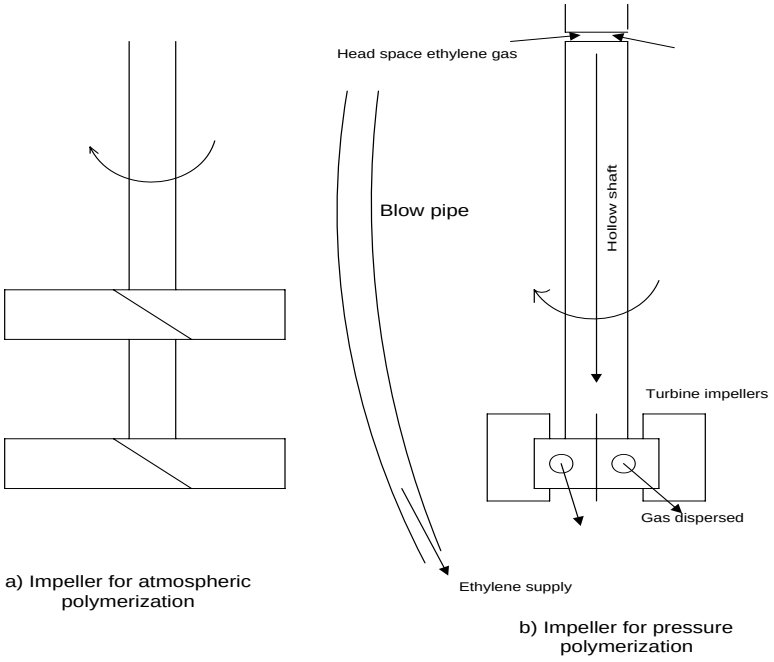


Figure 4.4 Impellers

4.1.3 Feed tanks and pumps

CHAPTER 4 DESIGN OF PRESSURE REACTOR SYSTEM

Four pumps available to deliver up to four solutions to the reactor at precise feed rates (see Figure 4.5). These diaphragm metering pumps can work against high pressure. The oxidizer and reducer solutions are pumped through a slower feed rate pump while the monomer and soap solutions are fed through a higher feed rate pump. The feed rate of the pumps can be controlled by the speed and stroke of the pump. Rough settings for stroke and speed can be obtained from the calibration graphs. The exact feed rate can be monitored and manually checked by timing the drop in weight using the balance and stop watch. The tubings from the tanks to the pumps are made from opaque PP plastic, so that we can verify flow. These tubings will have to be high pressure rated stainless steel tubings if we want to pressurize the tanks, which is not possible in the current piping configuration. The tubings from the pumps to the reactor are high pressure rated stainless steel tubing.

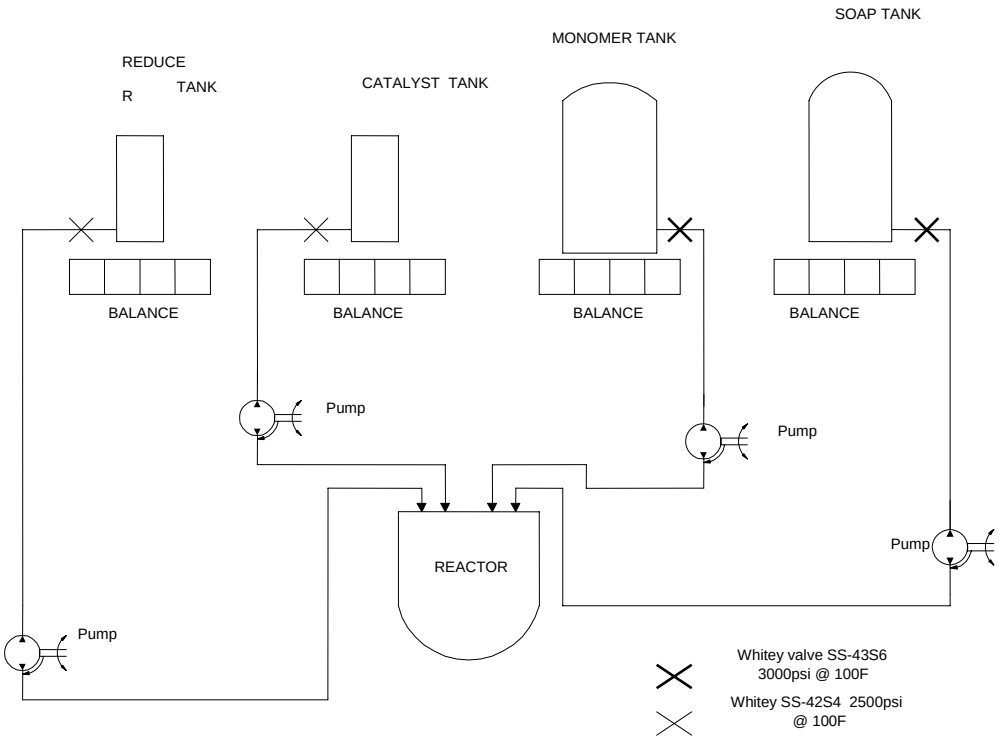


Figure 4.5 Feed tanks and pumps

4.1.4 Haskel pump

The Haskel pump is a gas booster pump which is driven by air. Using the Haskel pump, we can pressurize the intermediate 1 gallon ethylene gas feed cylinder up to the desired operating pressure even though the main 30 lbs ethylene cylinder is at a lower pressure (See Figure 4.1 and 4.6) . We can draw empty the 30 lbs ethylene cylinder using the Haskel pump.

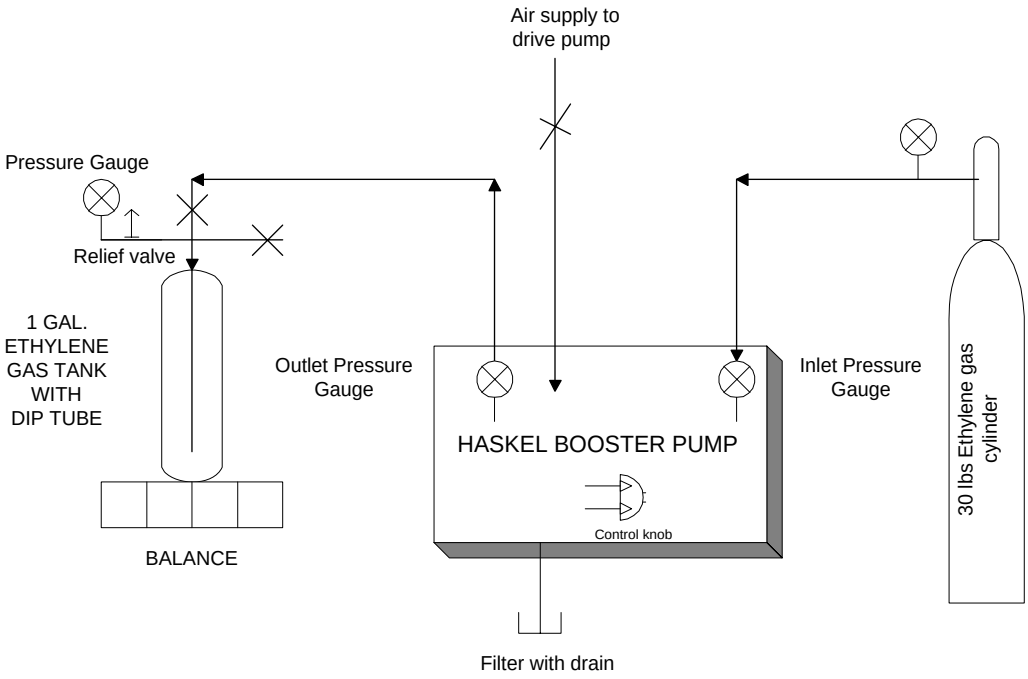


Figure 4.6 Haskel pump and transfer of ethylene.

4.1.5. Temperature control

The temperature in the reactor is maintained by the jacket temperature. Circulating water is constantly fed from the tempered water bath to the reactor jacket such that the jacket temperature is close to the water bath temperature.

To cool the reactor temperature, the bypass switch of the overtemp will actuate the solenoid to switch the 3-way switching valve to the cool city water. Once this bypass switch is turned off, the valve will switch the flow of water back to the tempered water bath. Sometimes during this switch-over, there may be excess water flowing

back from the jacket to the bath, causing the bath to overflow. Therefore, modification was made by using an overflow preventor device which consists of a float switch to actuate the solenoid valve that sends the excess water to drain. If the temperature of the reactor exceeds the set point temperature of the overtemp, it will also actuate the valve to cooling.

An optional cooling coil may be placed inside the reactor. The cooling water is regulated by the research motor valve.

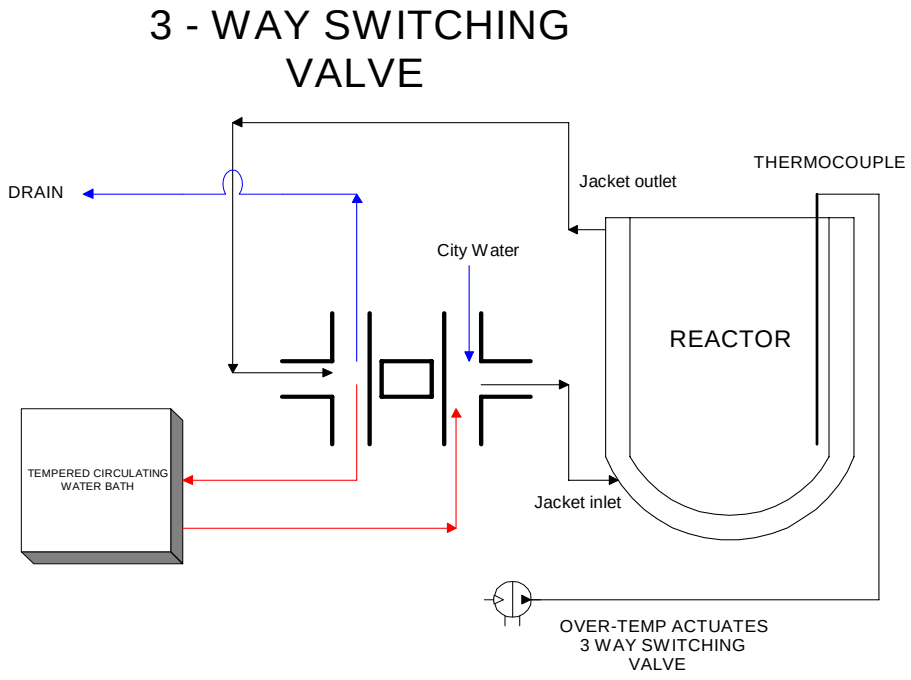


Figure 4.7 Temperature control

4.1.6. Research motor valves

The research motor valves are used to control the feeding of ethylene into the reactor. Two motor valves installed in series are used for this ethylene feed line. One is actuated on temperature and the other on pressure.

Only when both conditions are satisfied (i.e., temperature below set point, pressure below set point) will the ethylene be allowed through valves. The valves are "fail-safe" i.e., in emergency shut-down, the valves will be closed. There is also a line for nitrogen which is used during pressure test. A bypass is only used in the initial stage to bring the pressure to a desired level quickly.

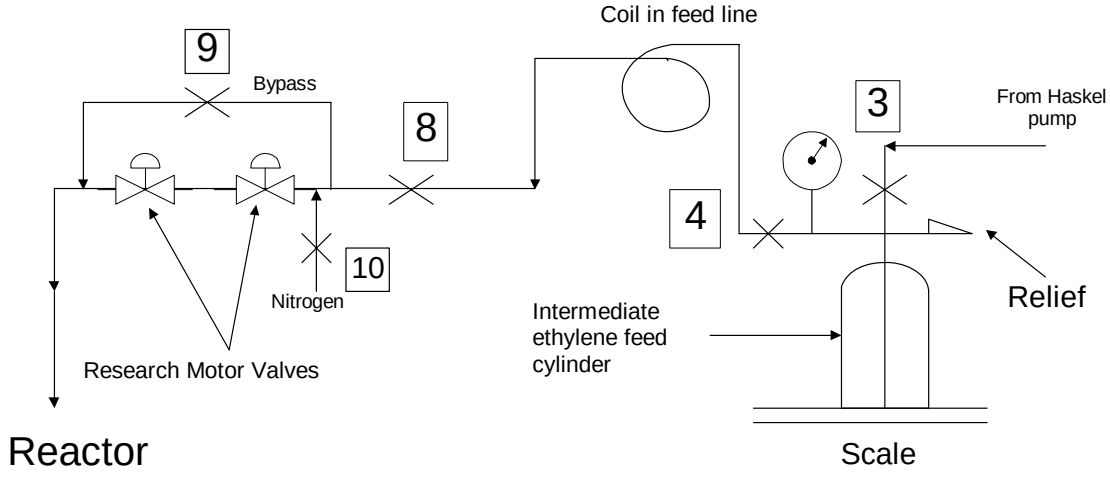


Figure 4.8 Research motor valves

A bigger motor valve is installed to the cooling coil as an option. This will only be used when we are using oil bath at temperature higher than 100 °C. During emergency shut down, this motor valve will be switched to “fail-safe” position, i.e., open for cooling down.

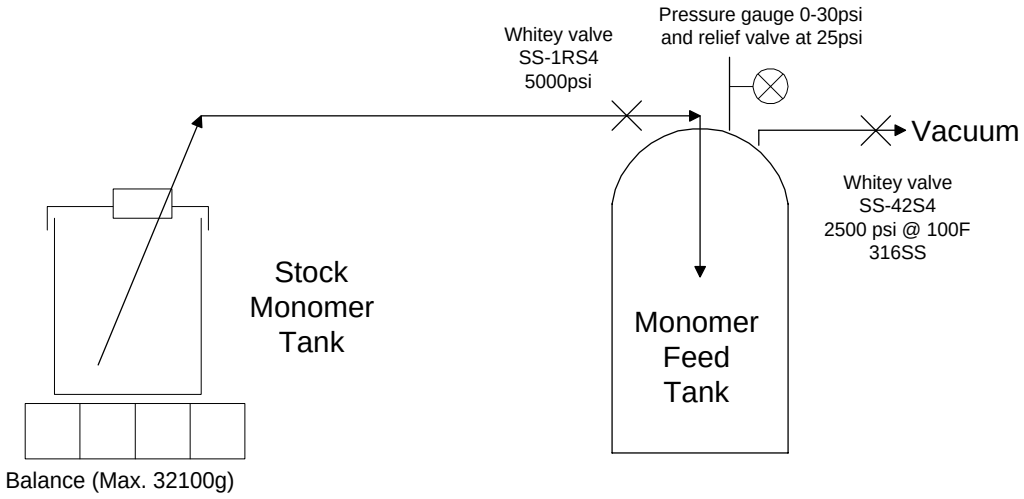


Figure 4.9 Monomer preparation system

4.1.7. Monomer preparation system

The monomer preparation is carried-out in a laboratory hood with the setup as shown in Figure 4.9. There is no need to handle the monomers by pouring them into the tank, which can cause spillage. Instead, the monomers from the stock monomer tank are being filled into the monomer feed tank through vacuum.

