

# STUDIES ON HIGH HEAT RESISTANT ACRYLIC ADHESIVE

A DISSERTATION

SUBMITTED IN THE PARTIAL FULFILLMENT OF THE  
REQUIREMENT FOR THE AWARD OF THE DEGREE OF

MASTER OF TECHNOLOGY

IN

POLYMER TECHNOLOGY

Submitted by:

**RADHA SACHAN**

**2K16/PTE/05**

Under the supervision of

**DR. ROLI PURWAR**

**DR. DEENAN SANTHIYA**



**DEPARTMENT OF APPLIED CHEMISTRY**

**DELHI TECHNOLOGICAL UNIVERSITY**

(Formerly Delhi College of Engineering)

Bawana Road, Delhi-110042

JUNE-2018

**DELHI TECHNOLOGICAL UNIVERSITY****(Formerly Delhi College of Engineering)****Bawana Road, Delhi-110042****CANDIDATE'S DECLARATION**

I Radha Sachan, 2K16/PTE/05 student of M.Tech Polymer Technology hereby declare that the project dissertation title “**STUDIES ON HIGH HEAT RESISTANCE ACRYLIC ADHESIVE**” which is submitted by me to the Department of Applied Chemistry, Delhi Technological University, Delhi in the partial fulfilment of the requirement for the award of the degree of Master of Technology, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any degree, Diploma Associateship, Fellowship or other similar title or recognition.

Place: Delhi

**RADHA SACHAN**

Date:

**DEPARTMENT OF APPLIED CHEMISTRY**  
**DELHI TECHNOLOGICAL UNIVERSITY**  
**(Formerly Delhi College of Engineering)**  
**Bawana Road, Delhi-110042**

**CERTIFICATE**

I hereby certify that the project dissertation title “**STUDIES ON HIGH HEAT RESISTANCE ACRYLIC ADHESIVE**” which is submitted by RADHA SACHAN, 2K16/PTE/05, Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Technology, is a record of the project work carried out by the student under our supervision. To the best of our knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

Place: Delhi

**Dr. Roli Purwar**

Date:

**Dr. Deenan Santhiya**  
**(SUPERVISOR)**

## ACKNOWLEDGEMENT

The success and final outcome of this project required a lot of guidance and assistance from many people and I am extremely fortunate to have got this all along the completion of this project work.

I wish to express my gratitude towards my project supervisor, **Dr. Roli Purwar and Dr. Deenen Santhiya, Department of Applied Chemistry, Delhi Technological University**, who provided me a golden opportunity to work under their able guidance. Their scholastic guidance and sagacious suggestions helped me to complete the project on time.

I wish to thank **Dr. Archana Rani, Professor and Head of the Department of Applied Chemistry, Delhi Technological University**, for her constant motivation and for providing able guidance.

I am thankful to and fortunate enough to get constant encouragement, support and guidance from all teaching as well as non-teaching staffs and of Department of Applied Chemistry and Polymer Technology, which helped me in successfully completing my project work.

Finally, yet importantly, I would like to express my heartfelt thanks to my beloved family and friends who have endured my long working hours and whose motivation kept me going.

**Radha Sachan**

## *ABSTRACT*

---

Acrylic copolymer was prepared by solution polymerisation technique using water as a solvent. The Cloisite 30B/Acrylic Copolymer nanocomposites with different loading of nanoclay (0.5-3.0%) were prepared by In-situ method. For compositional analysis fourier transform infrared spectroscopy (FTIR), Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) and Isothermal thermal gravimetric analysis have been studied and results show that a suitable copolymer has been formed with four monomers that are acrylic acid, methacrylic acid, butyl acrylate, methyl methacrylate.

Different parameters like solid content, solubility, appearance, acid value and pH values were checked for each nanofilled copolymer. Rheology was tested for pure and 0.5% filled copolymer and increase in viscosity with shear thickening behaviour at high shear rate was observed. All compositions were checked for thermal stability by thermal gravimetric analysis (TGA) analysis and found that 50 % wt. at 398 °C for 2.0% filled Cloisite 30B/ Acrylic nanocomposite. Epoxy resin was added as tackifier with curing agent with acrylic system. Peel strength was checked for two substrate: corona treated metallised biaxially-oriented polypropylene (bopp) and nylon cloth. Peel strength was increasing with nanofiller loading upto 2.0%.

## TABLE OF CONTENT

---

Candidate's Declaration	i
Certificate	ii
Acknowledgement	iii
Abstract	iv
Contents	v
List of Tables	vii
List of Figures	viii
List of abbreviations	ix
CHAPTER 1 INTRODUCTION	
1.1 Background	1
1.2 Problem	2
1.3 Motivation	3
1.4 Objective	3
CHAPTER 2 LITERATURE REVIEW	
2.1 Introduction	4
2.2 Acrylic adhesive	7
2.2.1 Reactive solvent based acrylic adhesive	8
2.2.2 Water based acrylic adhesive	9
2.3 Acrylic Nanocomposite	13
2.3.1 Cloisite 30B	14
2.3.2 Synthesis of nanocomposite	16
2.4 Acrylic – Cloisite 30B nanocomposite adhesives	17
CHAPTER 3 EXPERIMENTAL	
3.1 Material	19

3.2 Methodology	19
3.3 Method	20
3.3.1 Synthesis of copolymer	21
3.3.2 Rheology	22
3.3.3 Determination of acid value	23
3.3.4 Infrared spectroscopy	23
3.3.5 NMR spectroscopy	24
3.3.6 Thermal analysis	25
3.3.7 Substrate preparation	25
3.3.8 Adhesive sample preparation	26
3.3.9 Curing	26
3.3.10 Peel Strength	26
CHAPTER 4 RESULT AND DISCUSSION	
4.1 Composition of Copolymer	28
4.2 Properties of resins	29
4.3 Compositional Analysis	
4.3.1 FTIR	29
4.3.2 <sup>1</sup> H NMR	31
4.3.3 Isothermal TGA	32
4.4 Thermal Analysis	33
4.5 Rheology	35
4.6 Peel Strength	36
CHAPTER 5 CONCLUSION	38
References	

## LIST OF TABLES

---

<b>Table no.</b>	<b>Content</b>	<b>Page</b>
2.1	Monomers commonly used to synthesize water borne acrylic adhesive	10
4.1	Composition of adhesives	28
4.2	Properties of acrylic resins	29
4.3	Adhesion property in terms of Peel strength of Nanocomposite adhesive	35
5.1	Final composition of adhesive	38



## LIST OF FIGURES

---

<b>Figure no.</b>	<b>Content</b>	<b>Page</b>
2.1	Cross section of an adhesive bond	4
2.2	Illustration of different states of clay dispersion in polymer matrices, with corresponding X-ray and TEM results	14
2.3	Schematic structure of a 2 : 1 clay mineral showing two tetrahedral sheets sandwiched between one octahedral sheet within the clay-stacking pattern.	15
2.4	Structure of Cloisite 30B	16
2.5	Schematic representation of In-Situ Polymerisation	17
3.1	Flow chart of working methodology	21
3.2	Experimental setup for synthesis of Acrylic Copolymer	22
3.3	Anton Paar – MCR 102	23
3.4	Nicolet 380 FT-IR Spectrometer	24
3.5	JEOL USA 400 MHz Nuclear Magnetic Resonance Console	24
3.6	Perkin-Elmer TGA 4000 analyser	25
3.7	UTM – Stable Micro Systems : TA-HD Plus Texture Analyser for peel strength analysis	27
4.1	FTIR analysis of Acrylic copolymer and its modification with Cloisite 30B	30
4.2	<sup>1</sup> H NMR of Acrylic Copolymer	31
4.3	Isothermal TGA curve of Neat Acrylic Copolymer	32
4.4	TGA curve of acrylic copolymer, its modification with Cloisite 30B and of Cloisite 30B	33
4.4	Effect of Cloisite 30B loading	34
4.5	Rheology of Neat (0%) Acrylic copolymer and Acrylic/0.5% Cloisite 30B Nanofilled copolymer	36

## LIST OF ABBREVIATIONS

---

<b>Symbol</b>	<b>Notation</b>
AA	Acrylic Acid
MAA	Methacrylic Acid
MMA	Methyl Methacrylate
BA	Butyl Acrylate
APS	Ammonium per sulphate
VOC	Volatile organic compound
MMT	Montmorillonite
ASTM	American society for testing and materials
DIN	Deutsches Institut für Normung
UV	Ultraviolet
PSA	Pressure sensitive adhesive
$T_g$	Glass transition temperature
TEM	Transmission electron microscopy
PEHA	Pentaethylene hexamine
FTIR	Fourier transform infrared spectroscopy
$^1\text{H}$ NMR	Proton nuclear magnetic resonance
TGA	Thermal gravimetric analysis
GSM	Grams per square meter
BOPP	Biaxially-oriented polypropylene
UTM	Universal testing machine

# CHAPTER 1. INTRODUCTION

---

The use of polymeric adhesives to join components for structural, semi-structural, and non-structural applications has expanded significantly in recent years due to the irreplaceable advantages. Polymeric adhesives offer for certain assembly processes and the development of new adhesives with upgraded strength and environmental suitability. The increasing complexity of present assembled structures and the different types of materials used have led to many joining applications that would not be possible with further conventional joining techniques. Adhesives are also being used either in combination with or to replace mechanical fasteners and welds. Reduced weight, sealing capabilities, reduced part count and assembly time, as well as enhanced fatigue and corrosion resistance, these all feature provide the trendy with desirable for customisable opportunities for assembly. The fabrication of many modern vehicles, devices, and structures are dependent on the use of adhesives.

With the rise of the chemical industry and man-made polymers, the range of adhesive formulations burst out. Presently, adhesives can be classified in several different ways, such as by cure (bonding) mechanism, chemistry involved, and on the basis of application (e.g. structural vs. non-structural).

A number of acrylic resins are used for bonding cloth, plastics, leather, and, in some cases, metal foils. The acrylic monomers most commonly used in adhesives are ethyl acrylate, methyl acrylate, methacrylic acid, acrylic acid, acrylamide, and acrylonitrile. They provide good weather resistance, resistance to hydrolysis, gloss and color retention in exterior applications. Acrylic resins can be thermoplastic or thermoset and are available in organic solvent born, waterborne, powder and radiation-curable type[1]

Now a days low VOC and water based adhesive are under high attention. Waterborne adhesives are very popular and are considered as an environmentally friendly and economically viable alternative to solvent-based adhesives. One of the major advantages of waterborne adhesives is the absence of volatile organic compounds (VOCs). Furthermore, water can be used to clean excess adhesive off of mated parts and to clean

the equipment. These adhesives are usually considered very environmental friendly. Water based acrylic resin generally prepared by solution or emulsion polymerisation by free radical mechanism. In this direction people have developed water based acrylic adhesive for different application such as high heat resistant for fluorescent lamp[2], automotive polyolefin parts[3], pressure sensitive adhesives[4][5], diapers and sanitary napkins[6], labels and stickers and tape on skis[7][8] which requires water resistance[9][10] also.

To improve the mechanical, thermal and rheological properties of adhesive nanofillers used to add. Different nanofillers have been used such as carbon nanotubes[11][12] metal and its derivative nanoparticles[13][14], aluminosilicate[15][16] etc. Among these nanofillers, nanoclay are most popular as research topic due to following reason: easy availability, high aspect ratio and specific surface area and lower price[17]. Nanoclays are ubiquitous nanofiller and belong to a wider group of clay minerals. Clay minerals are hydrous silicates and can be described as fine-grained particles with sheet like structure stacked over one another. Mostly Cloisite and Nanomer MMT clays with plane geometry are used by the researchers. Though Cloisite 30B provide better tack in comparison to Na<sup>+</sup> MMT/blank acrylic copolymer[18].

Acrylic itself has good adhesive properties, but it doesn't by itself adhere well to polyolefin used in packaging industry. So that epoxy resin is added to provide initial tack of water based adhesives and also improves heat resistance[3]. As a crosslinking agent amino resin used to add with epoxy which helps in curing of adhesive and makes the system thermosetting. High heat resistance adhesive required in various field like packaging industry where laminating adhesive need heat resistance at the time of heat seal. Fabric adhesive also need heat resistance to be used in fabric like nylon, aramid for parachute manufacturing; adhesive is always a better method over stitching. Fluorescent lamp also requires high heat resistant adhesive with long life.

