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Copolymerized Urea Formaldehyde Based Binder and their Characterization

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ABSTRACT

Modified urea formaldehyde (MUF) resin was prepared by the copolymerization of urea formaldehyde (UF) with polyvinyl acetate (PVAc) and butyl acrylate (BA) using various ratios i.e., 50:50, 60:40, 70:30 of (UF: PVAc) and 50:50, 60:40, 70:30 of (UF: BA). The physicochemical properties were determined by the standard methods. The comparison of the physical properties of the modified urea formaldehyde resin showed the improvement in viscosity, density and melting point at 70:30 ratio of (UF: PVAc). Copolymerized urea formaldehyde resin with polyvinyl acetate significantly reduced the formaldehyde emission at 70:30 (UF: PVAc) ratio as compared to similar ratio of butyl acrylate binder 70:30 (UF: BA). Findings indicate that MUF can be utilized as cheap binder for emulsion paint formulation due to its lower level of formaldehyde emission.

Keywords: Urea-formaldehyde, Polyvinyl acetate, Butyl acrylate, Copolymerization, Formaldehyde emission.

1. INTRODUCTION

Urea-formaldehyde is a thermosetting resin which has high heat distortion temperature, surface hardness, tensile strength, elongation at break, volume resistance and low water absorption. These resins have applications in particle board, MDF, adhesives, finishes, molded objects, in automobile tires to enhance the bonding of rubber to tire cord, in paper to improve tear strength and in molding electrical devices[1-2]. Urea formaldehyde can be utilized in the coating industry if the problems associated with the UF resin are eliminated[3].

Polyvinyl acetate also known as wood glue is a rubber like thermoplastic polymer with the formula $(C_4H_6O_2)_n$. Polyvinyl acetate emulsions are used as adhesives for wood, paper, cloth, as industrial coatings, as a binder and in textile finishing[4]. Acrylics are the thermosetting plastic substances made from acrylic acid or methacrylic acid. Polymethyl acrylate is used in lacquer, textile finishes and adhesives[5]. Paints containing greater amounts of acrylic resins ensure the stain protection, water resistance, improved adhesion, resistance against cracking and blistering[6-8].

Formaldehyde emission is the major environmental challenge with UF resins and hence creating problems of environmental pollution. Hence, the reduction of this pollutant is an important environmental requirement[9-10]. For the safety purpose, alternative raw materials are being used to produce the new formulation and to control the amount of volatile organic compounds. Many efforts are being made in amino resin technology to reduce the formaldehyde emission during the last few decades. It will result in the production of formaldehyde free products and to meet the standard requirements for each type of composite.

An approach to reduce the formaldehyde emission by decreasing the mole ratios of F/U was used, which not only reduced the formaldehyde but also affected the other properties[11]. Osemeahon et al used 2:1 ratio of F/U to reduce the formaldehyde emission. Other modifications with other additives are also reported[12]. Previous applications include the lowering of formaldehyde emission by using acetals. Different studies have turned the attention to formaldehyde free adhesives i.e. soy-bean and isocyanate based adhesives. Study of soy protein as formaldehyde scavenger has also been reported[13]. Copolymerization of methylol urea and polyester in the presence of varying concentrations of TEA (Triehanolamine) produced a copolymer composite with a considerable reduction in formaldehyde emission[14].

Coating industry is now using the synthetic resin instead of natural resin because of the applications associated with the synthetic resin such as hardness, durability and resistance to water. Various modifications have set a new trend of research in the resin synthesis[15-16]. For the enhancement of the outstanding physical, mechanical and chemical properties, blending is an important process. By blending we can achieve a wide range of inaccessible applications[17]. It is an important way of getting new materials having properties slightly different from the pure components. Modifications of urea formaldehyde resin resulted in the production of the efficient binder in emulsion paint formulation[18-25].

This study investigated the chemical structure of modified urea formaldehyde resin. The aim of this study is to undertake the copolymerization of urea formaldehyde with polyvinyl acetate and butyl acrylate to form a reduced formaldehyde coating product.