4.2 Safety Features

4.2.1. Safety devices

There are several safety features installed for the safe operation especially during pressure polymerization (See Figure 4.10). The polymerization room is a walk-in hood having a face velocity of at least 100 ft/min. There is an air flow meter with "beeping" alarm system to ensure that the face velocity is always within the requirement. Any hazardous chemicals will quickly be dispelled from the walk-in hood. There is also an ethylene (or combustible gas) detector and a "ringing bell" alarm system to detect any combustible gas. The rupture disc ensures that the pressure of the reactor does not go beyond an undesirable level. The effluent handling system channels the effluent to a catch tank if the rupture disc should burst. The pressure switch will automatically shut down all the pumps and Honeywell controllers (motor valves to safe-shut) in the event the pressure exceeds 1350 psig or 9.3 MPa (as calibrated). The overtemp controller will activate cooling water to the reactor jacket when the temperature is too high.

SAFETY FEATURES

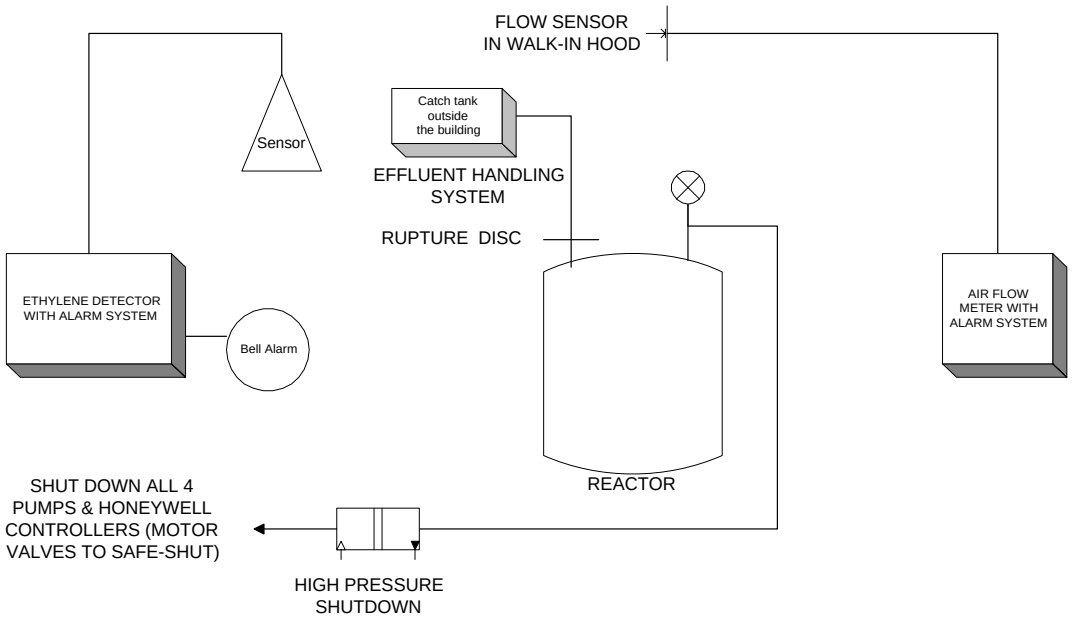


Figure 4.10 Safety features

4.2.2. Effluent handling system

(Refer to Figure 4.11)

The rupture disc will burst when the reactor pressure is higher than the bursting pressure of the disc (10.5 MPa at 22°C or 9.9 MPa at 260°C). In such situation, the effluent from the reactor will move through the high pressure flexible hose and expand/foam through the 3" pipe.

Eventually some effluent will be captured in the catch tank. Any hazardous vapors will be trapped by the mist eliminator made from wire mesh. There is a valve at the bottom of the tank for draining and cleaning purposes.

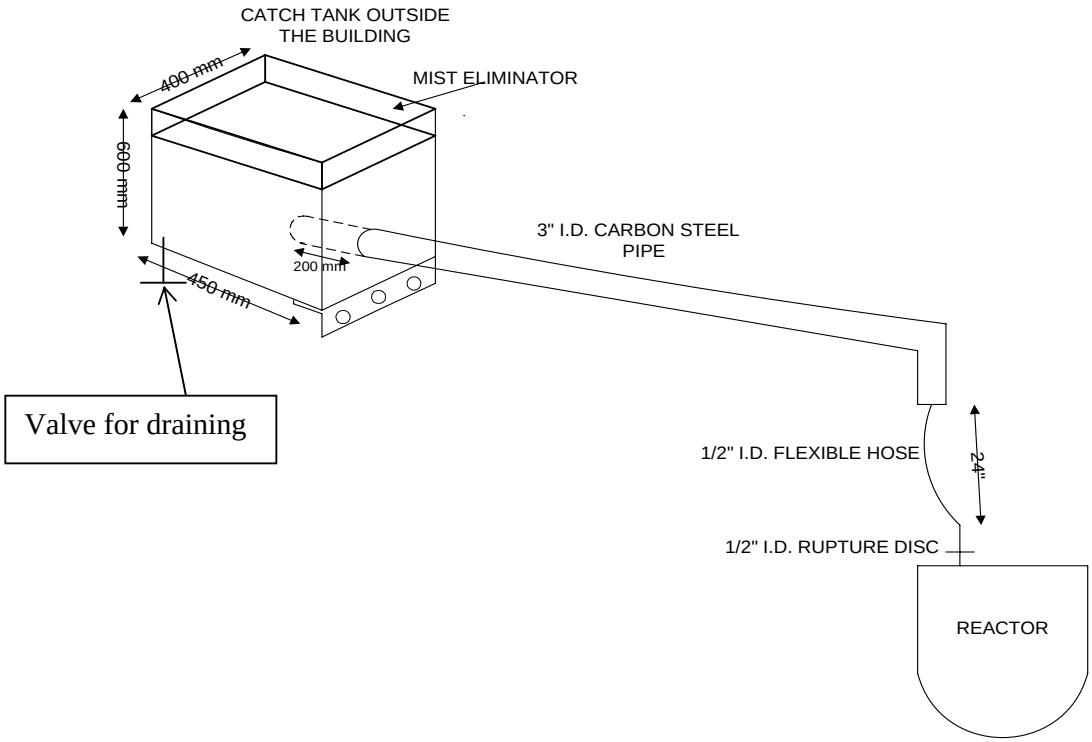


Figure 4.11 Effluent handling system

5 PHYSICAL PROPERTIES OF LATEXES

5.1 Introduction

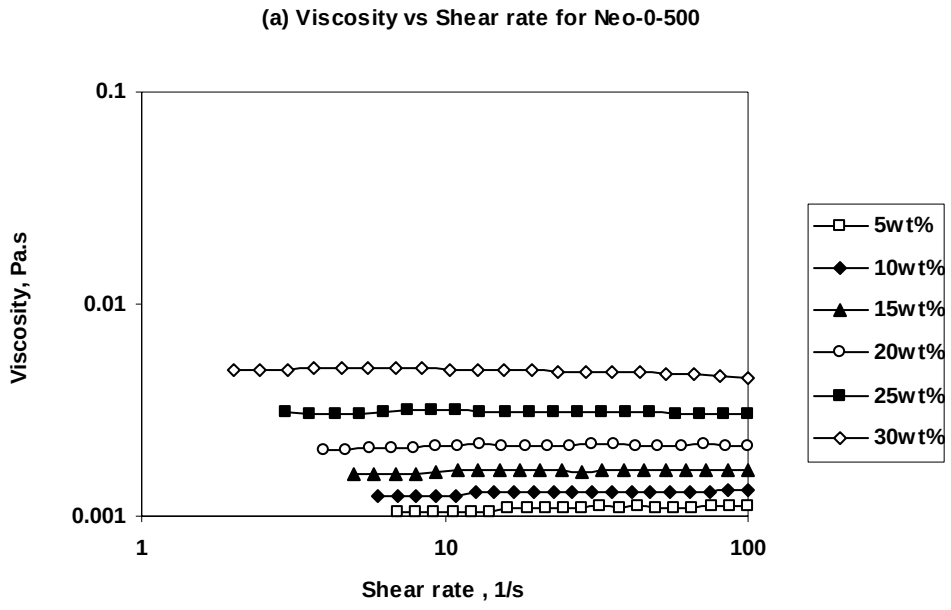
In this study, the author demonstrated the feasibility of preparing BEEVA latexes through proper design of the pressure reactor system and careful formulation of recipes consisting of vinyl acetate, ethylene and branched vinyl ester monomers. Three series of model BEEVA latexes were synthesized. Very low pressure of 200 psig or 1.4 MPa and medium pressure of 750 psig or 5.2 MPa were used in these BEEVA latexes as compared to much higher pressure of >1000 psig (or >6.9 MPa) in a typical ethylene-vinyl acetate copolymerization. Branched vinyl esters such as Neo9, Neo10 and Neo11 monomers were used.

The characterization of the physical properties of these latexes will facilitate in our understanding on the impact of varying the several key variables of the polymerization such as with or without branched vinyl ester monomer, the type of branched vinyl ester, the amount of branched vinyl esters and the polymerization pressure used. Several typical properties evaluated were glass transition temperature (T_g), rheological behaviour, contact angle and compositional evaluation through the use of high resolution proton Nuclear Magnetic Resonance (NMR). The monomer compositional changes will affect the glass transition temperature of these latexes. Understanding the rheological behaviour of these latexes will also be of interest and will be studied.

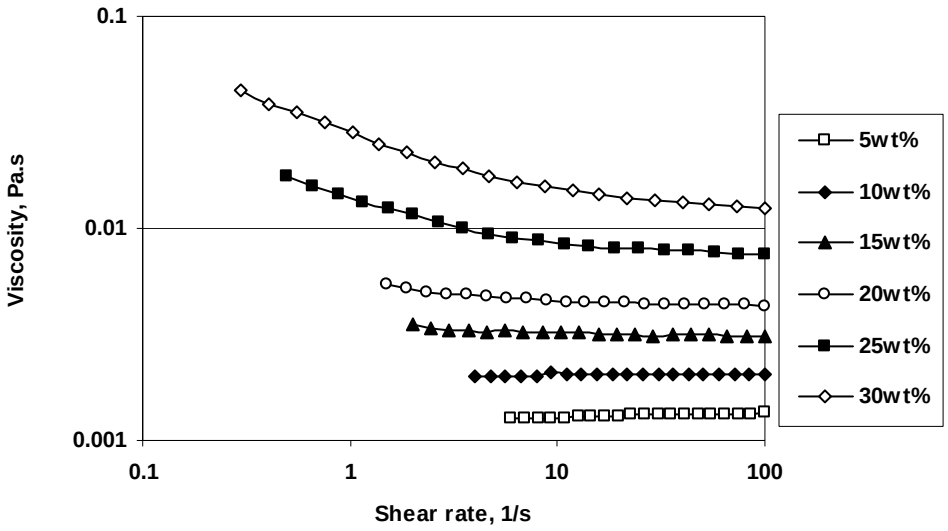
The hydrophobic property of the branched vinyl esters will also affect the contact angle of the polymeric film and this will be evaluated. The amount of ethylene incorporated into the BEEVA polymer can be more accurately determined using H^1 NMR.

5.2 Rheological Properties

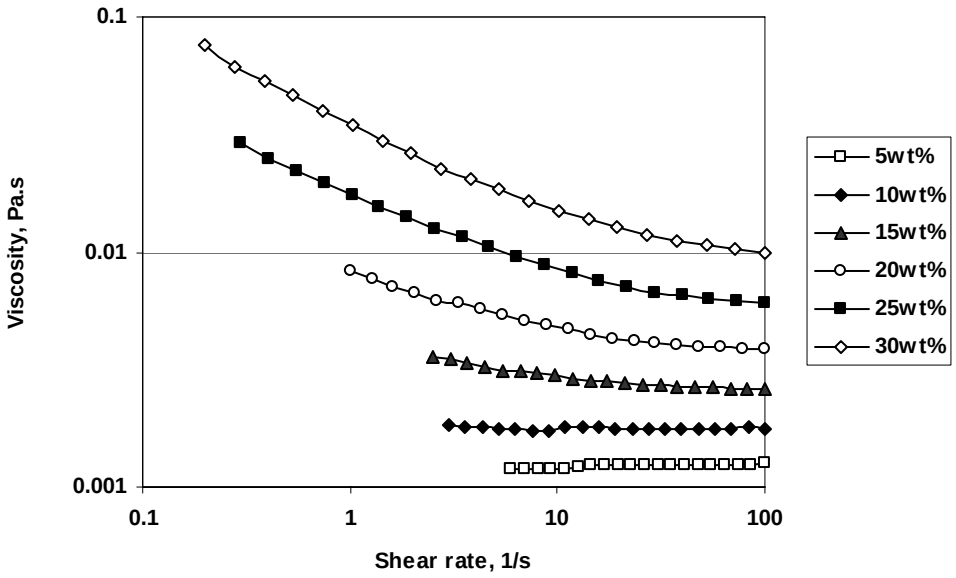
The study of rheological properties of these latexes has relevance in industrial processing behaviour of the polymers. The viscosity of a material can be significantly affected by variables such as shear rates [Barnes et al., 1989].