## 1.2 Problem

The necessity of high performance product is always looked-for in every field. In the field of acrylic adhesive requirement of environment friendly high heat resistant adhesive is required by different application area. These areas are fluorescent lamp, packaging, and

parachute fabric. Thus the problem is associated with the acrylic adhesive with high heat stability which should be water soluble.

### **1.3 Motivation**

The motivation of this project is completely industry oriented. U-Flex needs an adhesive which could be an acrylic copolymer and have heat resistance upto (400°C).

### **1.4 Objective**

Development of high heat resistant water soluble adhesive with acrylic copolymer.

To achieve this objective the sub-objectives are as follows:

1. Selection of monomers for adhesive preparation.
2. Synthesis of acrylic copolymer and its modification with Cloisite 30B.
3. Characterisation and testing for adhesive application.

## CHAPTER 2. LITERATURE REVIEW

---

### 2.1 Introduction

An adhesive is a material that is applied to surfaces to join them everlastingly by adhesion bonding practice. It is having ability to form bond with both the surfaces when the final object be made up of of two parts or section to be joined together[19][Modified from ASTM D 907-82, Standard Definitions of Terms Relating to Adhesives]. Bonding is the process of joining two substrates using an adhesive and depends on holding strength, peel strength and shear strength of adhesive. According to DIN EN 923, an adhesive is defined as a non-metallic binder that acts by means of adhesion and cohesion. ASTM D907-06 defines an adhesive as "a substance capable of holding materials together by surface attachment".

The adhesive contact between an adhesive and a substrate not only depends on the actual area of contact (adhesion zone) of the adhesive and substrate but also depends on the state of the adhesive in the vicinity of the surface of the substrate (transition zone).

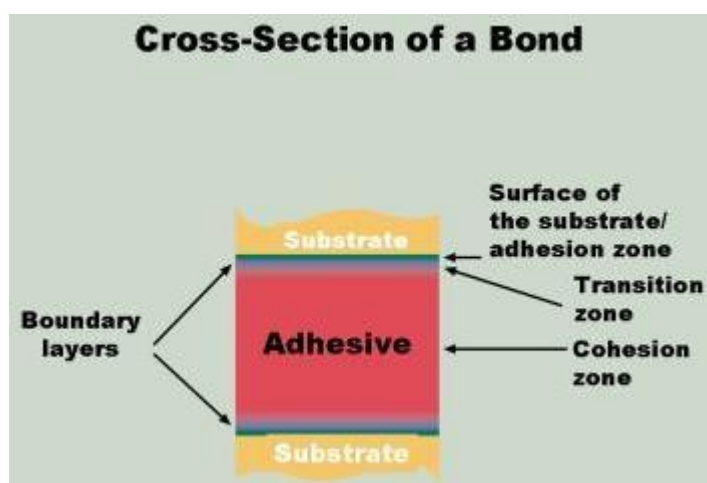


Fig 2.1 Cross section of an adhesive bond

- In the cohesion zone, the adhesive exists in its standard state.
- In the adhesion zone, the adhesive has an altered structure and composition due to its adhesion to the surfaces of the substrates. This structure and composition is different from the standard state in the cohesion zone. As an outcome, the macroscopic properties of the adhesive in the adhesion zone are also altered.
- The structure, composition and macroscopic properties of the adhesive constantly change in the transition zone which is in between the adhesion zone and the cohesion zone. There could be separation of the components of the adhesive due to diffusion of the small components of the adhesive into surface pores. The optimum composition of the adhesive is hence adversely affected.

Adhesives are classified by different classification systems:

1. Classification by structure
2. Classification of adhesives by curing method
3. Classification of adhesives by origin

Properties of some adhesives

1. Classification by structure

- **Thermosetting adhesives**

Thermosets molecules are cross-linked by strong covalent intermolecular bonds, forming one giant molecule. Cross-linking is irretrievable therefore thermosets cannot be processed again (re-melt). Cross-linking is achieved by curing process initiated by heat, chemical agents, radiation or evaporation of solvents. Curing results in sharp increase of strength, elasticity and stability. Most of thermosetting adhesives are based on epoxies, polyesters, polyimides and phenolics.

- **Thermoplastic adhesives**

Thermoplastics are polymers, which become softer (become flexible and plastic) and melt when heated. No new cross-links form (no chemical curing) when a thermoplastic cools and hardens. Thermoplastics may be reprocessed many times by heating or smearing a solvent. Molecules of most of thermoplastics association long polymer

chains alternating with monomer units. Polyamides, cyanoacrylates, polyacrylates, polyvinyl acetate (PVA) are typical thermoplastic adhesives.

- **Elastomeric adhesives**

Elastomers are polymers having high elasticity – can be stretched at high degree. Elastomer comprises of long lightly cross-linked molecules. Elastomers are strengthened by thermal curing or solvent evaporation. Curing results in increase of cross-linking of the molecules. Typical elastomeric adhesives are based on natural rubbers, silicones, acrylonitrilebutadiene (nitrile), neoprene, Butyl, polyurethane, styrene-butadiene.

## 2. Classification of adhesives by curing method

- **One-part adhesives**

- **Heat activated curing adhesives.** Adhesives of this type (epoxies, urethanes, polyimides) consist of a ready mixture of two components.
- **Light/UV activated curing adhesives.** Light activated adhesives are cured under a visible or UV light of proper wave length. Adhesives of this type generally contain photoinitiators to enhance curing reaction. It consists of Acrylic, cyanoacrylates and urethane chemistry.
- **Moisture activated curing adhesives.** These adhesives are cured when react with a moisture present on the substrate surface or in the air. It consists of RTV Silicones, cyanoacrylates and urethane chemistry.
- **Anaerobics.** Acrylic based adhesives cured between metallic substrates, surfaces of which are deprived of oxygen.
- **Pressure sensitive adhesives (PSA).** Adhesives of this type do not cure. Adhesive bonding forms as a result of a pressure applied to the substrates. The adhesion strength is determined by the pressure applied to the substrates. Usual example of pressure sensitive adhesive is self-stick tape.

- **Two-part adhesives.** A two-part adhesive is cured when its two (or more) components are mixed. The components react chemically forming cross-links of the polymer molecules. Examples of this are epoxies, urethane, acrylics and silicones.



### 3. Classification of adhesives by origin or raw material

- **Synthetic adhesives.** Typical synthetic adhesives are epoxies, polyurethanes, cyanoacrylates, polyimides, silicones, acrylics, polyamides, cyanoacrylates, polyacrylates, polyvinyl acetate (PVA), nitrile, and neoprene.
  
- **Natural adhesives (glues)**
  - **Animal glue.** Animal glue is prepared by boiling animal bones and connective tissues containing protein.
  - **Casein.** Casein is made of skimmed milk. The main component of casein is protein contained in cow milk.
  - **Fish glue.** Fish glue is made of fish skin containing protein (collagen).
  - **Vegetable-based glues (tapioca paste, soybean glue, starch glue)** - aqueous dextrine-based glues.
  - **Natural rubber (latex) glue.** Natural rubber glues are prepared from water-based latex emulsion of plant sap.

#### 2.2 Acrylics Adhesives

Acrylic adhesives are key to large sections of modern industry, providing high strength bonds that work well as an alternative to rivets or other more mechanical joining techniques. Where acrylic cements are adhesives that join acrylics together by fusing the two surfaces, acrylic resins are adhesives that are actually made from acrylic acid. Acrylic adhesives are either thermoplastics, which can be moulded above a certain temperature, or thermosetting polymer, which 'cure' once and cannot be remoulded. 'Curing' means 'toughening' or 'hardening', and can be induced through heat, electron beams, ultraviolet radiation, or chemical additives. Acrylic adhesives also look good, and bond easily to a number of different materials means they are good at bonding surfaces that are a little oily or a little dirty, and they will bond with plastics, metals and glass. This gives them a great flexibility in terms of applications, because of that they are used so widely. All-in-all, acrylic adhesives are extremely flexible and can be used for a great many applications. This is their substantial advantage over other forms of adhesive.

Acrylic adhesives can be divided broadly into water-based (referred as emulsion or dispersion) and solvent-based. Water-based are slow in drying rate as compared to solvent-based systems but mostly solvent-based acrylic systems have better resistance to other solvents, chemicals and water. Comparatively, water-based systems are less expensive than their solvent-based counter parts.

### **2.2.1 Reactive Solvent Based Acrylic Adhesives:**

Reactive solventborne acrylics are the most common solventborne adhesives next to urethanes. They have good aging properties and are resistant to many common media. They also are more heat and chemical resistant than their water based counterparts. Though, solvent-based acrylics have usually lower shear strength and are usually more expensive than water based (emulsion/dispersion) acrylics.

The most common acrylic monomers are ethyl acrylate, butyl acrylate, and ethylhexyl acrylate. Most of the time blends of all three monomer are copolymerized. Every now and then other ingredients are added, such as plasticizers to lower the glass transition temperature, tackifiers to increase tack, fillers to lower cost and to modify performance, and flame retardants and antioxidants to improve heat resistance. Sometimes other monomers are added such as acrylic acid or methacrylic acid to improve adhesion to metals.

Acrylic solventborne adhesives are mostly used for pressure sensitive adhesives (labels and tapes), and as construction adhesives for tile bonding and sealing (grouts) and as laminating and packaging adhesives. They are also used in architectural and industrial coatings. Other chemistries used for solvent based adhesives include reactive modified acrylics, silicones, and epoxy-amines. However, these adhesives are usually more expensive and find fewer applications.

In solvent based adhesive field lot of research is going continuously. Zbigniew Czech synthesize and modified solvent based pressure sensitive adhesive (PSA) based on acrylates. In that he checked effect of different parameters such as amount and kind of multifunctional isocyanate crosslinkers, modification with ethoxylated amines, modification with polyalkylene oxides and UV-crosslinking on the removability (peel adhesion) on steel, glass, polyamide (PA), polyvinyl chloride (PVC) and polypropylene

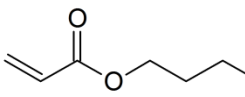
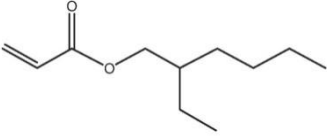
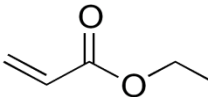
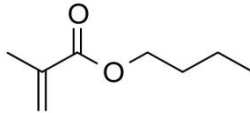
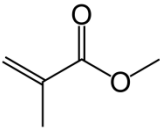
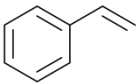
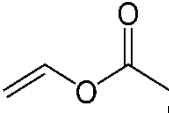
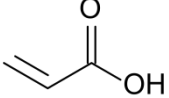
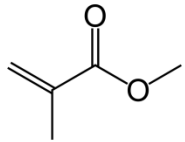
(PP) during the ageing time[20]. Solvent based pressure sensitive acrylic adhesives based on butyl acrylate, ethylhexyl acrylate and acrylic acid and peel strength was tested by Dominika Sowa et. Al. for different substrate stainless steel, poly(methylmethacrylate) (PMMA), polycarbonate (PC), polyethylene (PE), polypropylene (PP) and polytetrafluoroethylene (PTFE) known as Teflon[21]. In the same way solvent based thermo-resistance pressure sensitive acrylic adhesives based on butyl acrylate, vinyl acetate and acrylic acid monomer in presence of ethyl acetate was developed by Xingchen Lu et al. and was tested upto 150°C for peel strength[22]. Likely, Chung-Feng Jeffrey Kuo and Jiong-Bo Chen synthesise solvent borne pressure sensitive adhesive 2-Ethyl hexyl acrylate and acrylic acid monomer with high solid content and higher peel strength[23].

Xiaowen Zhang et al. prepared and studied rheological property of solvent based acrylic pressure sensitive adhesive with different crosslinking density[24].

### **2.2.2 Water Based Acrylic Adhesive:**

Waterborne adhesives are very popular and are conceived as an environmentally friendly and economically viable alternative to solvent-based adhesives. One of the major benefits of waterborne adhesives is the absence of volatile organic compounds (VOCs). Additionally, water can be used to clean excess adhesive off of mated parts and to clean the equipment. These adhesives are typically considered very environmental friendly.