2. MATERIALS AND METHODS

2.1 Reagents/Chemicals

All the reagents used during the study program were analytical grade. The reagents used include distilled water, urea, formaldehyde, sodium hydroxide, sodium dihydrogen phosphate, polyvinyl acetate, butyl acrylate etc.

2.2 Synthesis of urea formaldehyde resin

Urea formaldehyde was prepared by using the one step process (OSP) as reported by Osemeahon and Barminas[26]. The resin was prepared by treating 12 g of urea with 48.6 mL of formaldehyde 37% (w/v) by using 0.4 g of sodium dihydrogen phosphate as a catalyst. The initial pH was adjusted to pH 6 by using 0.1 M sodium hydroxide solution and temperature was raised to 70 °C for 1 hour with continuous stirring. The reaction was monitored through viscosity measurement. After cooling, it was kept for 24 hours at ambient conditions.

2.3 Copolymerization reaction

Polyvinyl acetate (48%) and butyl acrylate (52%) solutions were further diluted to 50% to make the desired concentration of the solution to react with urea formaldehyde resin. Copolymerization of urea formaldehyde was carried out by preparing the various concentration ratios with polyvinyl acetate and butyl acrylate i.e., 50:50, 60:40, 70:30 of (UF: PVAc) and 50:50, 60:40, 70:30 of (UF: BA) at 25 °C. Copolymerization was carried out after 24 hours of resin synthesis. The further tests of these six copolymerized resins samples were performed after 24 hours.

2.3.1 Determination of formaldehyde emission

25 mL of sodium sulfite (1 M) solution was taken in a flask. 1 g of the sample was put into the flask. 2 or 3 drops of phenolphthalein indicator were added into the flask and the solution was titrated against sulfuric acid (0.5 N). The amount of formaldehyde present in each sample was calculated by using the formula:

$$\text{HCHO emission} = N \times V \times 3.005/W$$

N= Normality of sulfuric acid, V= Volume of sulfuric acid used for titration, W= Weight of sample taken, End point: pink to colorless.[27]

After copolymerization their viscosity, density, turbidity, refractive index, moisture uptake,dry solid mass and formaldehyde emission were measured according to standard procedures. Their FT-IR spectra were also obtained for the confirmation of reaction.

3. RESULTS AND DISCUSSION

Modified urea formaldehyde (MUF) resin was prepared by the copolymerization of urea formaldehyde (UF) with polyvinyl acetate (PVAc) and butyl acrylate (BA) using various ratios i.e., 50:50, 60:40, 70:30 of (UF: PVAc) and 50:50, 60:40, 70:30 of (UF: BA). The physicochemical properties were determined by the standard methods. Results are described in the table-1.

Table 1. Characteristics of MUF Resin blends synthesized in this study

Sample Composition	Viscosity (cP)	Density (g/cm^3)	Melting Point (°C)	Turbidity (NTU)	Refractive Index	Moisture Uptake (g)	Solid Content (%)	HCHO Emission (%)
A. (50:50) UF:PVAc	25.8	1.117	220	38.15	1.3706	0.04	0.98	1.95
B. (60:40) UF:PVAc	38.3	1.139	240	50.73	1.3723	0.03	0.99	1.05
C. (70:30) UF:PVAc	90.9	1.154	260	56.1	1.3788	0.02	1.0	0.75
D. (50:50) UF: BA	21.09	1.096	230	71.5	1.3836	0.05	0.97	1.5
E. (60:40) UF: BA	34.21	1.097	240	77.7	1.3847	0.03	0.98	1.2
F. (70:30) UF: BA	86.23	1.134	250	83.2	1.3854	0.01	0.99	1.05
G. (100%) UF	98	1.192	200	126.1	1.4089	0.03	0.99	4.5

Influence of polyvinyl acetate and butyl acrylate concentration on the viscosity of UF (Fig. 1). In the beginning with the equal levels of UF with PVAc and BA, it was observed that viscosity lowered which may be due to polymer dissociation. Furthermore, increase in viscosity of MUF was observed by increasing the UF concentration.[28-30].