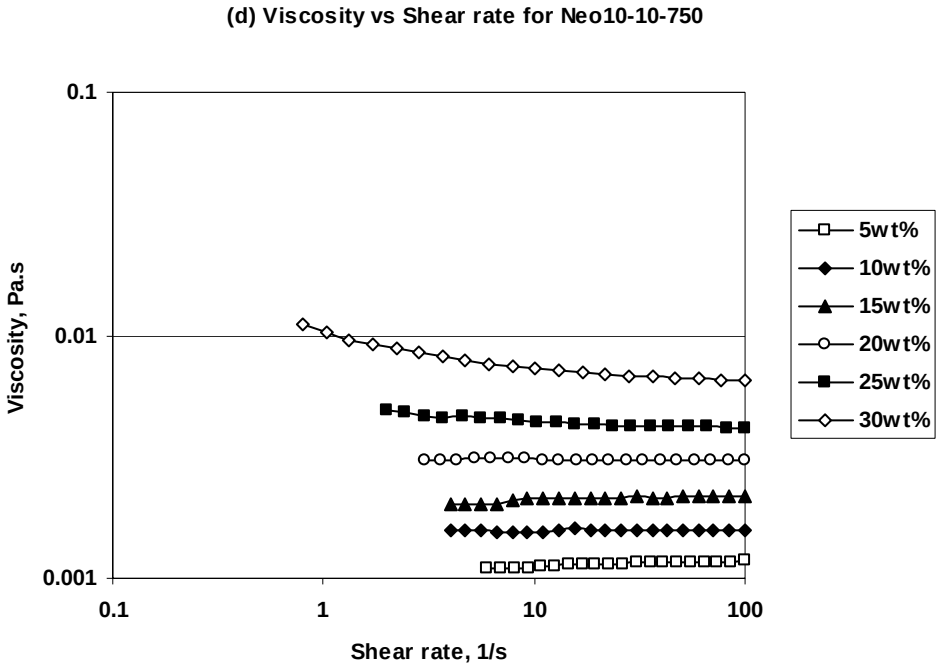


(b) Viscosity vs Shear rate for Neo10-10-500



(c) Viscosity vs Shear rate for Neo10-20-500





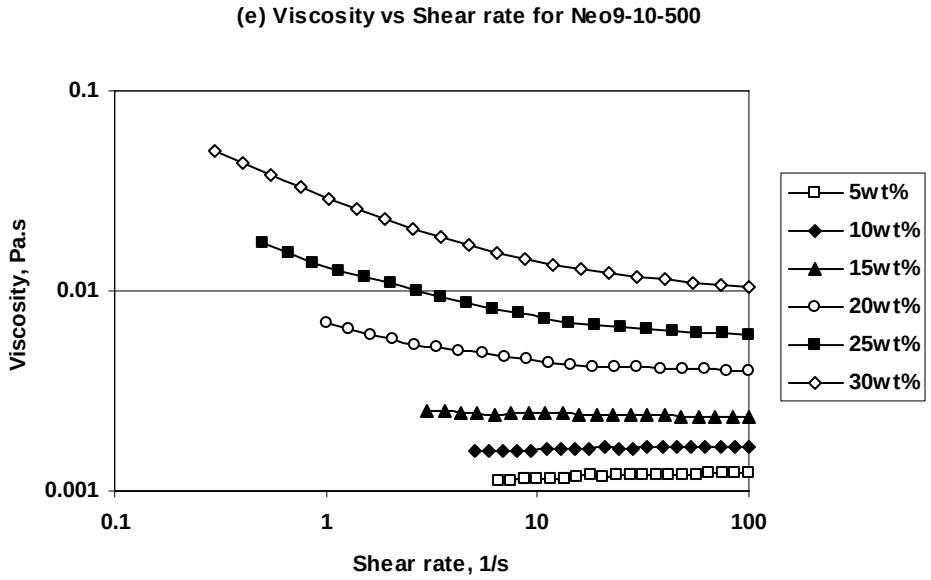


Figure 5.1 Shear viscosity versus shear rate of different polymer concentrations (wt%) of: : (a) Neo-0-500; (b) Neo10-10-500; (c) Neo10-20-500; (d) Neo10-10-750; and (e) Neo9-10-500.

Figures 5.1 (a) to 5.1 (e) show plots of shear viscosity versus shear rate at different concentration (wt%) of BEEVA polymer solutions. It can be observed that Neo-0-500 latex showed Newtonian flow behaviour at different concentrations. Neo-0-500 latex consisted of ethylene-vinyl acetate copolymer. For the ethylene-vinyl acetate-branched vinyl ester polymer solutions of Neo10-10-500, Neo10-20-500, Neo10-10-750 and Neo9-10-500, these exhibited Newtonian flow at low concentrations (5-15wt%) but at higher concentrations (20-30wt%), significant shear-thinning was observed. At higher concentrations, Neo10-10-500 gave the highest viscosity (refer to Figures 5.2 and 5.3).

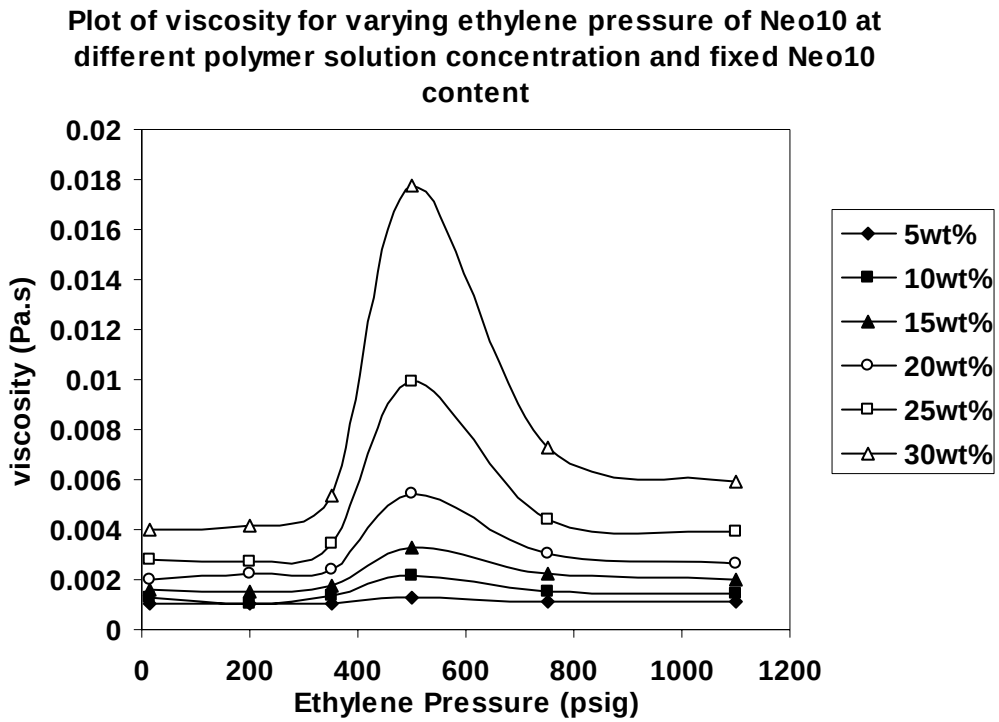


Figure 5.2 Plot of viscosity for varying ethylene pressure of Neo10 at different polymer solution concentration and fixed Neo10 content.

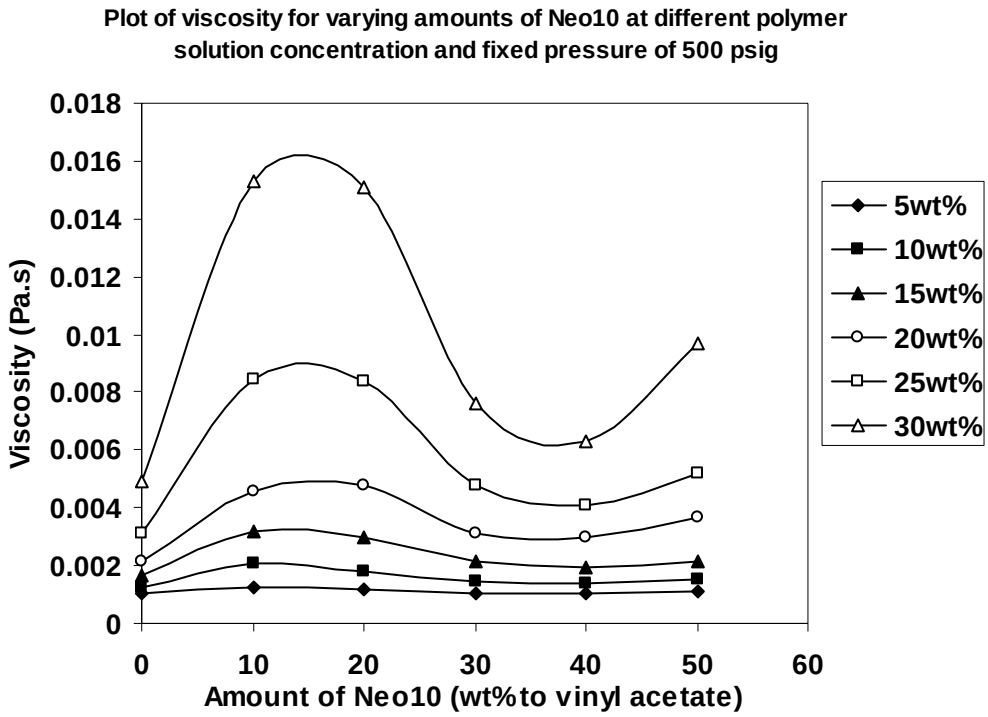


Figure 5.3 Plot of viscosity for varying amounts of Neo10 at different polymer solution concentration and fixed pressure of 500 psig.

Figure 5.2 showed that at ethylene pressure of 500 psig (or 3.4 MPa), the viscosity was the highest at fixed Neo10 amount of 10% by weight to vinyl acetate. It can also be observed that the amount of Neo10 between 10 to 20% (by wt% to vinyl acetate) gave the highest viscosity as shown in Figure 5.3. Higher degree of association from the hydrophobic groups on the particle surfaces could lead to higher viscosity.

As the polymer concentration increases, there is higher chance for flocculation of the polymer particles and greater particle-particle interactions, which will result in higher viscosity. As the shear rate increases, these clusters of flocculated particles will break into smaller clusters of flocculated particles which are responsible for the shear

thinning behaviour. Addition of branched vinyl esters into the polymer backbone provided more hydrophobicity to the polymer and some degree of association may have occurred leading to higher viscosity and more shear thinning at higher concentrations. The ability of the hydrophobic groups from the branched vinyl ester to associate intermolecularly can create a "crosslinked" supermolecule or a network. This is only possible at higher polymer concentration where there are greater particle-particle interactions. However, it is also worth noting that intramolecular associations between the hydrophobic groups that belong to the same polymer molecule, which do not contribute to the overall strength of the network, can also exist. These association junctions are dynamic through the continuous building and rupturing through Brownian process. The number density and functionality of the association junctions primarily determine the strength of the overall network, and hence, the rheological properties of the polymer solutions [Jenkins et al., 1991]. Neo10-10-500 polymer which has the highest viscosity, probably has high degree of association. This higher level of association could be due to significantly larger amount of hydrophobic endgroups extending out from the surface of the particles as compared to those embedded in the polymer particles.

There is insignificant difference in viscosity between the Neo monomer types as shown in Figure 5.4. The slight hydrophobicity differences between these Neo monomers did not significantly impact on the viscosity. However, at high polymer concentrations, there is a slight trend showing Neo11 monomer type having higher viscosity than Neo10 and Neo9. Neo11 monomer has higher amount of carbon atoms which can contribute to higher hydrophobicity and this can lead to some degree of

association between the hydrophobic groups on the particles giving rise to higher viscosity.

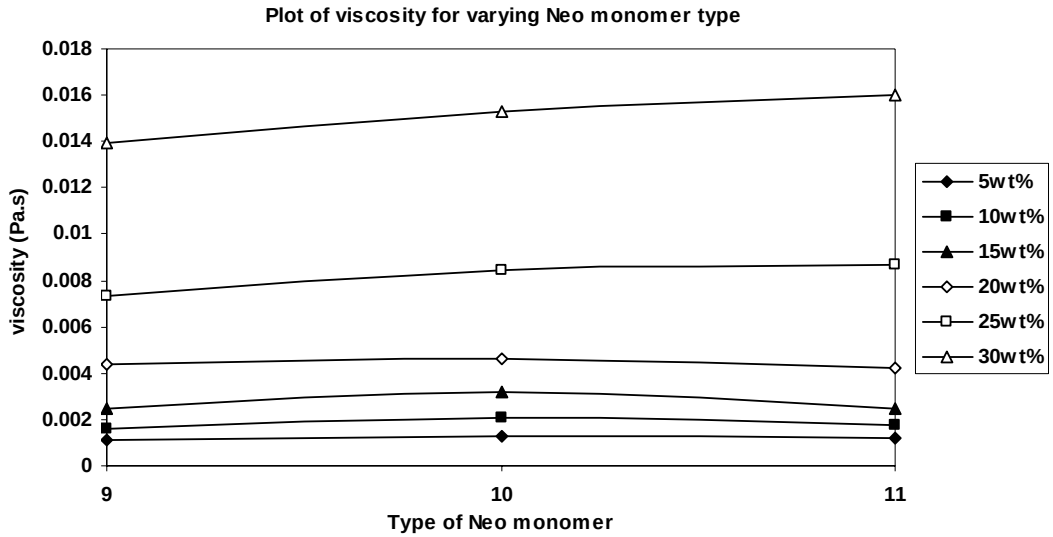


Figure 5.4 Plot of viscosity for varying Neo monomer type at different polymer solution concentration and fixed pressure of 500 psig.

5.3 Determination of ethylene weight percentage using H^1 NMR

One of the more accurate analysis of the amount of ethylene (wt%) incorporated into the BEEVA polymer is by using the high resolution proton nuclear magnetic resonance (NMR) spectrometer.

The proton peak of both CH groups (from branched vinyl ester and vinyl acetate) in the α position of the following copolymer structure appears at δ 4.9 ppm. (see Figure 5.5). The CH_2 proton peak from ethylene in the β positions appears at about δ 1.25ppm. Reference of polyethylene NMR similarly showed peak at 1.25ppm.

Branched vinyl ester and vinyl acetate copolymer (without ethylene) showed no peak at 1.25ppm (see Figure 5.6 (f)).

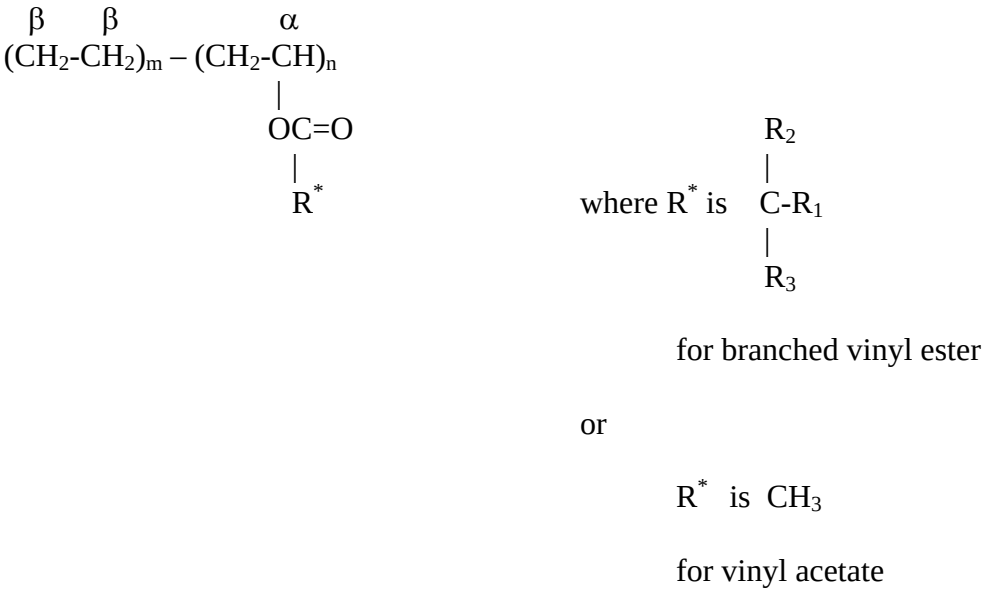


Figure 5.5 Location of protons for vinyl acetate and branched vinyl ester.