A variety of monomers are used to achieve desired performance properties such as tack, peel and shear. A common method for classifying the monomers is based on the glass transition temperature ( $T_g$ ) of their homopolymers. This approach divides monomers into the categories of functional monomer, soft, medium and hard monomers. Soft monomers produce homopolymers with  $T_g$  below -30°C, for hard monomers it is above 30°C and those monomers which produces homopolymers with  $T_g$  between these values are considered medium monomers. In table 2.1 few examples of monomers with classification are given. Hard monomers are added to enhance thermal resistance and cohesive strength of adhesive film as well. Functional monomers provide charge to adhesive polymer and a functional group by which it can be cross-linked[25].

Soft Monomers		Medium Monomers		
<b>n-Butyl Acrylate</b>	<b>2 Ethylhexyl Acrylate</b>	<b>Ethyl Acrylate</b>	<b>Butyl Methacrylate</b>	
				
Hard Monomers		Functional Monomers		
<b>Methyl Meth Acrylate</b>	<b>Styrene</b>	<b>Vinyl Acetate</b>	<b>Acrylic Acid</b>	<b>Methacrylic Acid</b>
				

**Table 2.1** Monomers commonly used to synthesize water borne acrylic adhesive

In this project two functional monomer acrylic acid and methacrylic acid, n-butyl acrylate as soft monomer and methyl methacrylate as hard monomer. Soft monomer and hard monomer are taken in 1:1 ratio to attain high thermal resistance acrylic resin. Properties of these monomers are listed below:

1. N-Butyl Acrylate
  - a) Soft Monomer
  - b)  $T_g$  is  $-57^\circ\text{C}$
  - c) Good Elasticity
  - d) Excellent Softness
  - e) Good resistance to solvents
  - f) Excellent heat resistance
  - g) Good wet rub fastness
  - h) Poor dry rub fastness

2. Methyl Methacrylate
  - a) Hard Monomer
  - b)  $T_g$  is  $105^\circ\text{C}$
  - c) Good Elasticity
  - d) Moderate Softness
  - e) Excellent heat resistance
  - f) Good dry rub fastness
  - g) Poor wet rub fastness
  
3. Acrylic Acid
  - a) Functional Monomer
  - b)  $T_g$  is  $106^\circ\text{C}$
  - c) Hygroscopic, brittle and colourless
  - d) Makes bond with cross linked monomers
  
4. Methacrylic Acid
  - a) Functional Monomer
  - b)  $T_g$  is  $228^\circ\text{C}$
  - c) Makes bond with cross linked monomers

Water based acrylic adhesive have diverse application as discussed earlier. Due to its environmental benefits scientist are doing research in every possible area of adhesive application. Now scientists are focusing on high performance adhesive of water based acrylic. In this direction P U Zhaobin et al. prepared water soluble acrylic resin for fluorescent lamp and found decomposition temperature at  $355^\circ\text{C}$  for resin[2]. High decomposition temperature of acrylic resin was required for fluorescent lamp working conditions and adhesive need to be high heat stable.

Webber et al. patented high bond strength, high heat resistant water based adhesive designed for bonding a vinyl substrate to a polyolefin surface. This water adhesive composition was comprised of three components. First is modified acrylic copolymer in an emulsion form. This acrylic copolymer emulsion made up of two monomers, one is ethyl acrylate and other is propylene chlorohydrin dimethyl ammoniummethyl methacrylate. Other two components of the adhesive are polyethyleneimine and epoxy

resin. Polyethyleneimine was used to improve bonding to a treated polypropylene surface and to crosslink the acrylic emulsion for higher heat resistance. Epoxy resin was added to improve heat resistance and to provide initial tack of water based adhesive. On the basis of this work epoxy resin was added in current project work to provide better tack and improved heat resistance[3].

In the field of water based pressure sensitive acrylic adhesives Dodge et al. patented formulation in 2013. They prepared pressure sensitive adhesive comprising of first a polymer or copolymer comprising polymerised monomers selected from the group consisting of acrylic acid, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, octyl acrylate, styrene, vinyl acetate and combinations. Second component consist of a tackifier resin selected from the group consisting of rosin ester resin, rosin acid resin, synthetic hydrocarbon resin, synthetic turpentine resin and its combinations. Third component comprises a second polymer consisting of ethylene acrylic acid copolymer, oxidized polyethylene, oxidized ethylene-vinyl acetate copolymer, maleated polyolefins and combinations. They had developed 4 different composition and checked for different properties of adhesive[4].

Corzani patented water based adhesive composition with bond retention in the presence of water for The Procter & Gamble Company. This adhesive used in the manufacturing of absorbent pads such as diapers and sanitary napkins. They had used different commercial acrylic polymer 20-60% and 40-80% tackifying resin. They prepared twelve different composition and tested for solid content, viscosity, water contact angle, bond strength and bond retention in water[6].

Kawabata et al. developed acrylic emulsion adhesive which features good adhesion and cohesion with high solid and high water resistance. This adhesive can be used as an adhesive sheet for surface protection. For acrylic emulsion monomeric mixture of alkyl methacrylate, acrylic acid, methacrylic acid and N-vinylpyrrolidone and surfactant mixture of an anionic and non-ionic surfactant were used[9].

Shimozato et al. prepared heat resistant emulsion copolymer of methylstyrene and acrylonitrile. The prepared resin was excellent in heat stability and mouldability when molded at high temperature[26]. While going through all these paper got an idea of monomer to be work on for preparation of acrylic resin which should be high heat

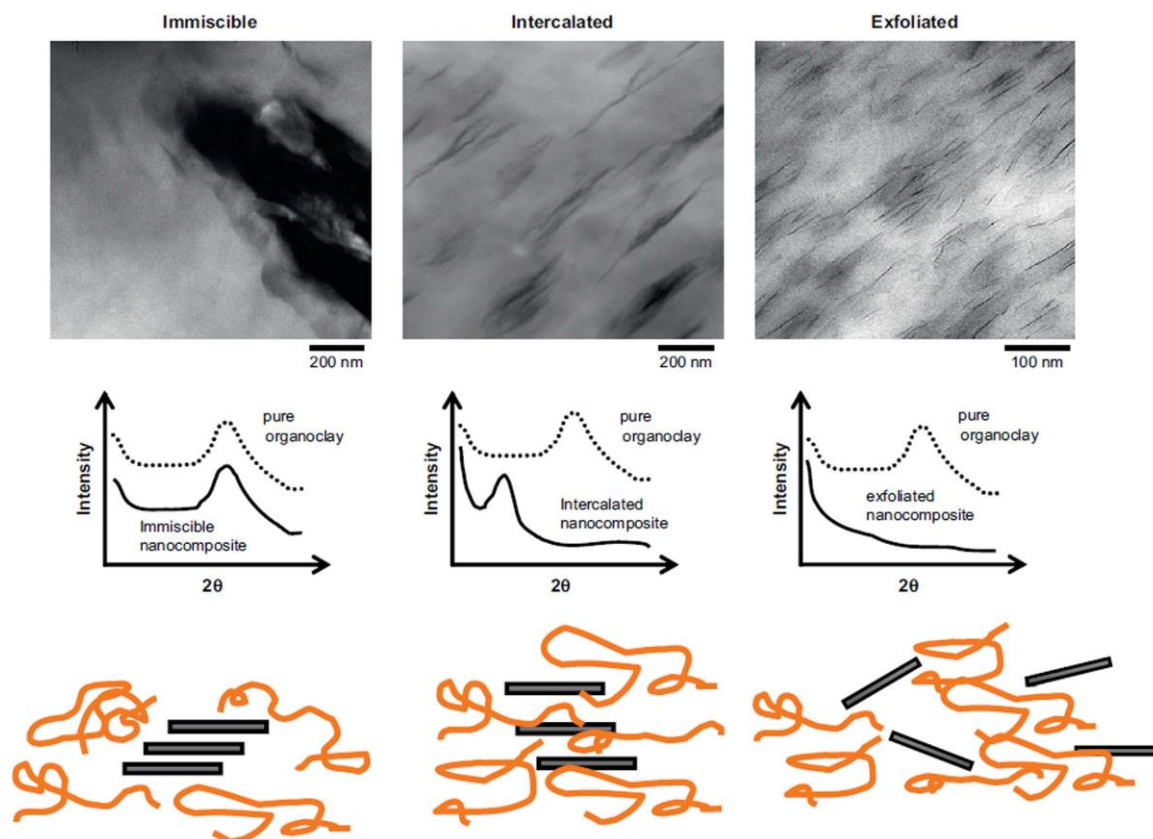
resistant. Most of the scientists used tackifying resin to improve initial adhesion so here in current project Epoxy resin was used as tackifier with crosslinking agent.

## 2.3 Acrylic Nanocomposite

Acrylic adhesives are under constant search for enhanced properties. On this search extensive study of nano-materials is going on since 20 years. As nanofillers lot of work could be found in publication about carbon nanotubes, nanoclays and metal and their derivative nanoparticles. Though among these nanofillers, nanoclays are most popular research topic. By advantage of layered silicate, prepared nanocomposites shows improvement in many properties like improves modulus and strength, higher heat resistance, better flame retardant property, enhanced barrier characteristics, and reduces gas permeability.

Depending on the microstructure of the clay dispersion in the polymer matrix, here different types of nanocomposites could be obtained as shown in fig. 2.2.

- 1) Phase separated or immiscible polymer/layered silicate systems, in which polymer doesn't penetrate between the silicate layers and the composition obtained has properties on the level of traditional microcomposites.
- 2) Intercalated nanocomposites, in which separate polymer chains penetrate between the silicate layers or polymer chains inserted into the interlayer spacing of the stacking silicate platelets, the *d*-spacing value of these well-ordered, polymer-silicate sandwich multilayers is greater than that of pristine clay. In this case some property enhancement could be observed.
- 3) Exfoliated nanocomposites, in which the clay layers are homogeneously and discretely dispersed in the continuous polymer matrix and enhanced properties are obtained[27].

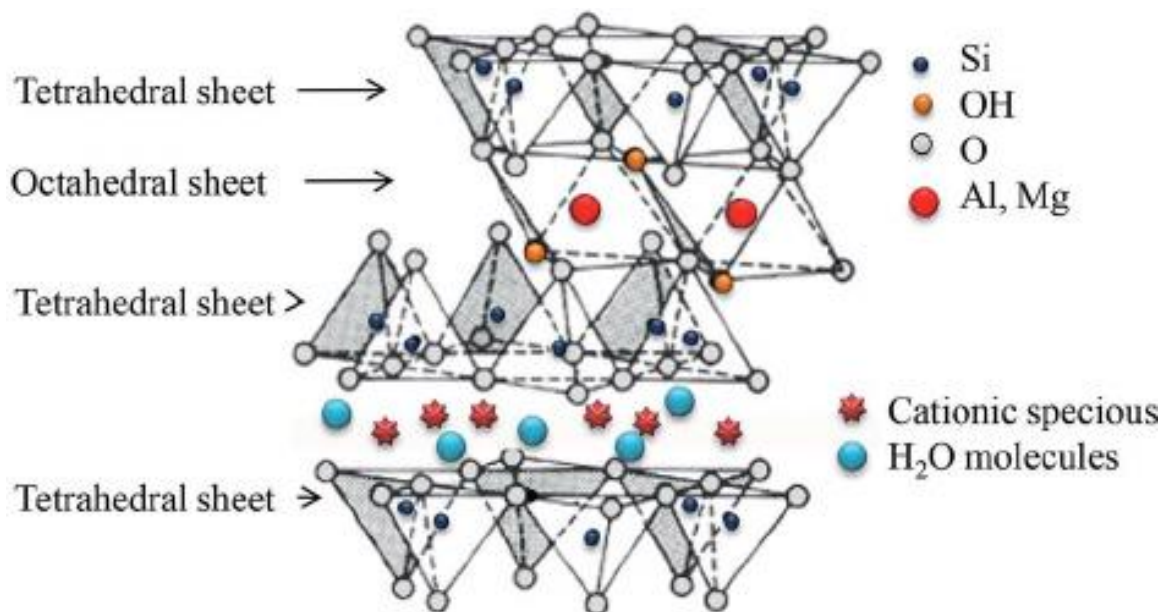


**Fig. 2.2** Illustration of different states of clay dispersion in polymer matrices, with corresponding X-ray and TEM results – reprinted from Polymer, Vol. 49, Paul D.R. and Robeson L.M., Polymer nanotechnology: nanocomposites, p.3187-3204, Copyright 2008.

### 2.3.1 Cloisite 30B

Smectite nanoclays are among intensely researched nanofillers in the field of nanocomposites. Among these smectite nanoclays, montmorillonite (MMT) has got prominence over other member nanoclays owing to its profusion, environmental affability and well-studied chemistry. MMT is a dioctahedral nanoclay with the 2:1 layer linkage. They are the most effective reinforcement fillers and their reinforcing capability is well documented in literature[28]. Their higher surface area and large aspect ratio are the outstanding features responsible for the reinforcement. Besides reinforcing effect of MMT, it is also viewed as rigid, impermeable filler. It creates a maze structure when dispersed in polymers, forces the moving gases/vapours to follow a tortuous path, and finally lowers their permeation rate. The structure of MMT is shown below in fig. 2.3.





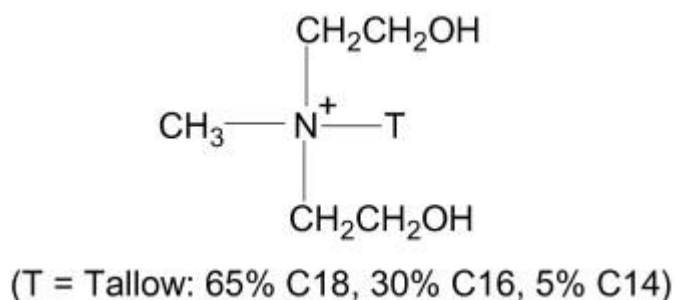
**Fig. 2.3** Schematic structure of a 2 : 1 clay mineral showing two tetrahedral sheets sandwiched between one octahedral sheet within the clay-stacking pattern.

The enhanced performance properties of MMT could only be recognized at nanoscale dispersion and to achieve nanoscale dispersion, delamination and, thereby exfoliation of these nanofiller platelets is essential. The clay minerals have solid tendency to form stacks owing to van der Waals' forces. Delamination is attained when there is affinity between the filler and polymer matrix, polymer chains intercalate to clay galleries and gets delaminate. Though, most of the polymers are not compatible with clay minerals owing to the differences in their surface energies; and the exfoliation of clay platelets is one of the main problems faced while preparing nanocomposites.

To overcome this issue, the surface energy of clay layers is lowered by their surface modification. In surface modification, surfactants having compatibility with the organic polymers are exchanged with exchangeable cations present in the clay, thereby expanding clay galleries and increasing spacing between the layers (d-spacing). The cations present in MMT galleries are usually exchanged with as alkylammonium or alkylphosphonium/onium.

Many intact and modified types of clays are commercially provided by a lot of suppliers. Structure of organo-modifier plays a vital role in delaminating and dispersing a nanoclay in a particular matrix. On that criterion Cloisite 30B was selected for current project work. Cloisite 30B is Quaternary Ammonium Salt Modified natural Montmorillonite, structure

shown in fig. 2.4 as per its supplier it acts as filler. It is organic intercalated nanoclay. It improves various physical properties, such as reinforcement, synergistic flame retardance, CLTE and barrier properties. Cloisite 30B offers good dispersion, provides miscibility with the thermoplastic systems. It enhances flexural and tensile modulus and suitable for injection moulding. They recommended it for automotive industry, flexible and rigid packaging such as films, bottles, trays blister packs as well as electronics like wire and cable. Its shore hardness on scale D is 83, specific gravity is 1.98 gm/cc, modifier concentration is 90meq/100gm of clay and the organic modifier is methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium and X-ray diffraction d-spacing is 18.5 Angstroms[29].



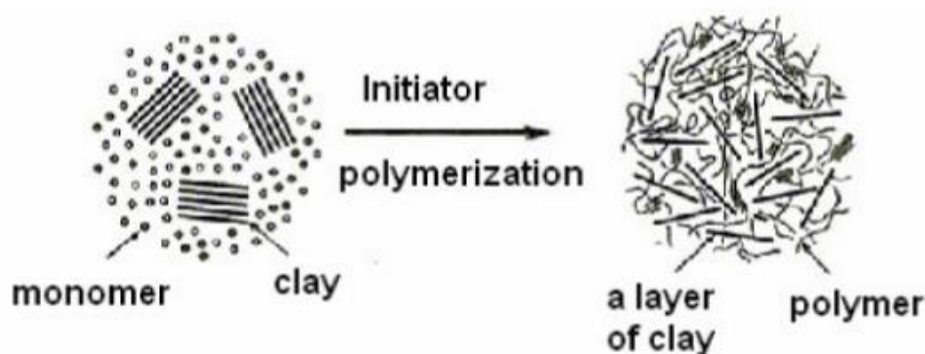
**Fig. 2.4** Structure of Cloisite 30B

### 2.3.2 Synthesis of Nanocomposite

Solution polymerisation technique was used for polymer synthesis. In which a solvent, a co-solvent and water soluble initiator APS was used. Solution polymerisation is preferred in current project over emulsion polymerisation due to its easiness, homogeneous system, fewer ingredients required which provide less contamination, ready to use resin as water soluble resin was required[30].

The nanocomposites could be prepared by different techniques including in situ polymerization, melt intercalation and direct mixing. In current project in situ method

was followed for the preparation of acrylic-cloisite 30B nanocomposite. The in-situ polymerization method has numerous benefits over the other two methods[27]. The schematic presentation is given below in fig. 2.5. The viscosity of the monomers during in situ polymerization is very low that they can easily intercalate the layered silicates. In in situ intercalated polymerization, the silicates layers are swollen within the monomer solution and can provide a high degree of exfoliation of the layer silicate aggregates in the nanocomposites.



**Fig. 2.5** Schematic representation of In-Situ Polymerisation

## 2.4 Acrylic-Cloisite 30B Nanocomposite Adhesives

Benefits of polymer/nanoclay composite over other nanofillers were discussed above. acrylic-cloisite 30B nanocomposites under research by scientists and different synthesis technique have been used so far. In this direction few publication are referred here for preparation of acrylic-cloisite 30B nanocomposite adhesives.

Gabriela Diaconu at al. synthesizes high solid content waterborne acrylic/MMT nanocomposites by miniemulsion polymerisation. They used two different commercial organically modified clays: cloisite 15A and cloisite 30B and methyl methacrylate and butyl acrylate as acrylic monomers. They obtained stable and coagulum free latexes with 30% solids content and with 2–4 wt.-% cloisite 30B and 3 wt.-% cloisite 15A. Testing shows that nanocomposites had improved glass transition temperature and at 50% weight loss there is almost 30°C rise in decomposition temperature. Cloisite 30B better dispersed in polymer matrix than cloisite 15A. The mechanical testing showed that the

nanocomposites gave a substantial improvement in storage modulus, a mild improvement in tensile strength and a loss in elongation at break compared to pure copolymer[31].

Matej Micusik et al. studied morphology of polymer/clay latex particles synthesized by miniemulsion polymerisation. They copolymerised BA/MMA (90:10 wt. %) in the presence of two different organomodified clays i.e. cloisite 30B and cloisite MA16. The adhesive properties, tack and shear resistance, and the gel content of the latexes were measured for some of the nanocomposite latex synthesized with the C30B and CMA16 organomodified clays. They determined the effect of the compatibility of the organoclay in the monomer mixture on the morphology of hybrid polymer/clay particles by using TEM. The nanocomposites synthesized with reactive CMA16 clay contained a higher amount of gel than those synthesized with cloisite 30B. The tack and shear resistances for the blank and nanocomposites revealed that latexes containing clay were just slightly less tacky, but they provided improved shear resistance, which was very noteworthy for latexes[32].

Dhurba J. Haloi et al. synthesise poly(2-ethyl hexyl acrylate)/ clay nanocomposite by In situ radical polymerisation. The best kinetic result with good control over molecular weight with narrow molecular distribution was observed in the case of cloisite 30B. The PEHA/clay nanocomposites have intercalated morphology as verified by WAXD and TEM studies. The PEHA/clay nanocomposites showed better thermal properties compared with the neat PEHA[33].

Wang L et al. [34] studied properties of the ternary adhesives consisting of epoxy/acrylic rubber blends and Cloisite 30B MMT. Epoxy resin used was a standard DGEBA-based one, and acrylic rubber was random copolymer consisting of acrylonitrile (AN), ethylacrylate (EA), butylacrylate (BA) and glycidylmethacrylate (GMA). Intercalation by solution technique accompanied by sonication was applied to obtain formulations with up to 5wt. % clay. Wang L et al. concluded that clay incorporation resulted in more complete phase separation of the epoxy-acrylic rubber systems, changed the size of the phases, allowing finer morphologies (with a decreased epoxy-enriched phase size) to appear. Such morphologies also directed to the clay platelets exfoliation and a remarkably improved strength and toughness characteristics, which resulted in the increase in the adhesive strength of the systems joints with copper foil and polyimide.

On the basis of findings in publications mentioned above cloisite 30B was chosen as nanoclay for preparation of nanocomposite with acrylic copolymer matrix. Epoxy resin also added after resin synthesis. Different properties like thermal, structural, compositional and bond strength have been studied.

## CHAPTER 3. EXPERIMENTAL

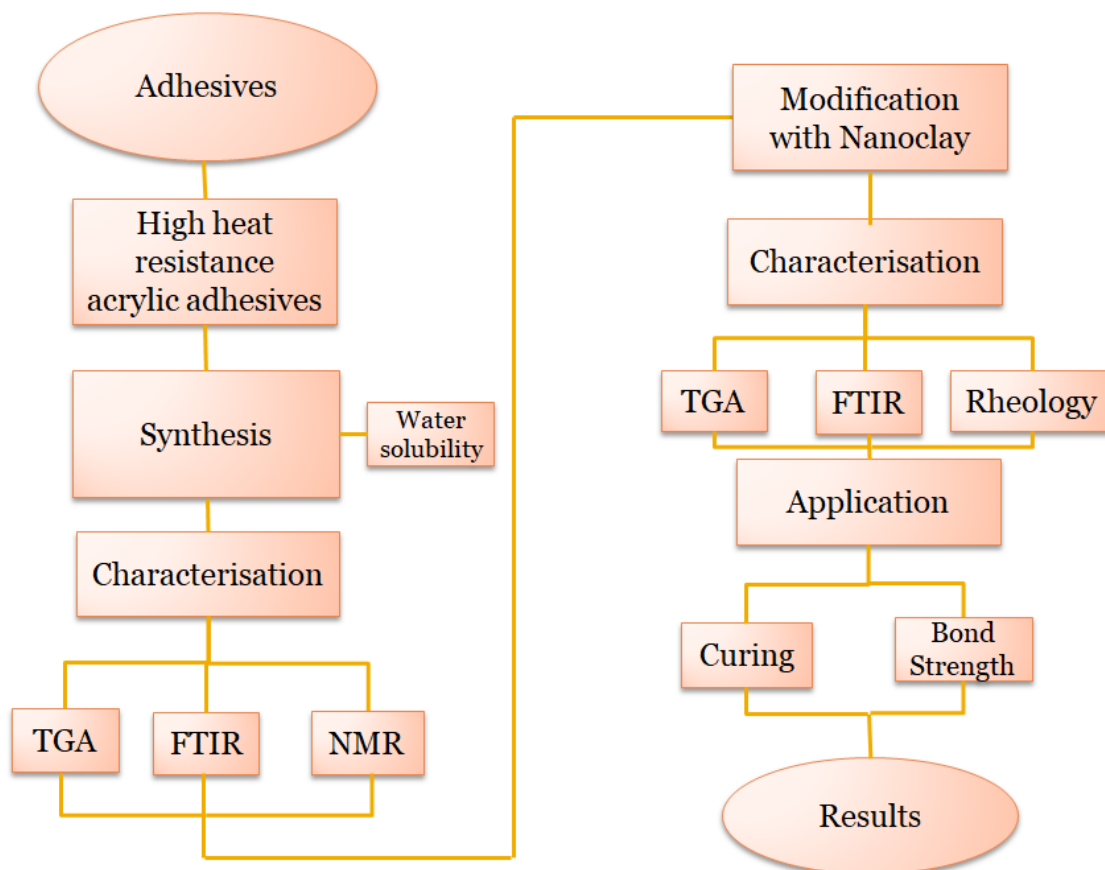
---

### 3.1 Material

Monomers used for synthesis of acrylic copolymers are; Acrylic acid (99.0%) LR grade from Central Drug House (P) Ltd. Delhi, Methacrylic acid (99.0%) LR grade from Central Drug House (p) Ltd. Delhi, Methyl methacrylate (99.0%) LR grade from central Drug House (P) Ltd. Delhi, and butyl acrylate (99.0%) from Loba Chemie pvt. Ltd. Mumbai, Initiator APS (98.0%) from Thermo Fisher Scientific, U.S. , cosolvent ethanol (99.9%) from Merck KGaA, Germany and liquor ammonia (about 25% NH<sub>3</sub>) from Thermo Fisher Scientific, U.S. as neutralising agent were used. Nanoclay Cloisite 30B. Epoxy resin (Bisphenol A) emulsion Epotec TW 5001C (65% solid in water) and waterborne curing agent modified polyamine Epotec THW 4506 (60% solid in water) from Aditya Birla Chemicals (Thailand) ltd. (Epoxy Division) were used. For application Corona treated metalized BOPP packaging films and Nylon fabric after washing with mild detergent were used.