Another possible way of analyzing the spectra is to examine the range from δ ranging from 1.1 – 1.8 ppm for all of the CH_2 along the polymer backbone consisting of 4 protons from ethylene and 2 protons from both vinyl acetate and branched vinyl ester. However, using this calculation, the results are inconsistent and inaccurate while the calculation using 1.25ppm as ethylene proton peaks gave more reasonable data. Nevertheless, this can only provide estimates because of the structure of branched vinyl esters such as Neo 9 or Neo 10 having several isomers. Scholten et al mentioned of the five isomers of Neo 9 (Veova 9) [Scholten et al., 1991].

The isomers of Veova 9 and their respective T_gs are as shown in Figure 5.6.

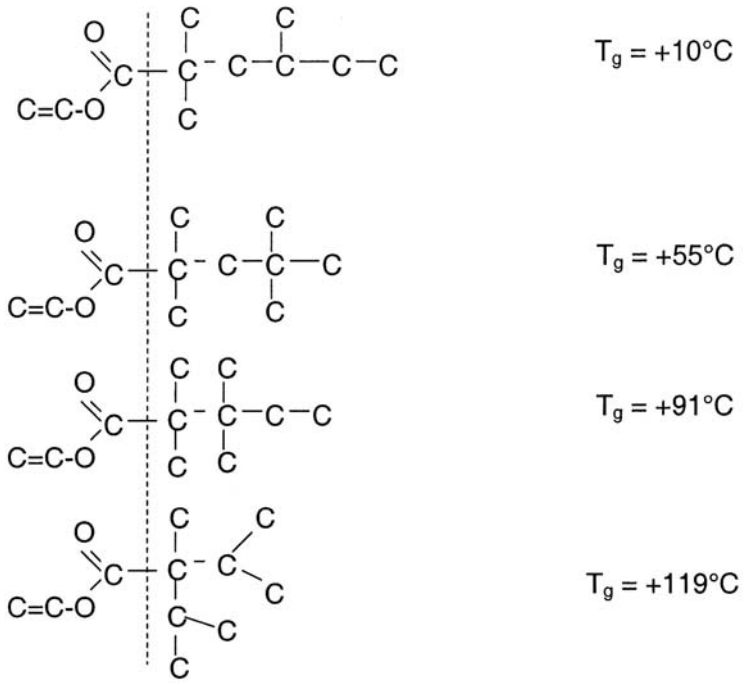


Figure 5.6 Isomers of Veova 9

We can calculate the ethylene wt.% in the BEEVA polymer as shown below:

Molar ratio of (Vinyl acetate + Neo monomer) to Ethylene

$$= \frac{\text{proton number at } \delta\ 4.9\text{ppm}}{(\text{proton number at } \delta\ 1.25\text{ ppm} / 4)}$$

Let Ethylene (wt%) = Ew

Therefore,

$$\frac{(Ew / 28)}{((1-Ew)/(\text{average M.W. of vinyl acetate + Neo copolymer}))}$$

$$= \frac{\text{molar fraction of ethylene (\%)}}{\text{molar fraction of vinyl acetate + Neo copolymer (\%)}}$$

The average molecular weight (M.W.) of the copolymers used for the calculation are as tabulated in Table 5.1.

Example of calculation for average M.W. of copolymer vinyl acetate / Neo 10 at 90/10 wt. % ratio:

100 / Ave. M.W. of copolymer = (90 / 86.09) + (10 / 198.31)

where M.W. of vinyl acetate is 86.09 and M.W. of Neo 10 is 198.31.

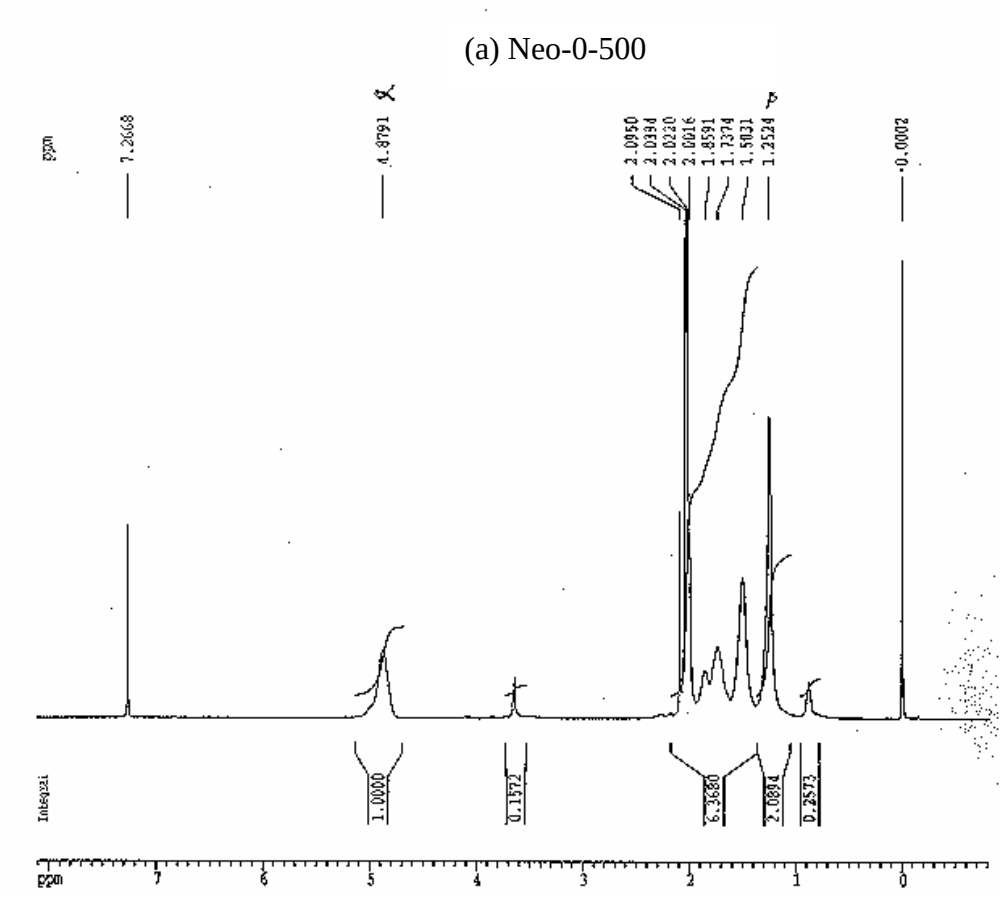
Copolymer ratio (by wt%)	**Average M.W.**
Vinyl acetate / Neo10 at 100 / 0	86.09
Vinyl acetate / Neo10 at 90 / 10	91.25
Vinyl acetate / Neo10 at 80 / 20	97.08

Vinyl acetate / Neo10 at 70 / 30	103.69
Vinyl acetate / Neo10 at 60 / 40	111.28
Vinyl acetate / Neo10 at 50 / 50	120.06
Vinyl acetate / Neo11 at 90 / 10	91.53
Vinyl acetate / Neo9 at 90 / 10	90.93
Ethylene	28

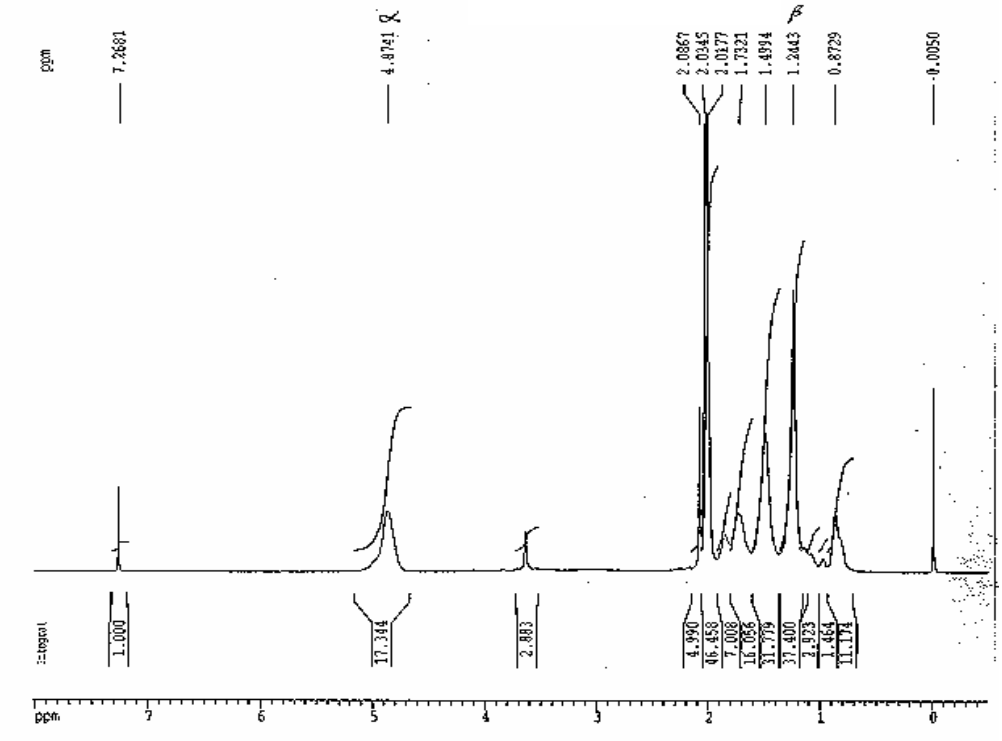
Table 5.1 The average M.W. of copolymers used in the NMR calculations

The proton NMR spectra are shown in Figure 5.6.