### 3.2 Methodology

The methodology which has been followed in this project is shown in the form of flow chart in fig. 3.1. The project was started from study about high heat resistance acrylic adhesives as described in chapter 2. Selection of monomer, its synthesis and to prepare a water soluble acrylic copolymer comprises lot of trial and changes in parameters. That follows up its testing and characterisation for confirmation of copolymer synthesis and solubility in water. Modification of copolymer with nanoclay (cloisite 30B) was carried out and all the properties and characterisation was studied.



**Fig. 3.1** Flow chart of working methodology

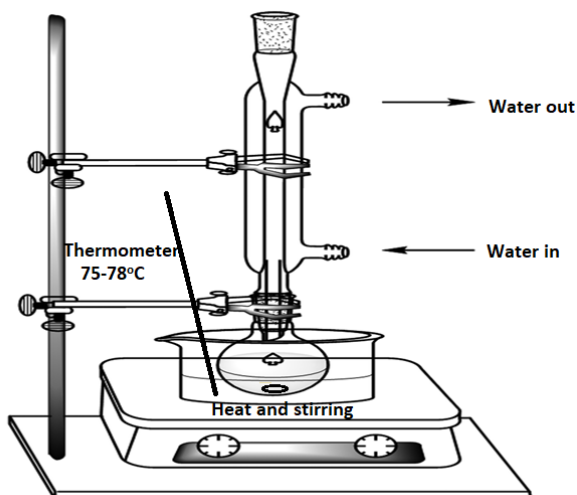
### 3.3 Method

#### 3.3.1 Synthesis of copolymers

In this project methyl methacrylate was used as hard monomer, butyl acrylate as soft monomer and acrylic acid, methacrylic acid as functional monomer. Deionised water was used as a solvent and ethyl alcohol as cosolvent. The polymerisation technique used here is solution polymerisation and APS was used as an initiator. The reactions were carried out in a 250 ml round bottom flask equipped with reflux condenser and magnetic bead for stirring. The reactor was placed in a temperature controller water bath (Shown in Fig. 3.1). Reactor is charged with DI water, cosolvent, monomer and initiator. After a series of experiments temperature and time conditions were optimized. Temperature of water bath maintained between 75-78°C, reaction was carried for 60 min at same temperature and then cooled till water bath temperature dropped to 60°C. At this point few drops of

liquid ammonia were added and mixed thoroughly to neutralise free acids, pH strips were used to confirm the neutralisation and pH was maintained within 7-8. After that water soluble acrylic resin with solid content at 40-45% (by mass) was obtained.

With same method acrylic resin was modified with Cloisite 30B (0.5-3.0% on the monomer content). Cloisite 30B first soaked overnight and ultrasonicated before addition. The clay added with monomer addition in reactor and in-situ polymerisation takes place.



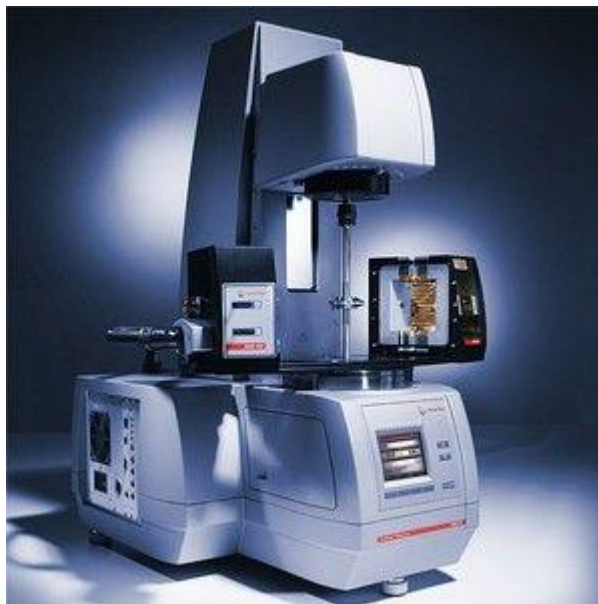
**Fig. 3.2** Experimental setup for synthesis of Acrylic Copolymer

### 3.3.2 Rheology

Viscosity is a measure of the ability of a material to resist flow, and reflects dissipation of deformational energy through flow. Material will respond to an applied force by exhibiting either elastic or viscous behaviour, or more commonly, a combination of both mechanisms. The combined behaviour is termed viscoelasticity. In rheological measurements, the deformational force is expressed as the stress, or force per unit area. The degree of deformation applied to a material is called the strain. Strain may also be expressed as sample displacement (after deformation) relative to pre-deformation sample dimensions.

The rheological behaviour of the acrylic copolymer of different weight percentage of Cloisite 30B nanoclay was measured using an Anton Paar rheometer (MCR 102, Anton Paar GmbH, Graz, Austria), which had recorded the viscosity and for varying shear rate.





**Fig 3.3** Anton Paar – MCR 102

### **3.3.3 Determination of acid value**

The procedure involves in determination of acid value is the dissolution of known weight of sample in DI water which is then titrated against a standardized solution of KOH(Potassium hydroxide) using phenolphthalein as end point indicator. At the end of titration, the colour of solution changes from colourless to pink. The acid values of polymers were determined by ASTM D1386 method.

### **3.3.4 Infrared Spectroscopy**

Infrared spectroscopy is very important characterisation when a polymer was synthesised. One of the great advantages of infrared spectroscopy is that virtually any sample in virtually any state can be examined. Fourier transforms infrared radiation (FITR) spectrometer calculates the transmission percentage of infrared. Here FT-IR spectrophotometer Nicolet 380 (shown in fig.3.3) was used to obtain IR spectra of prepared sample. For preparation of sample, synthesised resin first dried in oven and collected in powder form. In order to prepare pellet little quantity of potassium bromide (KBr) was segregated with powder sample and after that pressing of mixture was done. Analysis of that pellet was done using FITR by keeping the pellet in sample holder.



**Fig. 3.4** Nicolet 380 FT-IR Spectrometer

### 3.3.5 NMR Spectroscopy

Nuclear magnetic resonance frequency spectroscopy is a technique to determine molecule structure. It identifies the carbon-hydrogen framework of an organic compound which helps to determine molecular structure.  $^1\text{H}$ NMR spectra of the copolymer were recorded on a JEOL USA 400 Mhz spectrometer (shown in fig. 3.4) with upgraded console using  $\text{CDCl}_3$  as solvent and tetramethyl silane as internal standard.



**Fig. 3.5** JEOL USA 400 MHz Nuclear Magnetic Resonance Console

### 3.3.6 Thermal Analysis

Thermogravimetric analysis measures the amount and rate of change in mass of a sample as a function of temperature or time in a controlled atmosphere. The measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional analysis. The process was carried out in N<sub>2</sub> gas atmosphere. The compositional analysis can be done by the use of auto stepwise TGA where the TGA instrument automatically heats the sample at 3°C/min and then holds it under isothermal conditions when the instrument detects a significant weight loss. Thermogravimetric analysis can be utilising to determine the thermal stability of acrylic copolymer. If no weight change was observed in the polymeric sample in desired range of temperature then polymer will be considered as thermally stable. Thermogravimetric analysis(TGA) of acrylic copolymer and acrylic copolymer modified with Cloisite 30B was done on a Perkin-Elmer instrument (shown in fig. 3.5) from 25 to 600°C at a heating rate of 10°C/min by taking 1mg of powder sample. Cloisite 30B was analysed on thermograrvimetric analysis by heating rate 10°C/min between temperatures ranging from 25 to 900°C under nitrogen atmosphere.



**Fig. 3.6** Perkin-Elmer TGA 4000 analyser

### **3.3.7 Substrate preparation**

Surface treatment and right dimensions are important factors which affect bonding of adhesives with substrate. Two kinds of surface were used for the specimen. Corona treated metallised BOPP film and Nylon cloth (245GSM) after mild soap wash were used for testing of adhesive properties. Size of testing specimen was kept 50 x 200mm for metallised BOPP and 25 x 200mm for nylon cloth.

### **3.3.8 Adhesive sample preparation**

The sample of adhesive prepared by mixing the acrylic polymer/nanofilled polymer with epoxy resin Epotech TW 5001C in 75:25 ratio. The water based curing agent modified polyamine Epotec THW 4506 was added 80% on the basis of solid content of epoxy resin. Whole calculation was based on solid content of polymers. The prepared adhesive thinned upto application viscosity so that it could easily spread on substrate.

### **3.3.9 Curing**

Before testing of any sample complete curing is important. The prepared adhesive was applied on bopp substrate in the form of thin film on corona treated side. Then adhesive was covered with same corona treated side of bopp film and kept for drying at 40°C for 6 hours. All bopp sample were prepared by this curing method.

For nylon substrate, the prepared adhesive applied as thin film on surface of nylon and covered by other layer of nylon. The samples were kept at ambient condition for 48 hours to complete curing mechanism.

### **3.3.10 Peel strength**

ASTM D903 - 98(2010) is Standard Test Method for Peel or Stripping Strength of Adhesive Bonds. This test method covers the determination of the comparative peel or stripping characteristics of adhesive bonds when tested on standard-sized specimens and under defined conditions of pre-treatment, temperature, and testing machine speed.

The specimens were tested on an UTM – Stable Micro Systems: TA-HD Plus Texture Analyser tensile testing machine using standard testing fixtures. All samples tests were

carried out under monotonic loading at room temperature with speed of 10 mm/min. A minimum of three specimens for each surface condition was tested to achieve an average result. After each test, the failure load was recorded and fractured surfaces were examined visually.



**Fig. 3.7** UTM – Stable Micro Systems: TA-HD Plus Texture Analyser for peel strength analysis

## CHAPTER 4. RESULT AND DISCUSSION

### 4.1 Composition of Copolymer

S. No.	Ingredients	Weight%				
		1(0%)	2(0.5%)	3(1.0%)	4(2.0%)	5(3.0%)
1	DI Water	30.00	30.00	30.00	30.00	30.00
2	Ethanol	30.00	30.00	30.00	30.00	30.00
3	Acrylic Acid	6.00	6.00	6.00	6.00	6.00
4	Methacrylic Acid	6.00	6.00	6.00	6.00	6.00
5	Methyl Methacrylate	16.00	16.00	16.00	16.00	16.00
6	Butyl Acrylate	20.00	20.00	20.00	20.00	20.00
7	APS	0.40	0.40	0.40	0.40	0.40
8	Cloisite 30B	-	0.24	0.48	0.96	1.44

**Table 4.1** Composition of adhesives

The adhesives were prepared in round bottom flask placed in water bath kept in temperature 75-78°C. Time of reaction given is 1 hour at 75-78°C then cooled it down upto 60°C. and liquid ammonia was added to neutralise acidic groups. Different percentage of nanoclay Cloisite 30B was added 0.5%, 1.0%, 2.0% and 3.0% on the basis of monomer weight to modify acrylic resin. Measured weight of clay soaked in water for 24 hour then sonicated for 30 min before addition. In round bottom flask clay and cosolvent were added first then monomers were added under stirring followed by initiator addition. Temperature and time parameter was kept same as of neat acrylic resin synthesis and different modification of acrylic resin were obtained.