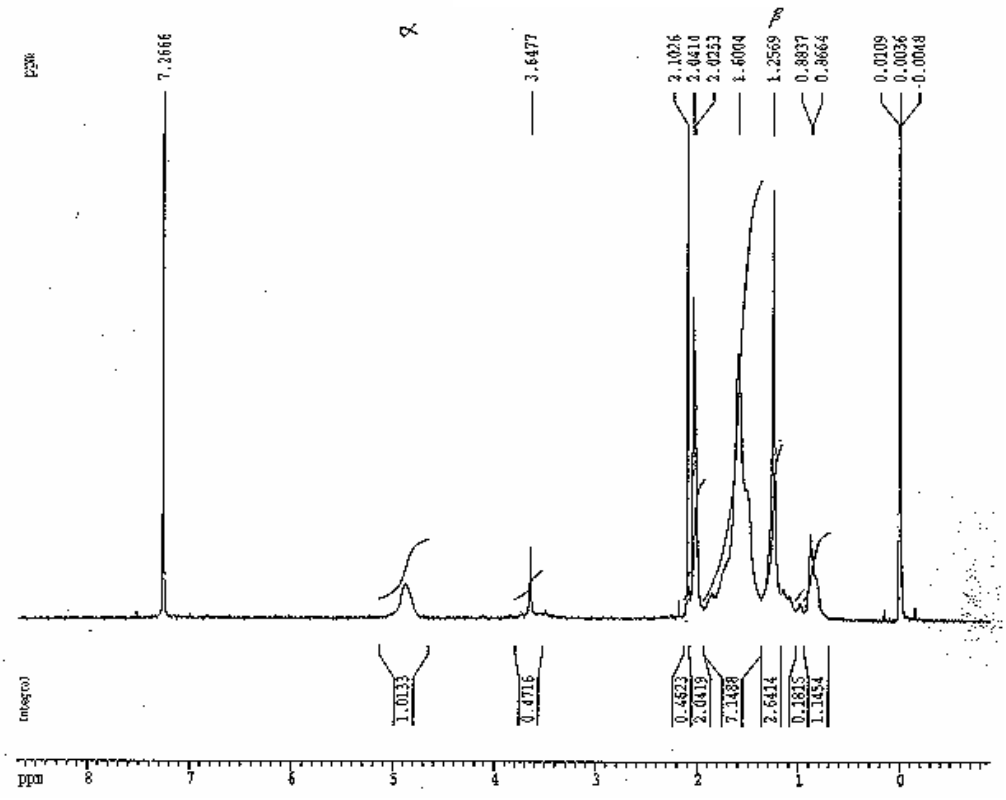
(a) Neo-0-500



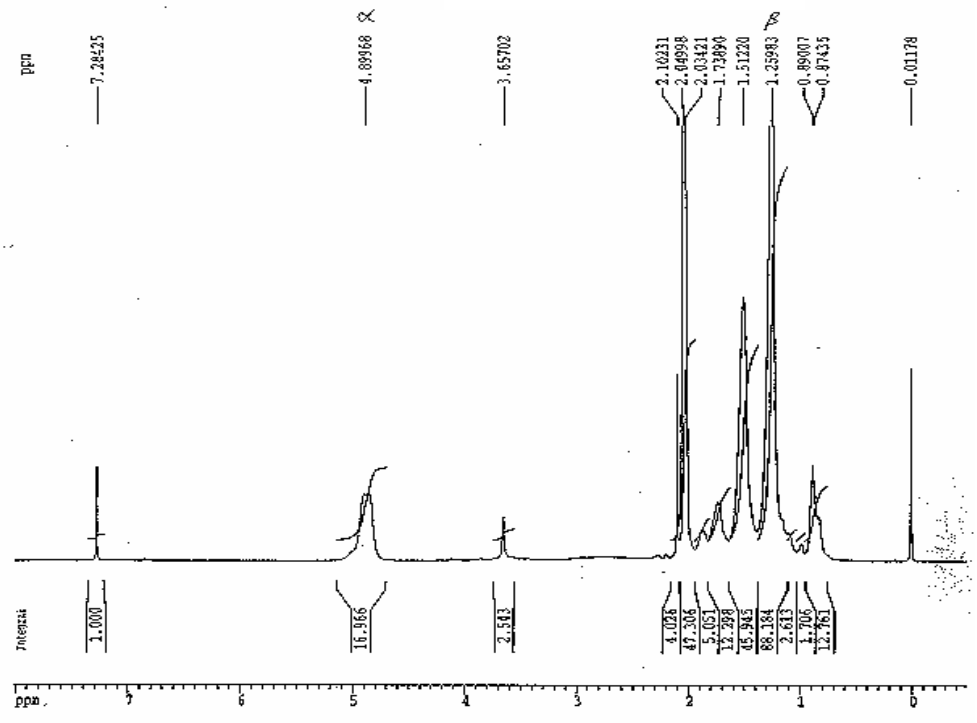
(b) Neo10-10-500



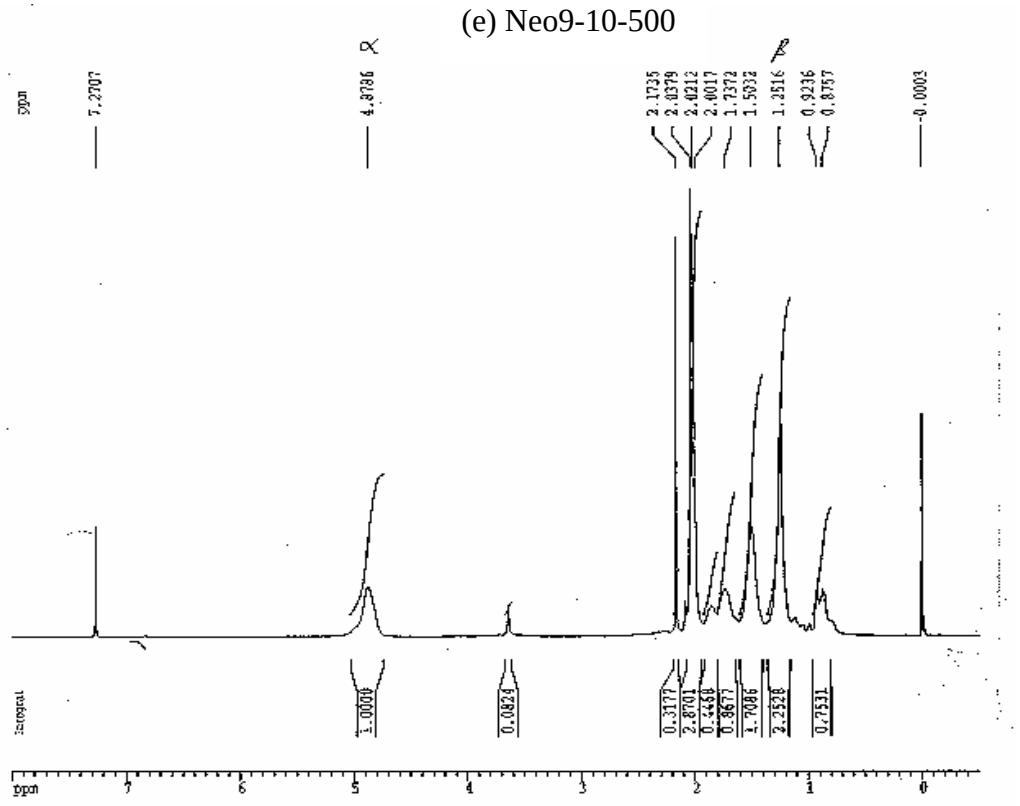
(c) Neo10-20-500



(d) Neo10-10-750



(e) Neo9-10-500



(f) Neo10-10-atm

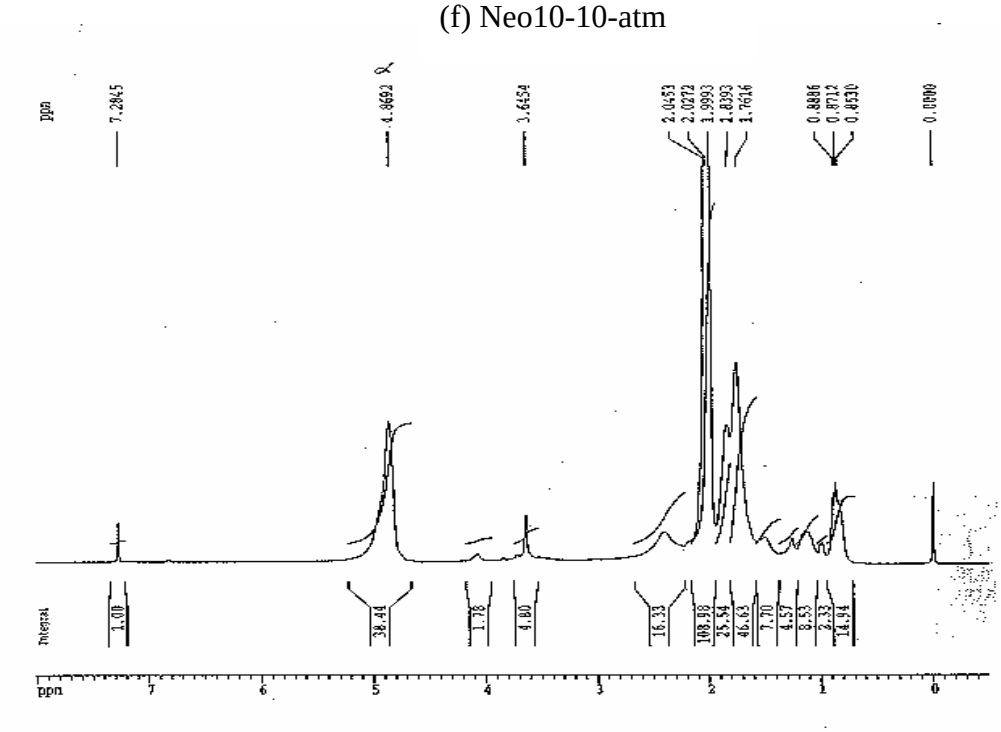


Figure 5.7 Proton NMR spectra of : (a) Neo-0-500; (b) Neo10-10-500; (c) Neo10-20-500; (d) Neo10-10-750; (e) Neo9-10-500 and (f) Neo10-10-atm.

The wt% of ethylene in the BEEVA polymers determined by NMR as in Table 5.2 showed relatively high amount of ethylene incorporation even at low pressure.

BEEVA polymer	Ethylene (wt%)
Neo-0-500	14.5
Neo10-10-500	14.2
Neo10-20-500	15.8
Neo10-30-500	19.8
Neo10-40-500	17.1
Neo10-50-500	16.3

Neo10-10-200	12.9
Neo10-10-350	10.4
Neo10-10-750	28.5
Neo10-10-1100	21.5
Neo9-10-500	14.8
Neo11-10-500	16.9

Table 5.2 Ethylene (wt.%) in the BEEVA polymers.

At very low pressure of 200 psig or 1.4 MPa, about 13 wt% of ethylene was incorporated which was quite significant. About 14-15 wt% of ethylene are incorporated in the BEEVA polymers at low pressure of 500 psig (3.4 MPa). At higher pressure of 750 psig (5.2 MPa), the amounts of ethylene incorporated increased significantly. Neo10-10-750 has about twice the amount of ethylene than Neo10-10-500. Figure 5.8 showed that the amount of ethylene incorporated into the BEEVA polymer beyond 750 psig or 5.2 MPa, did not increase any further. The ethylene incorporation was the highest at 750 psig or 5.2 MPa at fixed Neo10 amount. Low ethylene pressure from 200 – 500 psig gave quite similar ethylene amount at about 13-15 wt%.

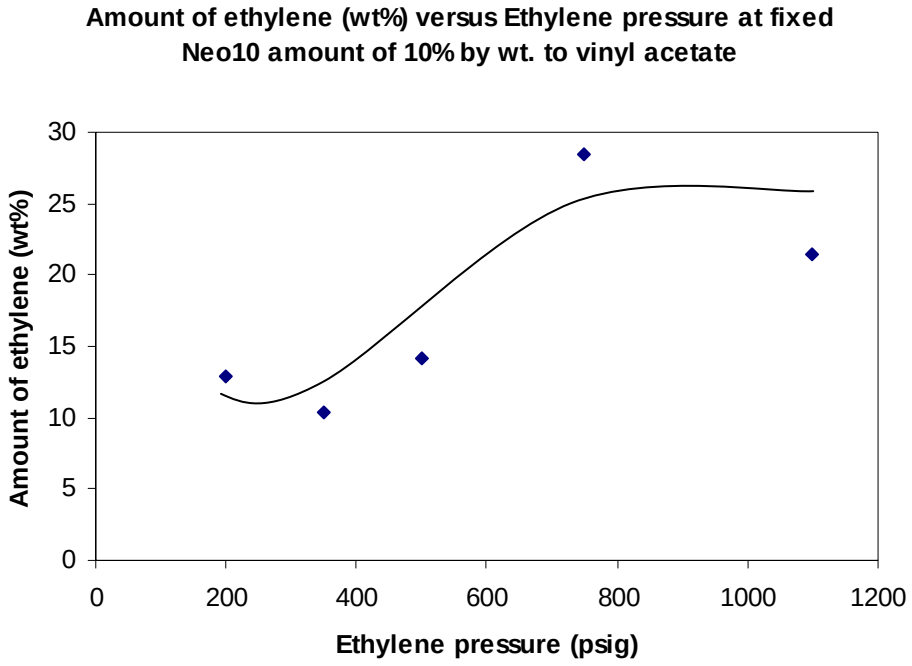


Figure 5.8 Amount of ethylene (wt%) versus ethylene pressure at fixed Neo10 amount of 10% by weight to vinyl acetate.

As higher amount of Neo monomer was used, the amount of ethylene incorporation increased slightly. Neo-0-500 (i.e., without Neo monomer) has 14.5 wt% of ethylene while Neo10-20-500 has 15.8wt% of ethylene. This could be due to the ability of the hydrophobic Neo monomer to facilitate the mass transfer of ethylene to the polymerization site. However, for Neo10 content greater than 30 wt% (to vinyl acetate) it did not show any further increase in ethylene incorporation as shown in Figure 5.9.

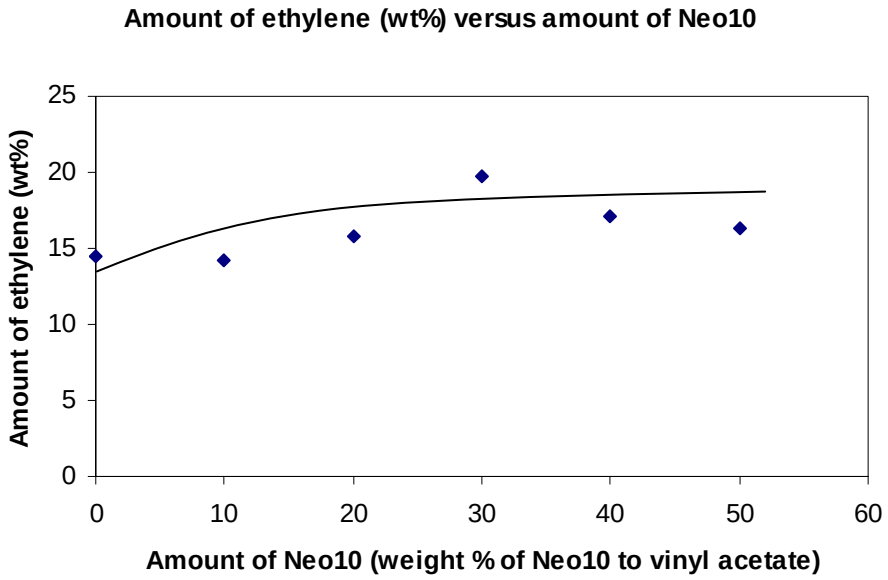


Figure 5.9 Amount of ethylene (wt%) versus amount of Neo10 at fixed pressure of 500 psig.

Neo9-10-500 has about the same amount of ethylene as Neo10-10-500 indicating that the different types of Neo monomers vis-à-vis Neo9 and Neo10 has little impact on ethylene incorporation. However, Neo11 monomer did show slight increase in amount of ethylene incorporated as shown in Figure 5.10.

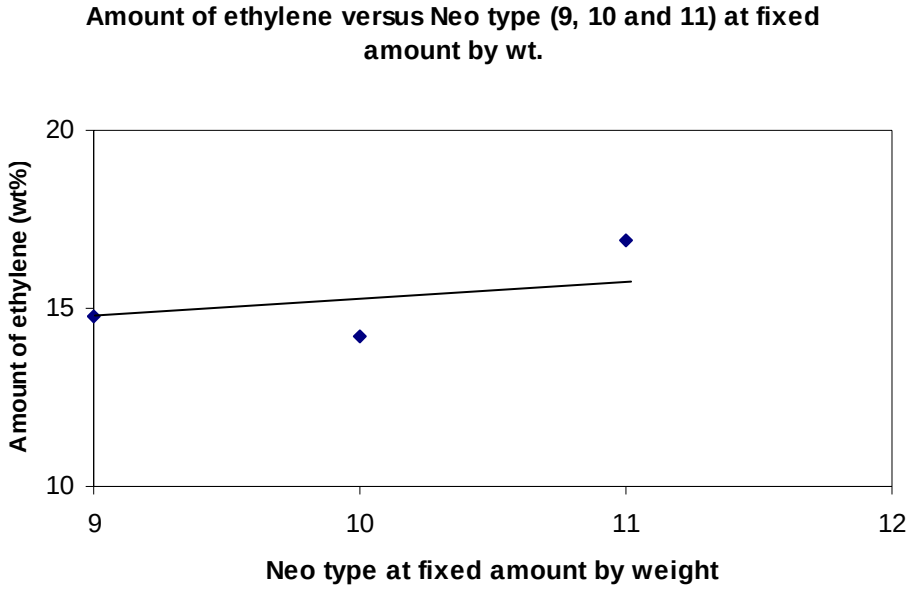


Figure 5.10 Amount of ethylene versus Neo type (9, 10 and 11) at fixed amount by weight and fixed ethylene pressure.

5.4 Glass transition temperature

Differential scanning calorimeter (DSC) was used to determine the glass transition temperature (T_g) of the BEEVA polymer. DSC is a thermal technique in which differences in heat flow into a substance and a reference are measured as a function of sample temperature while the two were subjected to a controlled temperature program. The glass transition temperatures of BEEVA polymers are tabulated in Table 5.3 while the DSC thermograms are shown in Figures 5.11 and 5.12.

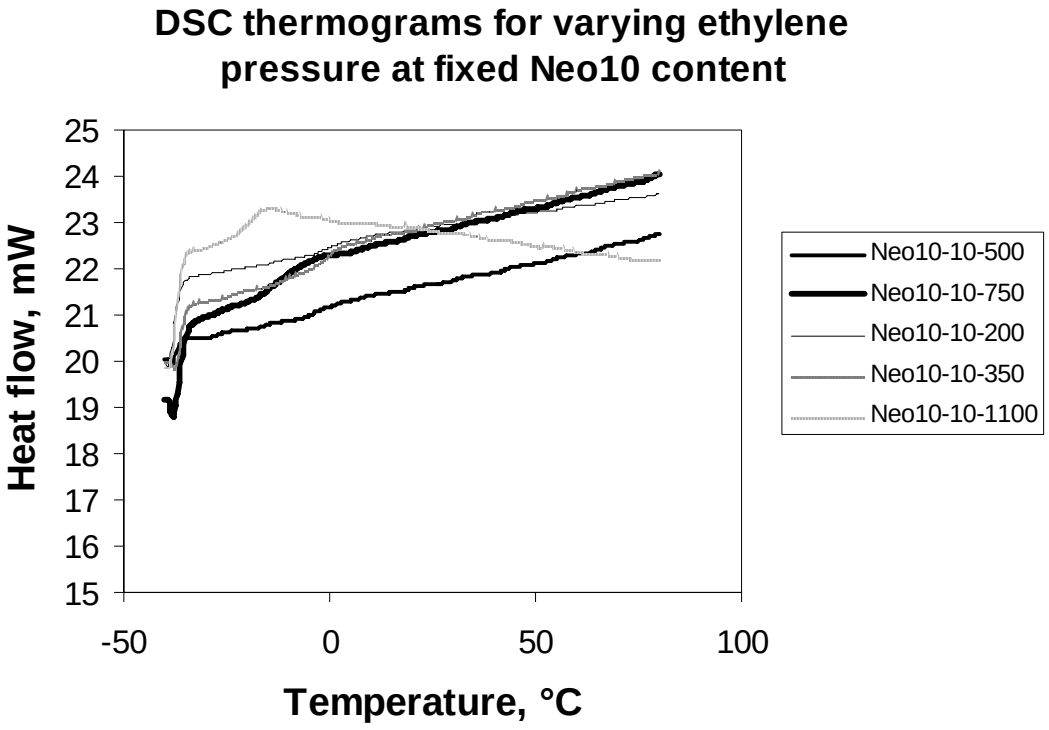


Figure 5.11 DSC thermograms for varying ethylene pressure at fixed Neo10 content.