## 4.2 Properties of Resin

Different properties of prepared acrylic resins were checked. Solid content, acid value, solubility, and pH were checked to evaluate these resins and results are shown in table 4.2. Here pH plays an important role in solubility of polymer in water. At low pH, the carboxylic acid group of the copolymer are un-ionised and the polymer molecules become inefficiently hydrophilic. As pH increases the acidic group ionise and the polymer become hydrophilic and capable to inflate in water easily [35].

S.no	Properties	0% (Neat)	0.5%	1.0%	2.0%	3.0%
1	Solid Content	47.2%	47.6%	47.86%	48.42%	49.20%
2	Acid value	36-38	36-38	36-38	36-38	36-38
3	Solubility	Completely in Water	Completely in Water	Completely in Water	Completely in Water	Completely in Water
4	Appearance	Transparent	Turbid	Turbid	Turbid	Turbid
5	pH	7-8	7-8	7-8	7-8	7-8

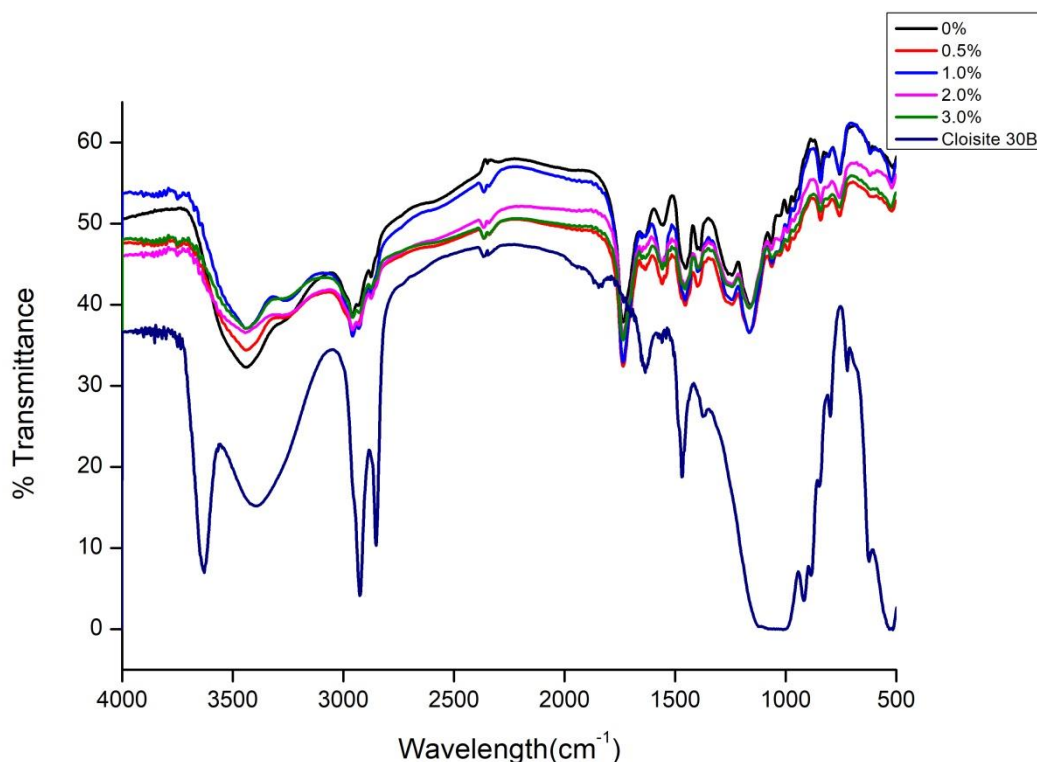
**Table 4.2** Properties of acrylic resins

## 4.3 Compositional Analysis

### 4.3.1 FTIR

All the prepared resin were characterised with IR to check functional group present. The results of IR shows that the peak around  $3437\text{cm}^{-1}$  wavenumber was assigned to the symmetric stretching vibration of primary amide N-H, the peak around  $1736\text{ cm}^{-1}$  wavenumber is assigned to the stretching vibration of C = O, the peak around  $1452\text{ cm}^{-1}$  wavenumber was assigned to the stretching vibration of C-N and the peak around  $1065\text{ cm}^{-1}$  is assigned to the stretching of C-O-C. The peak of  $3437\text{ cm}^{-1}$  shows that addition of liquid ammonia turned carboxyl into amide group. The presence of amide provides good water solubility of acrylic resins[36].

As Acrylic resin modified with cloisite 30B, FTIR analysis of cloisite 30B was also done. FTIR spectra of organo-modified layered silicates (cloisite 30B) show some characteristic peaks at 3629 and 3392  $\text{cm}^{-1}$  assigned to O–H stretching for the silicate and NH stretching of secondary amine respectively. The main characteristics of peaks of cloisite 30B were found, at 1012 and 1468  $\text{cm}^{-1}$ . These were assigned to Si–O–Si bending and methylene groups of the cloisite 30B, respectively[35]. The peaks at 2852–2925  $\text{cm}^{-1}$  were associated with C–H stretching.



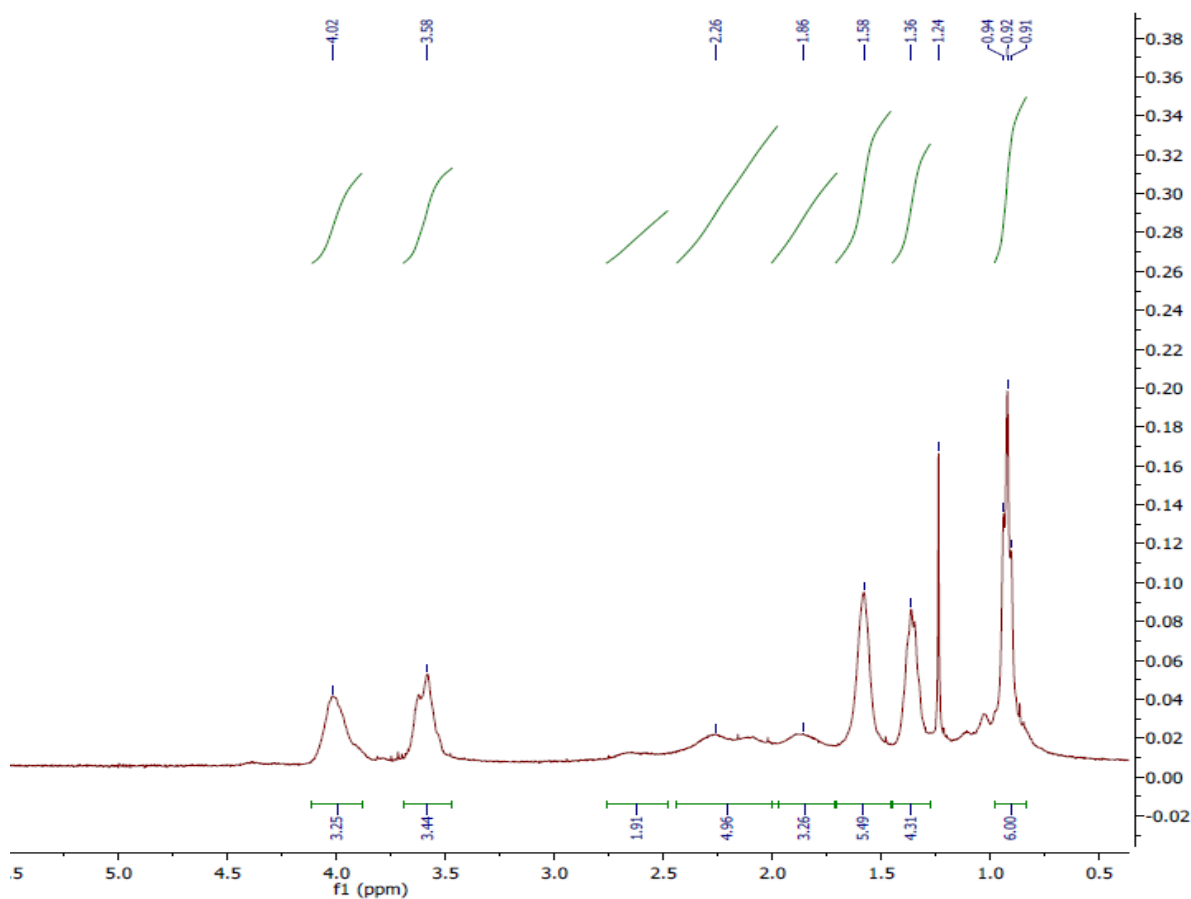
**Fig. 4.1** FTIR analysis of Acrylic copolymer and its modification with Cloisite 30B

In comparison of all these six spectra, it can be concluded that there is no obvious difference in the FTIR of acrylic resin and its modification with Clay. The acrylic/cloisite 30B didn't show the characteristic band of aluminosilicates (3629  $\text{cm}^{-1}$  for O–H stretching and 1012  $\text{cm}^{-1}$  for Si–O–Si stretching) which is because the polymer has multiple bands in the same spectral range and by far Acrylic is attached in large content to clay surface[37].



### 4.3.2 $^1\text{H}$ NMR

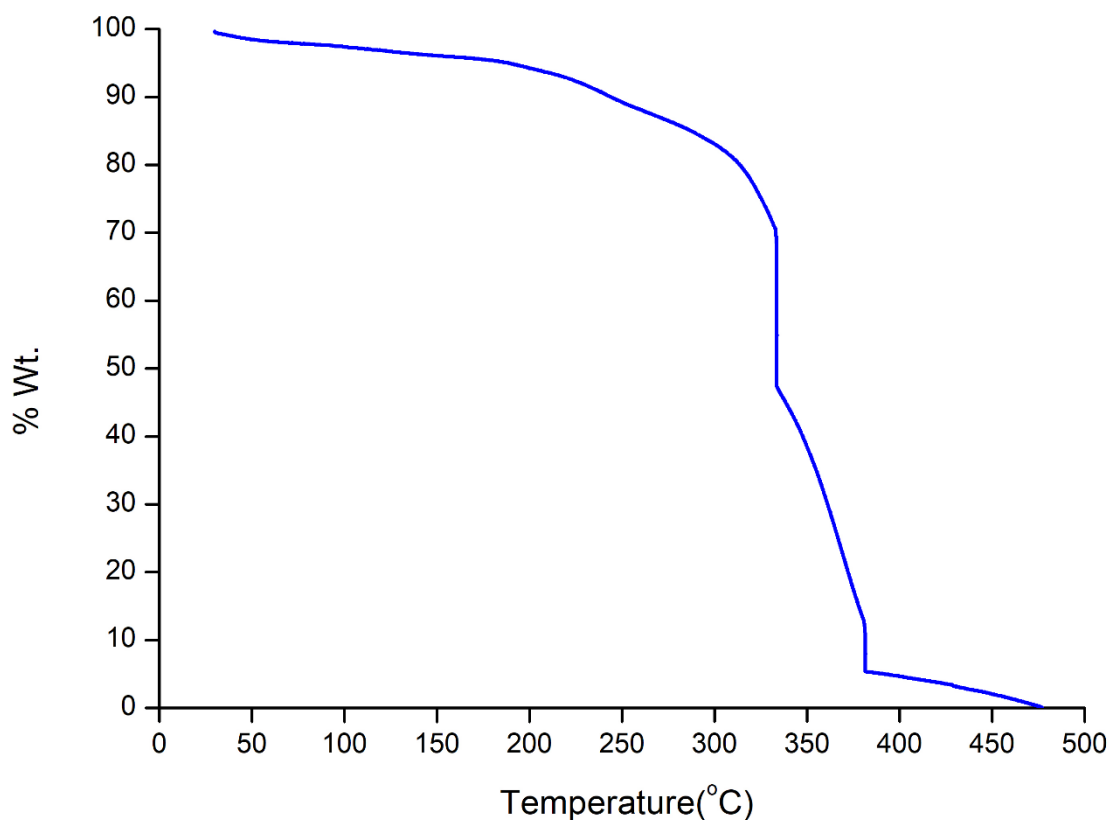
The NMR method has been used successfully in the study of homopolymers as well as acrylic copolymers. Model samples with a composition ladder provide a intense illustration of the effects of nearest and next nearest neighbours in the chemical shifts of species of interest. Fig. 4.2 shows  $^1\text{H}$  NMR spectra of Acrylic copolymer. The resonance signal due to  $-\text{O}-\text{CH}_3$  protons at  $\delta = 3.6$  ppm and  $\delta = 1.86$  are of MMA. The signal due to  $-\text{O}-\text{CH}_2$  proton of BA was observed at  $\delta = 4.0$  ppm[38]. The signal at  $\delta = 2.3$  ppm and at  $\delta = 1.6$  ppm are of AA[39]. A complex multiple was observed from  $\delta = 0.91$  ppm due to methylene groups of BA and  $-\text{CH}_3$  protons of MMA, MAA. With these chemical shifts it can be concluded that appropriate copolymer was formed with four monomers.