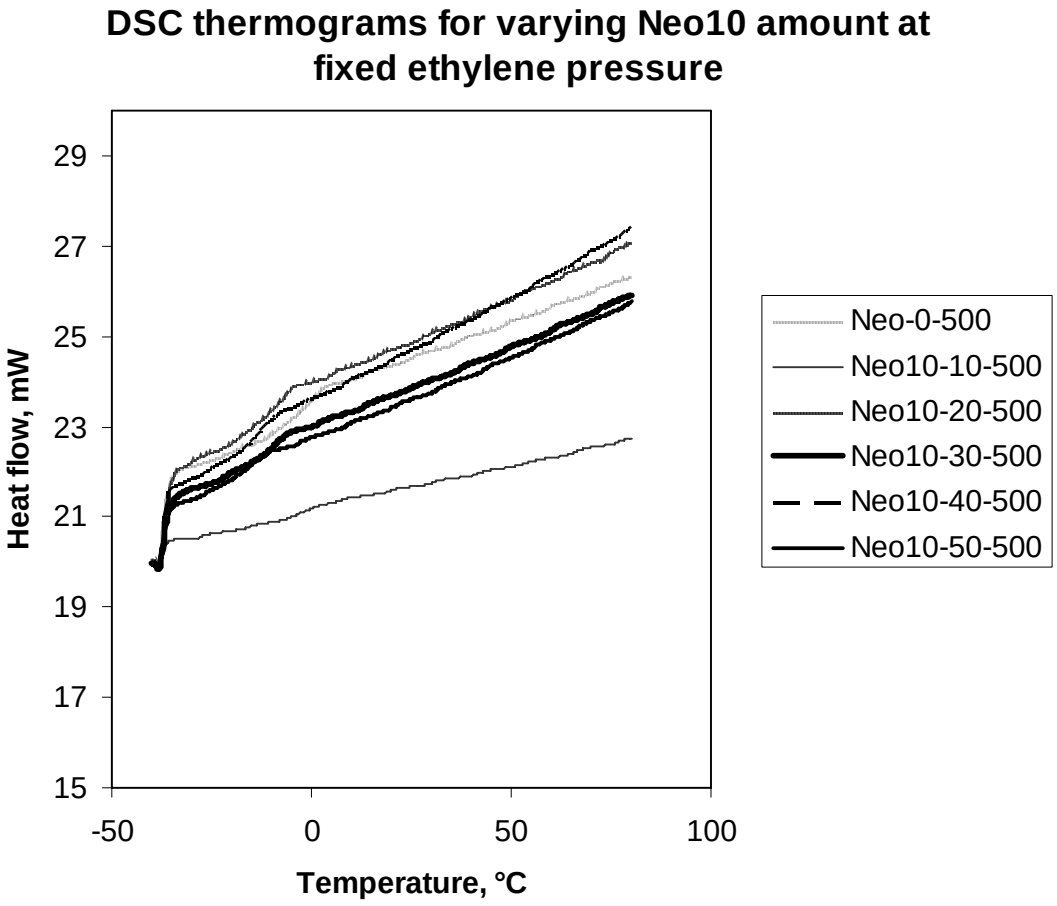


Figure 5.12 DSC thermograms for varying Neo10 amount at fixed ethylene pressure.

The T_g of Neo10-10-750 at -11.4°C was much lower than Neo10-10-500's T_g at -5.3°C. The T_g dropped significantly when the pressure was increased above 500 psig as shown in Figure 5.13. This showed that as the ethylene pressure was increased during the polymerization, the amount of ethylene incorporated into the polymer increased significantly, which contributed to a lower T_g. The T_g of polyethylene is the lowest at ca. -125°C. Increasing the ethylene pressure is a very effective method to enhance ethylene incorporation into the BEEVA polymer. As the ethylene content of the polymer was increased, a decrease in T_g was observed, illustrating the

plasticization effect of ethylene. The introduction of ethylene into polyvinyl acetate increases the separation of the acetate groups within the copolymer chain, thereby increasing the flexibility of the polymer chains, which accounts for the observed decrease in T_g [Scott et al., 1993].

BEEVA polymer	**T_g, °C (midpoint)**
Neo-0-500	-3.0
Neo10-10-500	-5.3
Neo10-20-500	-9.7
Neo10-30-500	-11.5
Neo10-40-500	-14.1
Neo10-50-500	-16.1
Neo10-10-200	-2.8
Neo10-10-350	-4.4
Neo10-10-750	-11.4
Neo10-10-1100	-28.0
Neo9-10-500	-2.4

Table 5.3 Glass transition temperature of BEEVA polymers.

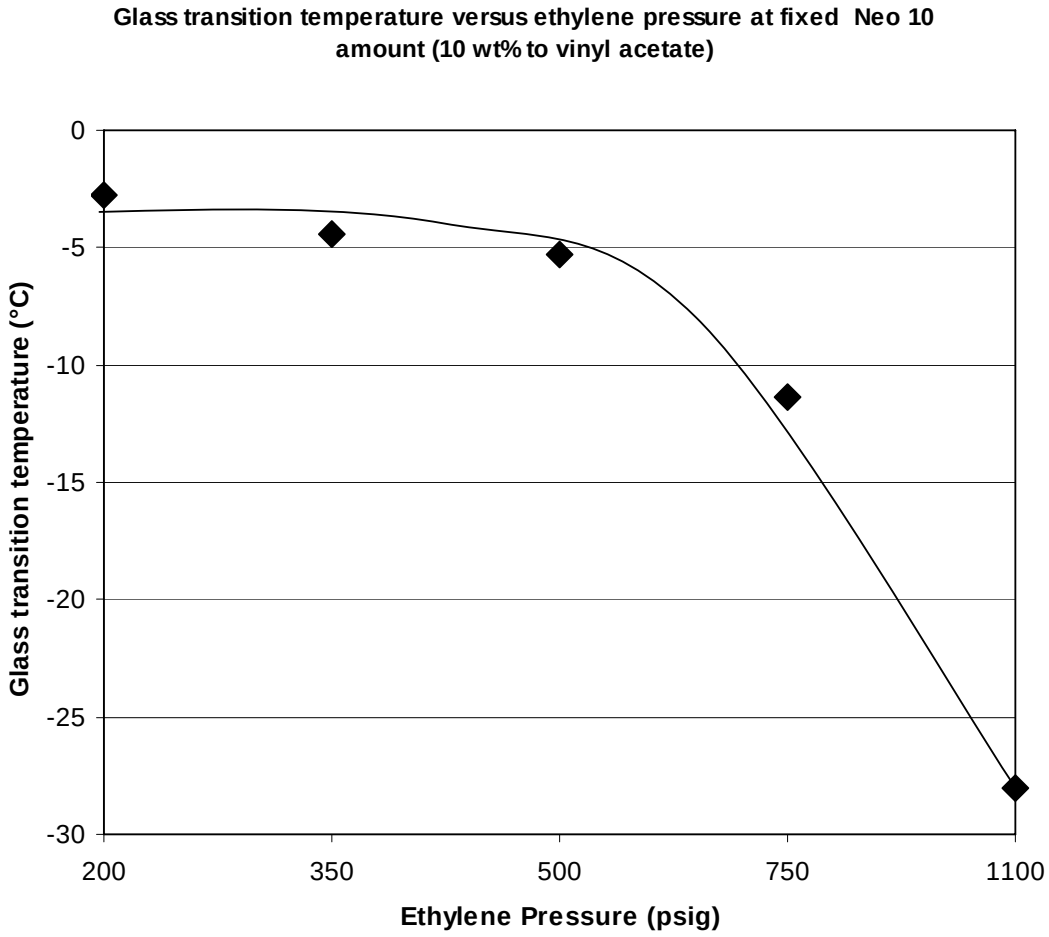


Figure 5.13 Glass transition temperatures versus ethylene pressure at fixed Neo10 amount (10 wt% to vinyl acetate).

The T_g of Neo-10-500 at -5.3 °C was slightly lower than that of Neo-0-500, which is at -3 °C. The amount of ethylene incorporated for both these polymers are quite similar as determined by NMR. Therefore, the slightly lower T_g of Neo-10-500 as compared to Neo-0-500 was due to the lower T_g of Neo10 monomer as compared to vinyl acetate (refer to Table 2.1). The T_g reduction with increasing Neo10 amount is linear as shown in Figure 5.14. There is a drop of about 3°C with each increase of 10 wt% of Neo10.

As the ethylene amounts in Neo9-10-500 and Neo10-10-500 were quite similar, the higher T_g of Neo9-10-500 at -2.4°C as compared to Neo10-10-500's T_g at -5.3°C was due to higher T_g of Neo9 monomer as compared to Neo10 monomer (refer to Table 2.2).

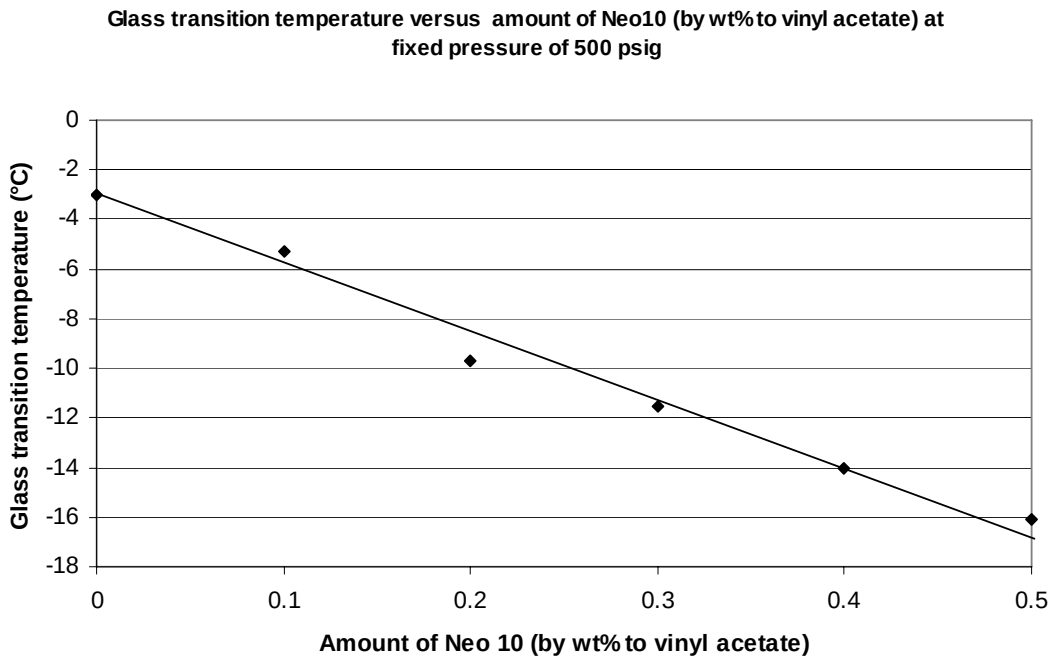


Figure 5.14 Glass transition temperatures versus amount of Neo10 (by wt% to vinyl acetate) at fixed pressure of 500 psig.

5.5 Contact angle

The contact angles of Neo10-10-500 and Neo10-20-500 are higher than Neo-0-500 which could be due to differences in hydrophobicity of the polymers as shown in Table 5.4.

The possibility of non-homogeneity of the distribution of the hydrophobic branched vinyl esters and ethylene on the polymer surface makes it difficult to relate hydrophobicity of the polymer to contact angle. The higher contact angle of Neo10-10-500 probably also suggests that there are considerably more hydrophobic component on the particle surface. This could also explain why Neo10-10-500 has the highest viscosity as mentioned in Section 5.2. The hydrophobic polymer chains on the surface of the Neo10-10-500 particles provided some degree of association leading to higher viscosity.

BEEVA polymer	Contact angle (mean)	Standard deviation
Neo-0-500	69.35	1.96
Neo10-10-500	75.97	0.73
Neo10-20-500	72.34	1.15
Neo10-30-500	73.79	0.48
Neo10-40-500	74.30	1.20
Neo10-50-500	72.26	1.46
Neo10-10-atm	22.26	1.59
Neo10-10-200	23.05	2.23
Neo10-10-350	71.43	0.84
Neo10-10-750	71.31	1.42
Neo10-10-1100	68.67	0.59
Neo11-10-500	49.11	3.92
Neo9-10-500	66.59	2.15

Table 5.4 Contact angle of BEEVA polymer

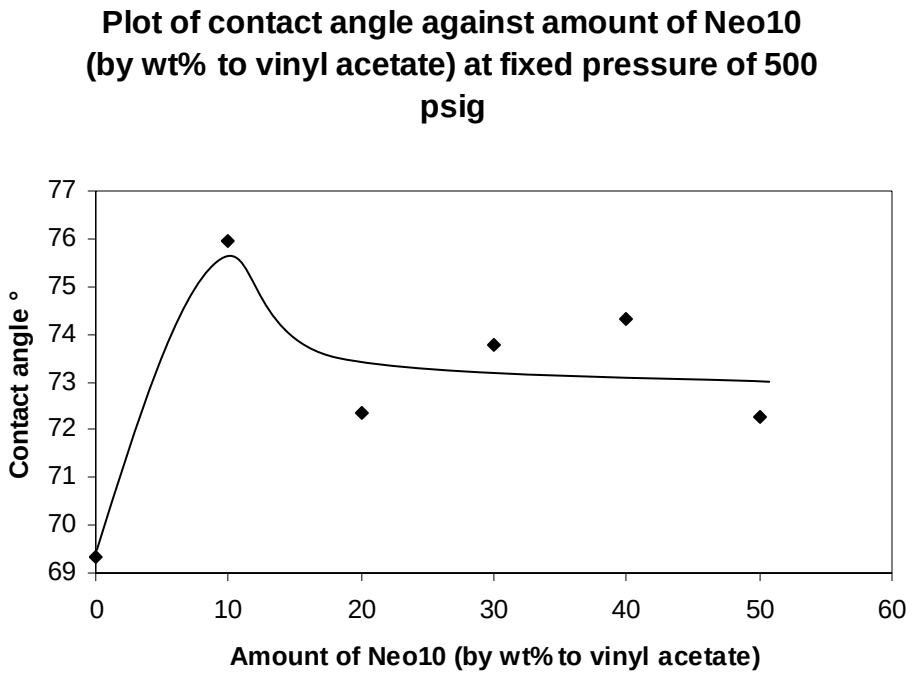


Figure 5.15 Plot of contact angle against amount of Neo10 (by wt% to vinyl acetate) at fixed pressure of 500 psig.

Figure 5.15 showed that 10% of Neo10 (by weight to vinyl acetate) gave the highest contact angle at fixed ethylene pressure of 500 psig or 3.4 MPa. Generally, the BEEVA polymers with high amount of Neo10 monomer had contact angles ranging from 72 to 76 degrees which were considerably higher than a vinyl acetate-ethylene copolymer (i.e., Neo-0-500) which had a contact angle of about 69 degree. This was due to increased hydrophobicity of the polymer as contributed by the branched vinyl ester (Neo10) monomer. The plot in Figure 5.16 showed that ethylene pressure of 500 psig or 3.4 MPa produced the highest contact angle at fixed Neo10 amount. Ethylene in the polymer contributed to the overall hydrophobicity which was reflected in the higher contact angle. The contact angle for Neo10-10-atm (i.e., without any ethylene)

was significantly lower as compared to the other BEEVA polymers. There was not much difference in contact angles between BEEVA polymers at high level of ethylene incorporation.

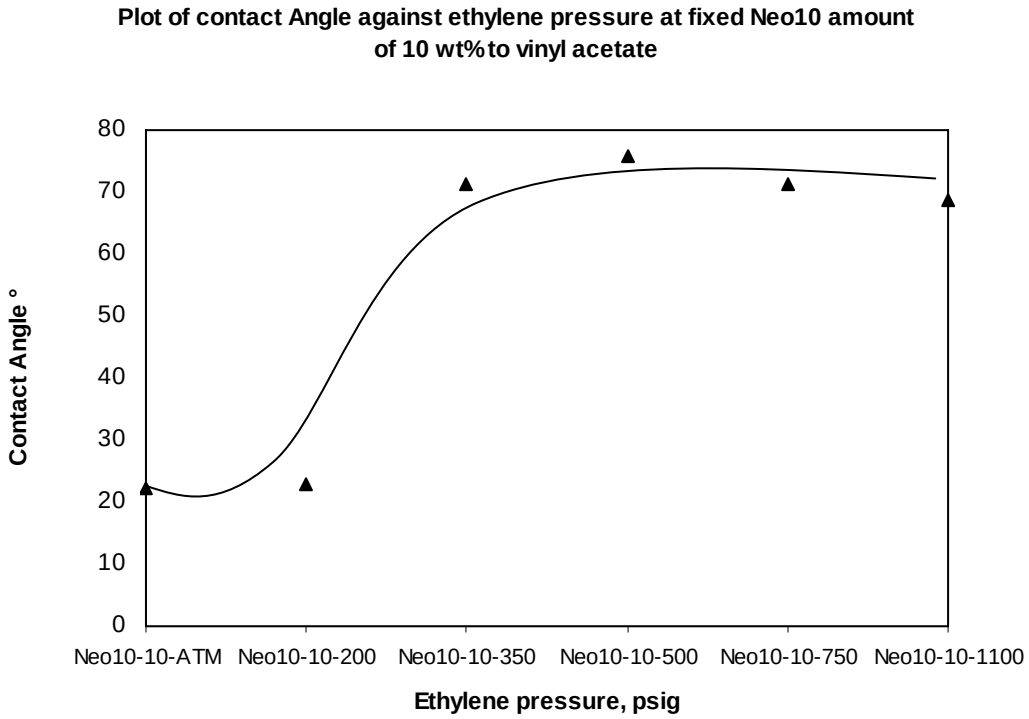


Figure 5.16 Plot of contact angle against ethylene pressure at fixed Neo10 amount of 10 wt% to vinyl acetate.

5.6 Zeta potential and particle size

Figure 5.17 showed that as pH was increased with the addition of sodium hydroxide (NaOH), the zeta potential for Neo10-10-500 increased more significantly than Neo10-10-atm latex.

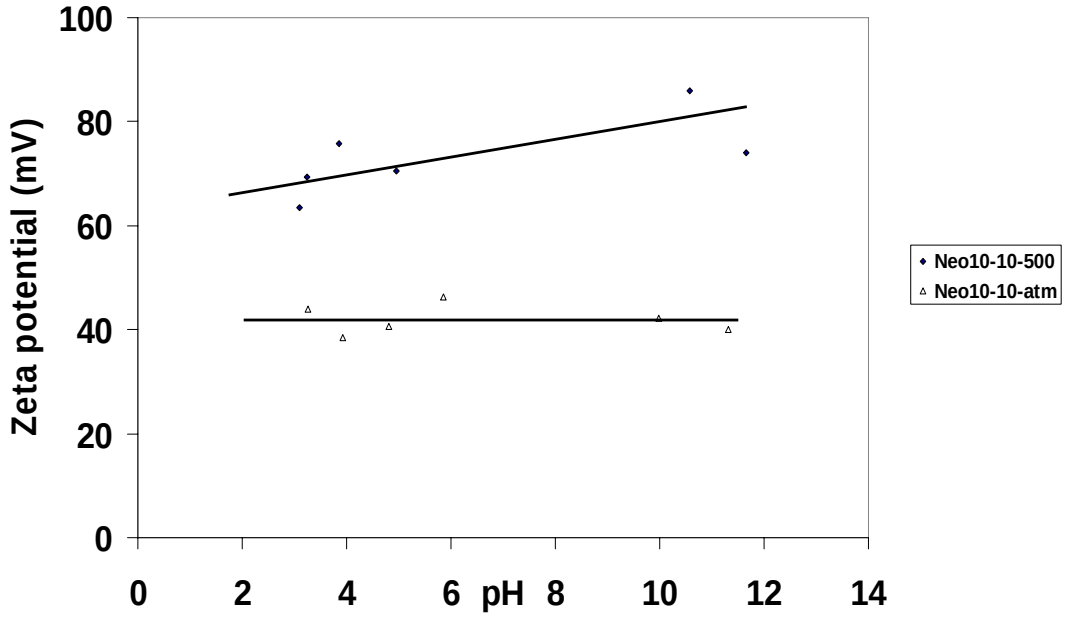


Figure 5.17 Zeta potential versus pH of Neo10-10-atm and Neo10-10-500.

BEEVA latexes were prepared using ammonium persulfate as initiator. When the surface sulphates in these latexes are high, the surface is hydrophilic and the zeta potential is predominantly a function of the degree of dissociation of the surface sulphates. However, the zeta potential is independent of the concentration of the surface sulphates when the concentration of these surface sulphates is relatively low [Ma et al, 1981]. Ma et al suggested that the controlling mechanism for the generation of surface potential in these cases is the tendency for the hydrophobic part of the surface, which represents a much greater fraction of the surface, to adsorb negative ions [Ma et al., 1981]. Therefore, it is probable that there are more hydrophobic groups on the particle surfaces of Neo10-10-500 as compared to Neo10-10-atm. These hydrophobic groups adsorbed hydroxyl ions from the addition of NaOH which related to higher zeta potential.

Neo10-10-atm and Neo10-10-500 latexes showed quite comparable particle diameters with a mean of 260 nm as shown in Figure 5.18. The particle size for these latexes did not change much with the addition of NaOH solution which indicated that there was no significant hydrolysis on these latexes.

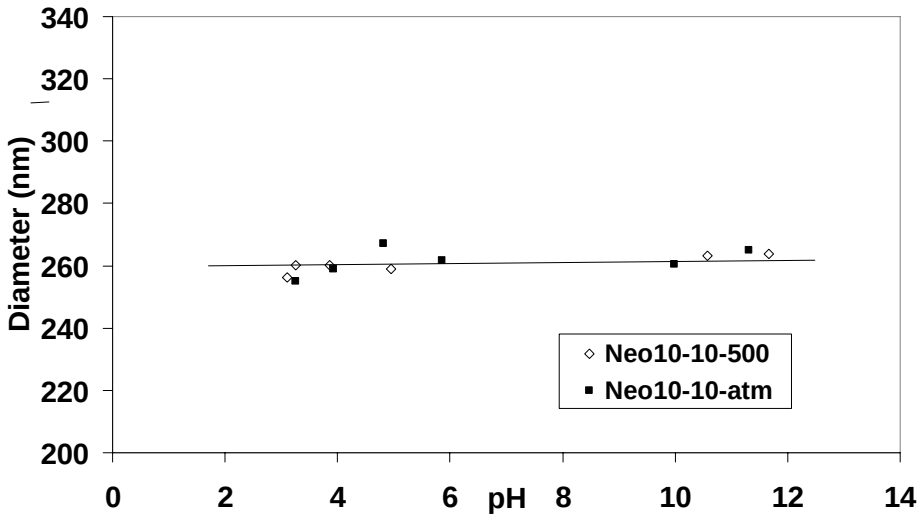


Figure 5.18 Particle diameter versus pH of Neo10-10-atm and Neo10-10-500

The trend of zeta potential with pH for varying Neo monomer types as shown in Figure 5.19 agrees with the results of contact angle. The zeta potential for Neo11-10-500 was the lowest while Neo10-10-500 had the highest zeta potential. Similarly, the contact angles for Neo11-10-500, Neo9-10-500 and Neo10-10-500 were 49, 66 and 72°, respectively (refer to Table 5.4). This difference was due Neo10-10-500 having more hydrophobic groups on the surface of the polymer particles as compared to Neo11-10-500.

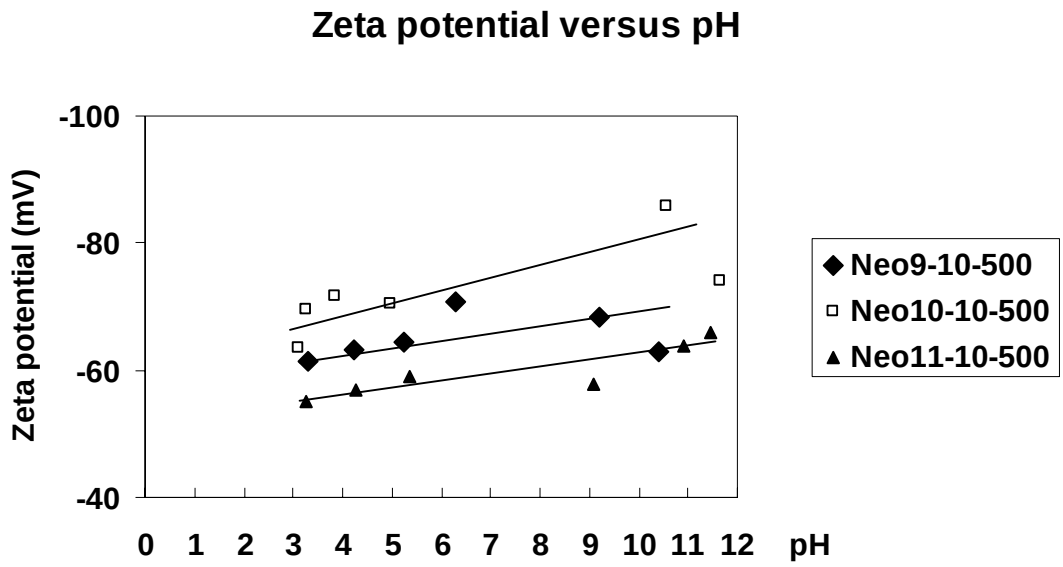


Figure 5.19 Zeta potential versus pH for varying Neo monomer types

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Three main areas of research have been described: (1) the design of a new pressure reactor system that is able to produce novel ethylene-vinyl acetate-branched vinyl ester emulsion polymers at varying pressures; (2) the preparation of model ethylene-vinyl acetate-branched vinyl ester (BEEVA) latexes; and (3) physical properties of these model latexes and their polymeric films by studying the rheological behaviour, glass transition temperature, contact angle, zeta potential and determination of ethylene composition by using proton NMR.

6.1.1 The design of a new pressure reactor system

The pressure reactor vessel was designed to have a maximum allowable working pressure of 1500 psig (10.3 MPa) since a typical ethylene-vinyl acetate emulsion copolymerization was higher than 1000 psig (6.9 MPa). The agitation speed at 600 rpm was sufficient to provide good mixing without too much foaming and coagulum formation. The radial or turbine impeller with hollow shaft and blow pipe provided good mixing of ethylene from headspace into the aqueous charge in the reactor. The turbine impeller gave low coagulum formation and good mixing at relatively high agitation rate of 600 rpm. High agitation with such impeller configuration enabled significant ethylene incorporation of about 14 wt% even at low pressure of 500 psig (3.4 MPa).

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

The Haskel gas booster pump was used successfully to increase the ethylene pressure in the intermediate 1 gallon ethylene tank to the desired ethylene operating pressure even though the 30 lbs ethylene tank was below the operating pressure. This enabled flexibility in running at higher operating pressure than the 30 lbs ethylene tank pressure and reduced wastage of residual ethylene gas in the tank.

The research motor valves provided good control of ethylene flow into the reactor by actuating both temperature and pressure conditions independently. When both of these conditions were satisfied, the valves were opened to allow the flow of ethylene from the intermediate ethylene tank to the reactor.

The temperature control was maintained effectively by controlling the jacket temperature of the reactor. The jacket was heated through hot water supplied from a temperature-controlled water bath and cooled by city water.

Effective safety devices were in place since this polymerization involved hazards such as handling highly flammable ethylene gas and working with high pressure reaction. These safety devices were walk-in hood installed with air flow detector and alarm system to house the pressure reactor system, rupture disc with safe shutdown when pressure exceeded MAWP of 1350 psig (9.3 MPa), flammable gas detector with alarm system and a safe effluent handling system in the event of an uncontrollable reaction.

6.1.2 The preparation of model ethylene-vinyl acetate-branched vinyl ester (BEEVA) latexes

Three series of model BEEVA latexes were synthesized varying in ethylene pressure, Neo-10 monomer amount, and Neo monomer type. All latexes produced were clean with negligible amount of coagulum in the reactor. No protective colloid was used but instead only anionic and non-ionic surfactants, which provided excellent mechanical stability during polymerization. Redox initiation system was effective to provide sufficient free radicals for emulsion polymerization of ethylene-vinyl acetate-branched vinyl ester and residual monomer levels were kept below 1000 ppm for the finished products.

Ethylene uptake during polymerization was noticed even at low ethylene pressure of 500 psig (3.4 MPa) while medium ethylene pressure of 750 psig (5.2 MPa) had significantly higher ethylene uptake rate.