**Fig. 4.2**  $^1\text{H}$  NMR of Acrylic Copolymer

### 4.3.3 Isothermal TGA

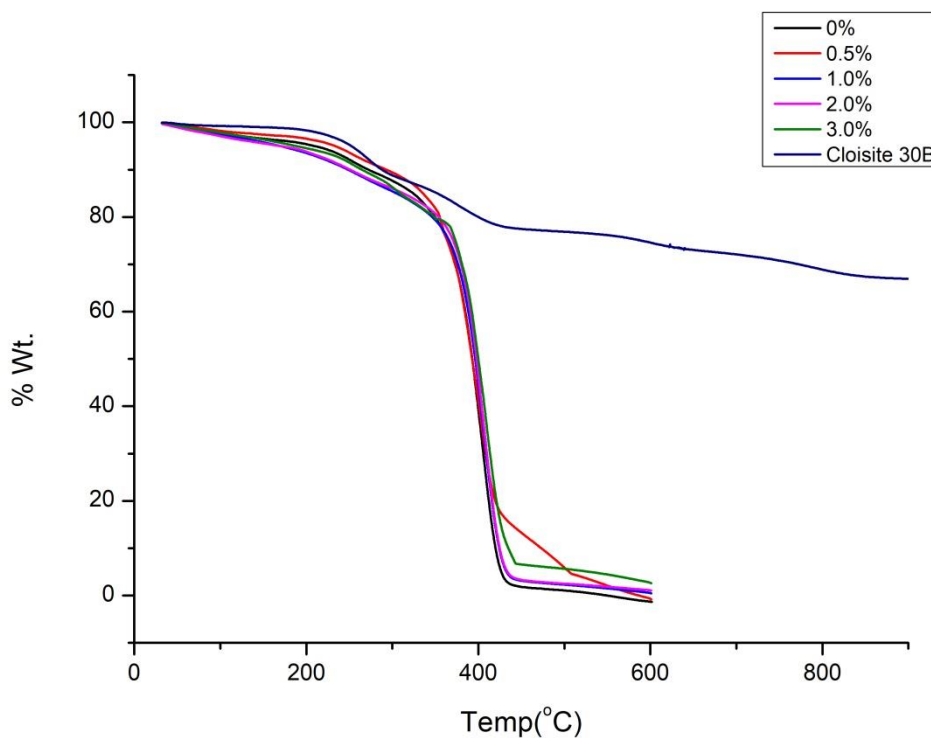
The compositional analysis can be improved through the use of auto stepwise TGA where the TGA instrument automatically heats the sample at 3°C/min and then holds it under isothermal conditions when the instrument detects a significant weight loss. Acrylic copolymer made up of four different monomers AA, MAA, BA and MMA. On the basis of thermal degradation curve of homopolymer [40][41][42][43] of individual monomer, this isothermal curve was analysed. Moisture was evaporated upto 100°C so the curve was divided into four segments after that. Through calculation it was interpreted that copolymer comprised of 11.50% of MAA, 12.00% of AA, 23.00% of MMA and 37.50% of BA which was well related with monomer feed ratio i.e. 12.5% of AA, 12.5% of MAA, 33.33% of MMA and 41.67% of BA. This result also confirms that copolymer is comprised of all four monomers.



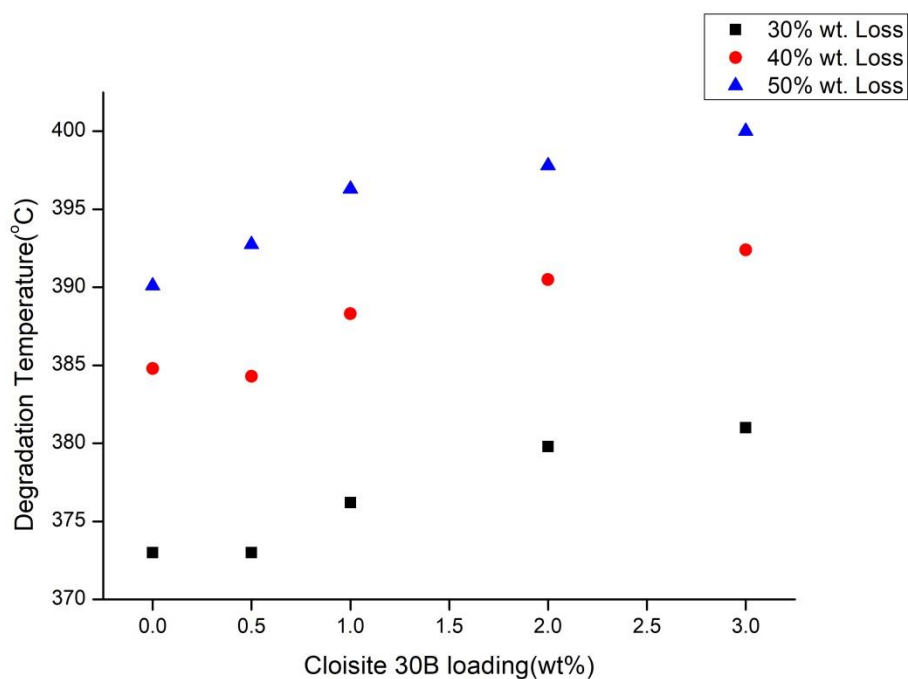
**Fig. 4.3** Isothermal TGA curve of Neat (0%) Acrylic copolymer

## 4.4 Thermal Analysis

Thermal analysis was done with Thermal gravimetric analysis. TGA under inert environment had been a popular and valuable technique for examining the effect of nanofillers on degradation of polymers. In all the cases, the curves showed single-stage degradation. The percentage weight decrease as function of temperature for the neat(0%) acrylic copolymer polymer and its cloisite 30B filled nanocomposites were shown in Figures 4.3. Compared to the neat (0%) polymer, a small shift in the degradation temperature was observed upon the addition of cloisite 30B. This was presented more clearly in Figure 4.4, where the degradation temperature was plotted as a function of cloisite 30B loading. For example, compared to the neat polymer, the degradation temperature at the 30% mass loss was increased by 8°C and at the 50% mass loss was increased by 10°C after the addition of 3wt.% cloisite 30B . This could be attributed to the good dispersion of nanoclay inside the acrylic matrix, which helped cloisite 30B nanoclay to act as a physical barrier against degradation of the acrylic matrix.



**Fig. 4.4** TGA curve of acrylic copolymer, its modification with Cloisite 30B and of Cloisite 30B



**Fig. 4.5** Effect of Cloisite 30B loading. The 30% of the initial weight loss data were defined as temperature where 30% of the initial mass of sample disappeared and similarly other curves

The enhancement in thermal stability could be due to the different reasons [27]. Silicate layers were impermeable to gases and therefore decreased the permeation rate of the volatile products formed during decomposition. Silicate layers could act as heat insulator to the polymer matrix because of the formation of carbonaceous silicate chars on the clay surface, and these silicate chars could also act as adsorbing sites for the volatile products formed during decomposition.

The degradation temperatures at the 30% mass loss were 391°C, 398°C and 400°C for the neat(0%), 2.0 wt% and 3.0 wt.% Cloisite30B/Acrylic samples, respectively. Similarly, in [33] D. Haloi et al. reported 6°C increase in  $T_{\text{onset}}$  (initial degradation temperature) and 2°C increase in  $T_{\text{max}}$  (temperature at which the degradation rate is fastest) for 2% Cloisite 30B loading in Poly(2-ethylhexyl acrylate) PEHA.

## 4.5 Rheology

Rheology of Acrylic polymer Neat (0%) acrylic copolymer and 0.5% cloisite 30B loaded acrylic copolymer were tested for rheological behaviour. The viscosities of samples have been tested for solid content of 25% to make it comparable. Rheological behaviour has been observed on varying shear rate. At low shear rate polymeric solution of acrylic copolymer in DI water shows Newtonian behaviour and Non-Newtonian (shear thickening) behaviour at high shear rate. These two parameters of polymeric solution followed Eyring model completely. The equation of Eyring model is given below:

$$\sinh\left(\frac{\tau_{yx}}{A}\right) = -\frac{1}{B} \frac{dv_x}{dy}$$

Where A and B are the two parameters.

in Eyring model, if  $\tau_{yx} \rightarrow 0$ , which means very low shear force, and at that point

$$\sinh\left\{\frac{\tau_{yx}}{A}\right\} \rightarrow \frac{\tau_{yx}}{A}$$

Therefore as  $\tau_{yx} \rightarrow 0$ , the model shows Newtonian behaviour

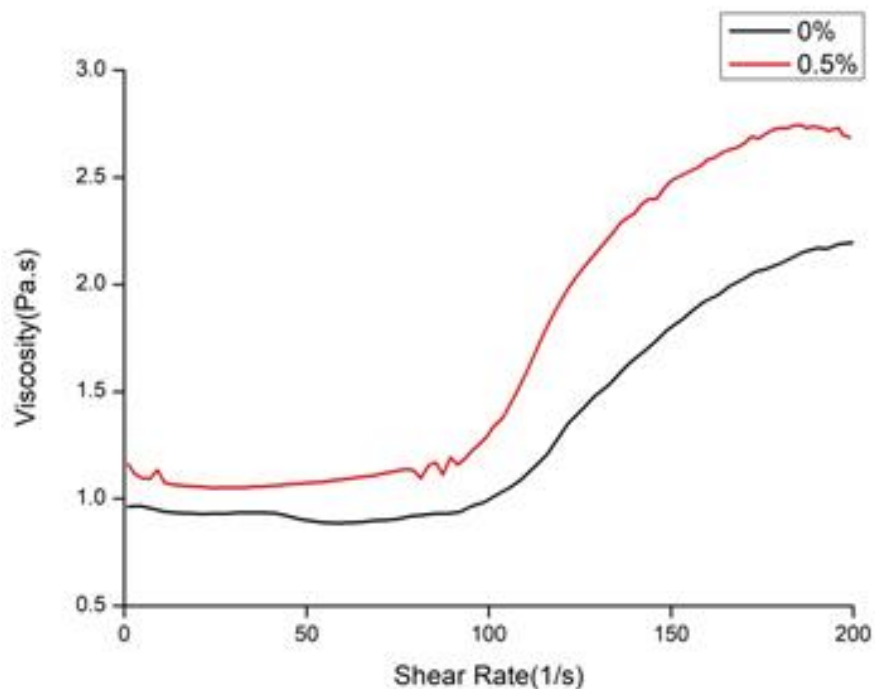
$$\tau_{yx} = -\frac{A}{B} \frac{dv_x}{dy}$$

Here viscosity = (A/B)

If  $\tau_{yx}$  is very large, the model shows Non-Newtonian behaviour. Which can be seen in Fig 4.6.

It is clearly seen in fig. 4.6 that shear rate upto  $100 \text{ s}^{-1}$  polymers are showing Newtonian behaviour and viscosity of neat acrylic copolymer and 0.5% nanoclay filled polymer is around 0.82 Pa.s and 1.10 Pa.s respectively. At higher shear from  $100 \text{ s}^{-1}$  to  $200 \text{ s}^{-1}$  Non-newtonian behaviour can be seen in fig. 4.6. for both the polymer and it ranges from 1.00 – 2.20 Pa.s for neat acrylic and 1.3 – 2.68 Pa.s for nanoclay filled polymer.

The viscosity of 0.5% nanoclay filled polymer has been increased equivalently this could be because nanoparticles of cloisite 30B filled up the space between polymeric chains and increased the viscosity of nanofilled polymer.