6.1.3 The physical properties of model BEEVA latexes

The amount of ethylene in the BEEVA polymer as determined by proton NMR showed that there was about 14-15 wt% ethylene when low ethylene pressure of 500 psig (3.4 MPa) was used. The amount of ethylene doubled to 28.5 wt% when medium ethylene pressure of 750 psig (5.2 MPa) was used. The amount of ethylene incorporation increased slightly when the amount of Neo-10 monomer was increased, which probably suggested the role the hydrophobic Neo monomer played in helping the mass transfer of ethylene into the polymerization site. A more accurate determination of ethylene in a BEEVA latex using proton NMR was difficult because Neo monomers have many isomers.

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Rheological study of these latexes showed that these latexes except Neo-0-500 (without Neo monomer) exhibited Newtonian flow at low concentrations (5-15 wt%) but at higher concentrations (20-30 wt%), significant shear-thinning was observed. Neo10-10-500 (i.e., at ethylene pressure of 500 psig and Neo 10 / vinyl acetate weight ratio of 10/90) had the highest relative viscosity. One possible reason was the flocculation of the polymer particles or higher degree of particle-particle interactions which resulted in a higher viscosity.

Ethylene contributed significantly to the lowering of glass transition temperature (T_g). The T_g of Neo10-10-750 (i.e., ethylene pressure of 750 psig) was the lowest at -11.4°C. The T_g of Neo 9 monomer was slightly higher than Neo 10 monomer.

The contact angle measurement of the polymeric BEEVA films gave a convenient indirect method to estimate surface energy of films and therefore, a qualitative assessment of the hydrophobicity of the polymeric films. Contact angles of BEEVA films containing hydrophobic branched vinyl esters (Neo monomer) were higher than ethylene-vinyl acetate latex without any Neo monomer (i.e., Neo-0-500).

The particle size measurements showed that the average particle size for Neo10-10-500 and Neo10-10-atm were 260 nm. Zeta potential measurements showed that Neo10-10-500 latex had higher zeta potential than Neo10-10-atm with addition of NaOH. This was probably due to adsorption of hydroxyl ions on the hydrophobic groups on the particle surfaces. This may suggest that Neo10-10-500 had higher amount of hydrophobic groups (mainly from branched vinyl ester) on its particle

surface. Association between these hydrophobic groups can also contribute to higher relative viscosity for Neo10-10-500. It is not clearly understood why Neo10-10-500 should have more hydrophobic groups on its particle surfaces than Neo10-10-atm. Though, we know that Neo 10-10-500 has ethylene incorporated which is relatively hydrophobic as compared to Neo10-10-atm.

6.2 Recommendations

As a consequence of this research, future studies of the following areas are recommended.

Research work involving a more detailed study on the physical properties of these polymers. By studying the physical properties of these model latexes, we can understand the optimum operating conditions to achieve desired properties such as water resistance, viscosity, film softness or tackiness, etc.

Since the Neo monomers have several isomers making ethylene determination less accurate using proton NMR, an identification study of the isomers of Neo monomer will be useful.

It is also not clearly known why certain BEEVA latex such as Neo10-10-500 possessed a high viscosity and contact angle. These could be due to the distribution of the hydrophobic Neo molecules on the polymer chain. These hydrophobic groups are possibly more concentrated on the surface of the polymer particles. Microscopic and surface analysis studies will help to better explain some of these observations. If the branched vinyl ester, ethylene and vinyl acetate polymers could be differentially

stained, then transmission electron microscopy could be utilized. Atomic force microscopy (AFM) can be used to study the surface morphology of the BEEVA polymeric film to understand the distribution of hydrophobic branched vinyl ester in the polymer.

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APPENDIX STANDARD OPERATING PROCEDURES

A. Standard Operating Procedures

Operating Procedure - Preparatory steps for ethylene polymerizations

We would need to ensure that the pressure of the nitrogen supply is sufficient (higher than the desired pressure during ethylene polymerization) for the pressure test. For safety purpose, we display the signal hazard placard for ethylene on the walk-in hood door to indicate ethylene polymerization is in progress.

Emergency Actions

Emergency Reactor Shutdown Procedure

- Immediately stop all feeds. Turn cooling water on (the overtemp city water).
- Activate the evacuation alarm, if in the judgment of the operator the situation is out of control, evacuation of the laboratory should proceed.

Response to an Evacuation or Fire Alarm

- Immediately shut down all feeds. Turn on cooling water and follow evacuation procedures of the laboratory / building.

Pressure Polymerization Procedures

A.1 Ethylene Transfer System

Ethylene Transfer Procedure from Source to Ethylene Feed Tank

(Refer to Figure 4.6)

- Leather protective gloves for frost protection and safety glass were worn.
- Valve from intermediate tank to motor valves was closed when doing ethylene liquid transfer.
- We then opened the valves at 30 lbs cylinder tank, both the 3-way valves (direction toward the line in use) and the valve to the intermediate cylinder.
- The pressure in the feed tank would equilibrate to slightly below the pressure of the source ethylene cylinder.

We used the Haskel booster pump since the source tank may have lower pressure than the required pressure to increase the pressure of the feed tank up to below 1500 psig or 10.3 MPa (the relief valve on the feed tank is set at 1750 psig or 12 MPa). When operating the Haskel booster pump, we opened the control knob of the pump to start the transfer to a higher pressure. The bigger the opening of the knob, the faster the transfer. [Note: DO NOT EXCEED 1500 psig!] After the transfer, we closed all valves (at 30 lbs cylinder tank, both 3-way valves, valve to the intermediate cylinder and the valve from the intermediate cylinder to the motor valves.

Connection of Ethylene Feed Tank to 5-gal. Reactor

(Refer to Figure 4.8)

The balance was zeroed before the start of feeding the ethylene. Valves #3 and #4 were closed. We used the by-pass valve #9 for faster charging of ethylene into the reactor to fill the reactor with ethylene to the desired pressure. To do so, valves #3 and #10 should be closed while valves #4, #8 and #9 should be opened. We would need to

carefully control valve #9 so as not to overfill the reactor to a pressure higher than what's desired.

Ethylene gas goes through both the motor valves and the by-pass into the reactor. When the pressure is near the desired pressure, valve #9 was closed to allow ethylene to go through the motor valves only. We need to work the motor valves (by opening and shutting the valves) if there were vapor lock which block the ethylene from going through the orifice of the valves.

A.2 Pressure Test

Operating Procedure - Leak Test Procedure or Pressure Testing Procedure

The pressure test was usually employed after the cleaning or re-assembling of a disassembled reactor. The procedure determines the location and rate of any leak in the system. Without this knowledge, the experimental results are questionable since the material balance on a gaseous component will not be satisfied. The importance of the pressure test cannot be overemphasized.

- We filled the reactor with 4 gallons water.
- We made sure that the drain valve was closed and that the vent valve was open. After the water addition was completed, we shut all valves.
- We slowly pressurized the reactor to the desired pressure during the ethylene polymerization plus 20% using nitrogen. A pressure 20% higher than that desired for the ethylene polymerization.
- We closed all valves to isolate the reactor from the nitrogen source. Then, we monitored the pressure. The pressure loss should not be greater than 3 psig per

30 minutes at constant temperature. Leak detectors (“Snoop”) was used to check reactor and fittings for gas leaks, and made repairs as needed.

- If a leak was detected in the head O-ring area, we would tighten the flange nuts. If the leak persisted, we would need to depressurize and replace the O-ring. If the leak was found in the tubing, we would depressurize and tighten the tubing, repressurize the system, and re-test. Another possible place where leaks could occur is at the packing glands of the research motor valves.
- When the pressure loss was less than 1 psig in 30 minutes at constant temperature and without agitation, we depressurized the reactor by slowly opening the vent valve. When the reactor pressure instrument showed 0 or 1 psig as the internal reactor pressure, we slowly opened the reactor drain valve to remove all water from the reactor.

Note: Maximum allowable pressure is 1350 psig for this test using nitrogen.

A.3. Preparation of monomers

Operating procedure - Preparation of monomers charge

(Refer to Figure 4.9)

The stock monomer tank was placed on the balance, and the transfer line was then attached to the 4-gal. monomer feed tank. With the valve to the transfer line shut, the vacuum line valve was slowly opened and until the reading on the pressure gauge drops to the minimum point.

The vacuum valve was then shut while the valve of the transfer line was kept opened until the monomer had completely filled the entire line. The valve was then shut and the balance was zeroed. We may continue to open the transfer line valve to let the monomer into the feed tank to the desired amount before shutting the valve.

Once the amount of monomer was correctly transferred into the feed tank, the transfer line valve was shut and the transfer line removed. The monomer in the transfer line would flow back into the stock monomer tank, hence, the transfer line was washed with acetone.

A.4 Ethylene-based Pressure Polymerization

Operating Procedure - Purging the 5-gal. Reactor

- The reactor must be purged with nitrogen to remove oxygen from the system, which may otherwise inhibit the reaction.
- After the initial aqueous reactor charge has been added to the reactor, all valves were shut. This aqueous charge would need to cover the bottom blades of the agitator. (Minimum amount of initial water is approx. 1650g for ethylene polymerizations).
- Vent-off line on top of the reactor was opened and nitrogen was added to the reactor for 5 minutes via the nitrogen line located directly above the reactor top assembly. The nitrogen purging was to lower oxygen content in the vapor space.

- A vacuum was pulled in the reactor to -9 to -10 psig by using the vacuum pump. Then, the vacuum was broken by using about 25g of ethylene (or 4-5 volumes of ethylene based on the reactor vapor space) which brought the pressure to about 10 psig to ensure ethylene-rich system.
- All valves were closed and held for 5 mins before venting the reactor.

Operating Procedure - Monomer Charge

After purging the reactor, we ensured that the reactor temperature had reached the desired set point temperature. The temperature of the reactor should be 3°C below the initial reaction temperature if ethylene was part of the initial monomer charge, or ethylene was to be charged before delayed feed start. (The addition of ethylene had a tendency to increase the temperature of the system)

1. Monomer Mix Charge

The initial monomer mix was added before the ethylene charge. The reactor monomer valve was opened, the monomer tank scale was zeroed and the monomer pump was started. When the desired initial monomer amount had been added, the reactor monomer valve and monomer pump were turned off, where the monomer pump and tubing were inspected for leaks.

2. Ethylene

The ethylene balance was zeroed. The ethylene valve to the reactor and the valve on the ethylene feed tank were opened. The two research motor valves on the ethylene feed line were opened to allow ethylene feed to the reactor if both the temperature and

the pressure set points were satisfied. Therefore, proper adjustments of the temperature and pressure set points were required before ethylene could be charged to the reactor. When the appropriate amount of ethylene had been charged to the reactor, the ethylene feed tank valve and the ethylene valve to the reactor were closed. When no ethylene was to be charged during the delayed feeds portion of the run, the ethylene feed tank valves were closed. The reactor head O-ring, tubings, research motor valves, ethylene cylinder etc. were checked for leaks using soap solution "Snoop".

[Note: This is an additional check since the reactor must have been previously been pressure tested and passed the pressure test.]

Due to solubilization of ethylene in the aqueous charge, there would be some drop in the pressure of the reactor. A period of about 15 minutes was allocated for solubilization of ethylene. If the pressure dropped by more than 5 psig, the ethylene valve to reactor was opened and the pressure was allowed to rise back to the desired level. Then the valve was then closed, and this procedure was repeated until the reaction mixture was saturated with ethylene monomer.

Operating Procedure - Starting the Reaction

The use of a gaseous monomer and/or redox catalyst system required special starting procedure. Before commencement of this procedure, it was expected that all initial reactor charging procedure had been successfully completed.

- When the temperature of the system had equilibrated 3°C below the desired reaction temperature, the reactor catalyst valves were opened and the catalyst pump was started.
- The reaction exotherm was monitored and the reaction temperature was allowed to decrease to the desired polymerization temperature before proceeding to the delayed feeds stage of the run.
- Once the temperature lined out with the desired polymerization temperature, the delayed feeds including ethylene were started. We would need to determine that ethylene was being consumed, and that the control valves actuated properly to maintain the temperature and pressure set points. The weight of the feed cylinder was observed to follow conversion. (If the reactor pressure remained constant for say 20-30 minutes. when only a few grams of ethylene had been fed, we would not change the pressure set point of the motor valve trying to add more ethylene - the catalyst most likely had difficulty getting charged to the reactor).
- If the reactor pressure should climb beyond the control point pressure, pressure was vented-off if it approaches 1300 psig. Venting was done cautiously to just prevent the pressure to go beyond 1300psig. Too much venting would cause the product to foam up excessively.
- When all the ethylene had been fed into the reactor, the valve on the ethylene feed tank and all ethylene monomer system valves were closed.
- When all monomer had been fed into the reactor, the valve on the monomer mix tank and all monomer mix system valves were shut.

- It was desired that the catalyst system (i.e., both oxidizer and reducer) fed-out after all monomer charges had fed-out. When the catalyst fed-out, the valve on the catalyst tanks and all catalyst system valves were closed.
- The system was allowed to post-heat for a desired length of time. After the post-heat step, we proceeded with the post-catalysis step.
- When the post-catalysis was completed, the reactor temperature controller was set to 30°C.
- When the temperature of the reactor reached 30°C, agitation was discontinued.

A.5. Recovery of Product

Operating Procedure - Dumping 5-gal. Reactor through Dump-out Pot

(Refer to Figure A.1)

We would proceed to recover the product at the end of a 5-gal. ethylene polymerization.

Respirator, safety glasses and butyl gloves were worn for this procedure. The transfer line from reactor flush valve was attached to an opening on the cover of the 15-gal. drum. Using the flush valve, we carefully controlled the transfer of product from reactor to the 15-gallon drum, to allow de-gassing and to minimize foaming. The product was left to de-foam for a day in the 15-gal. drum before transferring to sample container.

APPENDIX STANDARD OPERATING PROCEDURES

Dumping 5-gal. Reactor through Dump-out Pot

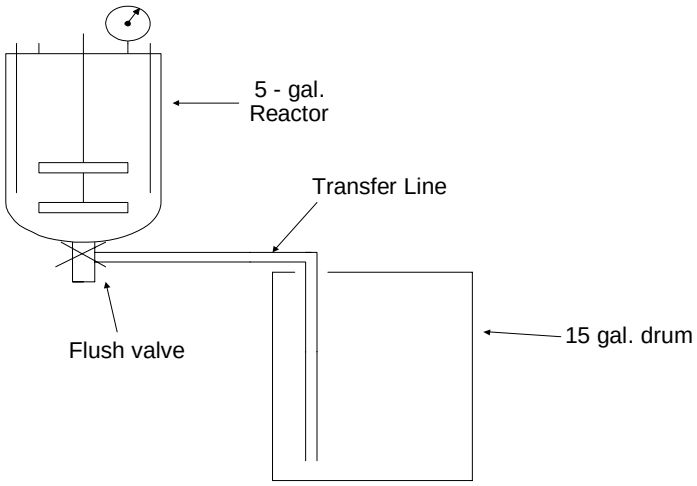

Figure A.1 Recovery of product