**Fig. 4.6** Rheology of Neat (0%) Acrylic copolymer and Acrylic/0.5% Cloisite 30B Nanofilled copolymer

## 4.7 Peel Strength

Peel strength is a method to determine bond strength of a material, particularly of an adhesive. Peel strength is the average load per unit width of bond line required to separate bonded materials where the angle of separation is 180 degrees. The adhesive strength is evaluated on the adhesion of bopp–bopp and nylon-nylon by the peel strength measurements.

Sample	180° Peel Strength (N/25mm) for Nylon cloth	180° Peel Strength (N/50mm) for Metallised BOPP Film
0% (Neat)	6.09 ± 0.5	5.99 ± 0.5
0.5%	7.90 ± 0.5	6.13 ± 0.5
1.0%	8.17 ± 0.5	6.70 ± 0.5
2.0%	11.02 ± 0.5	6.76 ± 0.5
3.0%	2.80 ± 0.5	4.68 ± 0.5

**Table 4.3** Adhesion property in terms of Peel strength of Nanocomposite adhesive

From the results in table 4.3, it can be determined that peel strength of nanocomposite with epoxy and crosslinking agent is increases upto 2.0% loading of nanoclay than decreases sharply in both the samples. In case of nylon cloth the roughness and air permeability of fabric plays an important role in higher bond strength in comparison to metallised BOPP film. The reason could be lesser roughness and no permeability of air which affect curing mechanism as well. So, upto 2.0% nanoclay could be added in acrylic copolymer to improve peel strength for different substrate.

## CHAPTER 5. CONCLUSION

---

This project was carried out with the aim of developing a water soluble high heat resistant Acrylic adhesive with nanofiller. The FTIR, NMR and isothermal TGA curve analysis shows that appropriate copolymer was formed with four monomers. The polymer formed was completely water soluble and its modification also. The solid content of each polymer was in the range of 45-50%. The viscosity of polymer was increasing with addition of nanofiller and shows shear thickening behaviour at higher shear rate. Degradation temperature at 50% wt. loss was successfully obtained 400°C (maximum) for 3.0% filled nanocomposite. Addition of nanoclay shows very slight improvement in degradation temperature. The peel strength results shows that there is improvement upto 2.0% loading of nanoclay then peel strength decreased drastically for 3.0% loading on that basis 2.0% formulation can be considered as best among these five variation and final composition is given as:

S. No.	Ingredients	Weight%
1	DI Water	27.43
2	Ethanol	27.43
3	Acrylic Acid	5.50
4	Methacrylic Acid	5.50
5	Methyl Methacrylate	14.62
6	Butyl Acrylate	18.28
7	APS	0.36
8	Cloisite 30B	0.88
	Total	100.00

**Table 5.1** Final composition of Adhesive



Nanoclay improved solid content, viscosity, and degradation temperature and peel strength. The results of this study indicate that the nanoclay(Cloisite 30B) filled acrylic copolymer consists of AA,MAA, MMA and BA has a good potential to use in high performance adhesive application area.

## REFERENCES

---

- [1] A. Pizzi, K.L. Mittal, “ *Handbook of Adhesive Technologies*,” Second Edition, Basel, Marcel Dekker, Inc. 2003.
- [2] P. U. Zhaobin, C. Yan, Z. Le, W. Lixi, and Z. Qitu, “Preparation of water soluble acrylic resin adhesive for fluorescent lamps and its modification,” vol. 30, pp. 1–4, 2011.
- [3] R. Cited, “United States Patent [ 191 Patent Number : Date of Patent :,” pp. 2–5, 1988.
- [4] H. P. Water-based and S. Adhesives, “N H e o w u t o r n s,” vol. 1, no. 19, 2013.
- [5] I. B. Yuan, P. A. Us, R. Lion, and P. A. Us, “( 12 ) United States Patent,” vol. 2, no. 12, 2013.
- [6] G. Company, “United States Patent [ 19 ],” 1999.
- [7] B. P. Corporation, “( 19 ) United States,” vol. 1, no. 19, pp. 1–5, 2012.
- [8] A. Data, “Ulllited States Patent [ 19 ] [ 11 ] Patent Number : [ 45 ] Date of Patent :,” pp. 4–8, 2000.
- [9] F. Application and P. Data, “IIIIIII-III,” no. 19, 1997.
- [10] G. H. Maplewood, D. S. Paul, J. White, B. Lake, and W. Stillwater, “United States Patent [ 191,” vol. 57030776, pp. 3–8, 1997.
- [11] Z. Spitalsky, D. Tasis, K. Papagelis, C. Galiotis, “Carbon nanotube–polymer composites:chemistry, processing, mechanical and electrical properties,” *Prog Polym Sci*, vol.35,pp. 357–401, 2010.

- [12] S. Bose, R.A. Khare, P. Moldenaers, "Assessing the strengths and weaknesses of various types of pre-treatments of carbon nanotubes on the properties of polymer/carbon nanotubes composites," *Polymer*, vol.51, pp.975–93, 2010.
- [13] S. Kango, S. Kalia, A. Celli, J. Njuguna, Y. Habibi, R. Kumar, "Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites—a review," *Prog Polym Sci*, vol.38, pp.1232–61, 2013.
- [14] O.M. Folarin, E.R. Sadiku, A. Maity, "Polymer-noble metal nanocomposites: review," *Int J Phys Sci*, vol.6, pp.4869–82, 2011.
- [15] S. Pavlidou, C.D. Papaspyrides, "A review on polymer–layered silicate nanocomposites," *Prog Polym Sci* vol.33, pp.1119–98, 2008.
- [16] A.A. Azeez, K.Y. Rhee, S.J. Park, D. Hui, "Epoxy clay nanocomposites – processing, properties and applications: a review," *Compos Part B: Eng*, vol.45, pp.308–20, 2013.
- [17] C. S. Triantafillidis, P.C. LeBaron, T.J. Pinnavaia, "Homostructured mixed inorganic– organic ion clays: a new approach to epoxy polymer-exfoliated clay nanocomposites with a reduced organic modifier content," *Chem Mater*, vol.14, pp.4088–95, 2002.
- [18] A. Bonnefond, M. Paulis, J. R. Leiza, and M. Mic, "Synthesis of waterborne acrylic / clay nanocomposites by controlled surface initiation from macroinitiator modified montmorillonite," vol. 48, pp. 896–905, 2012.
- [19] "Annual Book of Astm Standards."
- [20] Z. Czech, "Solvent-based pressure-sensitive adhesives for removable products," *Int. J. Adhes. Adhes.*, vol. 26, no. 6, pp. 414–418, 2006.
- [21] D. Sowa, Z. Czech, and Ł. Byczyński, "Peel adhesion of acrylic pressure-sensitive adhesives on selected substrates versus their surface energies," *Int. J. Adhes. Adhes.*, vol. 49, pp. 38–43, 2014.
- [22] X. Lu, G. Cao, Z. Niu, and Q. Pan, "Viscoelastic and adhesive properties of single-component thermo-resistant acrylic pressure sensitive adhesives," *J. Appl. Polym.*

- Sci.*, vol. 131, no. 7, pp. 1–10, 2014.
- [23] C. J. Kuo and J. Chen, “Synthesis of high-solid-content , acrylic pressure-sensitive adhesives by solvent polymerization,” vol. 46257, pp. 1–9, 2018.
- [24] X. Zhang, Y. Ding, G. Zhang, L. Li, and Y. Yan, “Preparation and rheological studies on the solvent based acrylic pressure sensitive adhesives with different crosslinking density,” *Int. J. Adhes. Adhes.*, vol. 31, no. 7, pp. 760–766, 2011.
- [25] C. Houtman, S. Severtson, J. Guo, H. Xu, and L. Gwin, “Properties of water-based acrylic pressure sensitive adhesive films in aqueous environments,” *TAPPI 8th Research Forum Recycling*, pp. 1–6, 2007.
- [26] M. Noro and P. E. J. Briggs, “United States Patent ( 19 ) U . S . Patent,” no. 19, 1987.
- [27] T. V. Brantseva, S. V. Antonov, and I. Y. Gorbunova, “Adhesion properties of the nanocomposites filled with aluminosilicates and factors affecting them: A review,” *Int. J. Adhes. Adhes.*, vol. 82, no. December 2017, pp. 263–281, 2018.
- [28] M. U. Chida, “Microstructure and Physical Properties of Acrylic Rubbers Filled with Montmorillonite in the Emulsion Polymerization Process by,” vol. 59, no. 7, pp. 553–559, 2010.
- [29] M. S. Nazir, M. Haa, and M. Kassim, “Nanoclay Reinforced Polymer Composites,” pp. 35–56, 2016.
- [30] V.R. Gowarikar, N.V. Vishwanathan, J. Shreedhar, “ *Polymer Science*,” Second edition, Delhi: New age interational publishers, pp. 60-61,1986
- [31] G. Diaconu, M. Paulis, and J. R. Leiza, “High solids content waterborne acrylic/montmorillonite nanocomposites by miniemulsion polymerization,” *Macromol. React. Eng.*, vol. 2, no. 1, pp. 80–89, 2008.
- [32] M. Mičušík *et al.*, “Morphology of polymer/clay latex particles synthesized by miniemulsion polymerization: Modeling and experimental results,” *Macromol. React. Eng.*, vol. 4, no. 6–7, pp. 432–444, 2010.

- [33] D. J. Haloi and N. K. Singha, "Synthesis of poly(2-ethylhexyl acrylate)/clay nanocomposite by in situ living radical polymerization," *J. Polym. Sci. Part A Polym. Chem.*, vol. 49, no. 7, pp. 1564–1571, 2011.
- [34] L. Wang, X. Shui, X. Zheng, J. You, and Y. Li, "Investigations on the morphologies and properties of epoxy/acrylic rubber/nanoclay nanocomposites for adhesive films," *Compos. Sci. Technol.*, vol. 93, pp. 46–53, 2014.
- [35] M. R. Bagherzadeh and T. Mousavinejad, "Preparation and investigation of anticorrosion properties of the water-based epoxy-clay nanocoating modified by Na<sup>+</sup>-MMT and Cloisite 30B," *Prog. Org. Coatings*, vol. 74, no. 3, pp. 589–595, 2012.
- [36] R. Cited *et al.*, "Preparation of water soluble acrylic resin adhesive for fluorescent lamps and its modification," vol. 1, no. 19, pp. 1–4, 2013.
- [37] P. Bhagabati, T. K. Chaki, and D. Khastgir, "Panoptically exfoliated morphology of chlorinated polyethylene (CPE)/ethylene methacrylate copolymer (EMA)/layered silicate nanocomposites by novel in situ covalent modification using poly( $\epsilon$ -caprolactone)," *RSC Adv.*, vol. 5, no. 48, pp. 38209–38222, 2015.
- [38] S. Mondal, B. Gupta, and H. Singh, "Acrylic monomers based emulsion copolymer for coating application," *Indian J. Fibre Text. Res.*, vol. 30, no. 2, pp. 184–189, 2005.
- [39] R. Laqo, P. J. Ortiz and R. Martinez, "Characterisation of acrylic copolymers by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy" vol. 38, no. 7, pp. 440–443, 1987.
- [40] M. C. Costache, D. Wang, M. J. Heidecker, E. Manias, and C. A. Wilkie, "The thermal degradation of poly(methyl methacrylate) nanocomposites with montmorillonite, layered double hydroxides and carbon nanotubes," *Polym. Adv. Technol.*, vol. 17, no. 4, pp. 272–280, 2006.
- [41] H. G. Schild, "Thermal Degradation of Poly (methacrylic acid): Further Studies Applying TGA/ FTIR," *J. Polym. Sci. Part A Polym. Chem.*, vol. 31, no. 9, pp. 2403–2405, 1993.

- [42] C. Samart, P. Prawingwong, S. Amnuaypanich, H. Zhang, K. Kajiyoshi, and P. Reubroycharoen, "Preparation of poly acrylic acid grafted-mesoporous silica as pH responsive releasing material," *J. Ind. Eng. Chem.*, vol. 20, no. 4, pp. 2153–2158, 2014.
- [43] H. Li *et al.*, "Synthesis and characterization of brush-like multigraft copolymers PnBA-g-PMMA by a combination of emulsion AGET ATRP and emulsion polymerization," *J. Colloid Interface Sci.*, vol. 453, pp. 226–236, 2015.