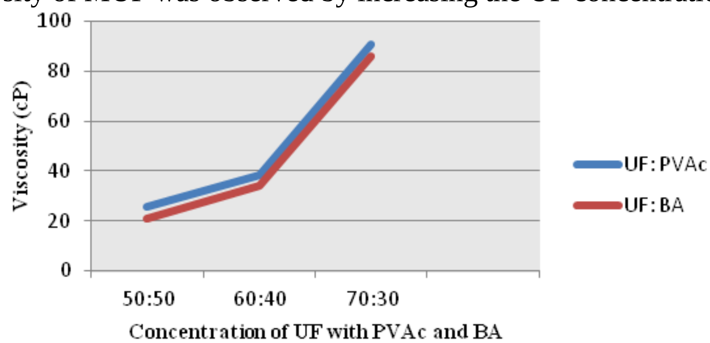

Figure 1. Effect of PVAc and BA Concentration on the Viscosity of UF

Effect of polyvinyl acetate and butyl acrylate concentration on the density of UF has been shown in the fig. 2. It can be observed that the density of modified UF increases with increase in UF concentration. Sharp increase is observed by increasing the composition of UF with BA from 60 to 70%. This result is attributable to the packing nature of resin molecules. Density depends on free volume and packing efficiency of molecular chains. The increase in density with increase in molecular weight indicates efficient molecular packing[31-32].

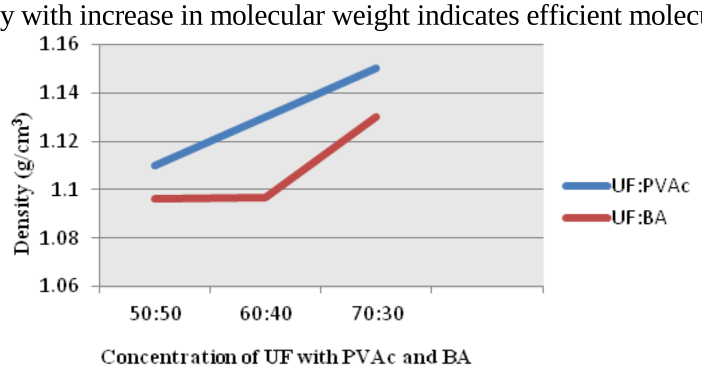

Figure 2. Effect of PVAc and BA Concentration on the Density of UF

Figure 3. shows the effect of PVAc and BA concentration on the melting point of UF resin. The increase in melting point at 70% composition of (UF:PVAc) as compared to (UF:BA) suggests that the increase in molecular weight makes the material harder due to the enhancement of the cross linking of the polymer. The melting point of a polymer has a direct effect on its thermal property. It is related to its molecular weight, degree of cross-linking and level of rigidity of the polymer[34]. Molar mass, rigidity, intermolecular interactions, and fundamental hard structure results in the increase of melting point[35].

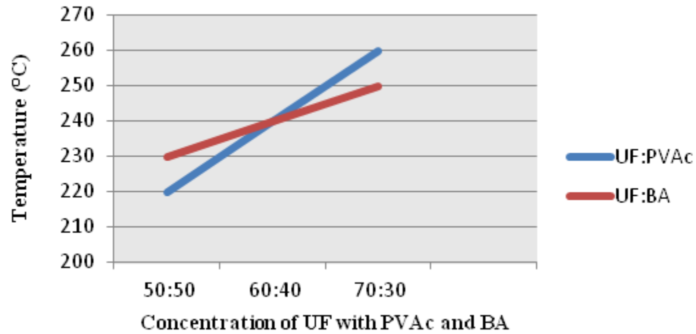

Figure 3. Effect of PVAc and BA Concentration on the Melting point of UF

Turbidity is an indication of the interchain cross-linking[33]. Turbidity value is generally low at 50% concentration because solution in this case is clear. As the concentration of UF increases, the large particles growth increases and hence the turbidity is increased. The more the UF concentration with BA, there is more scattering of light and hence increased turbidity is observed as shown in Figure 4.

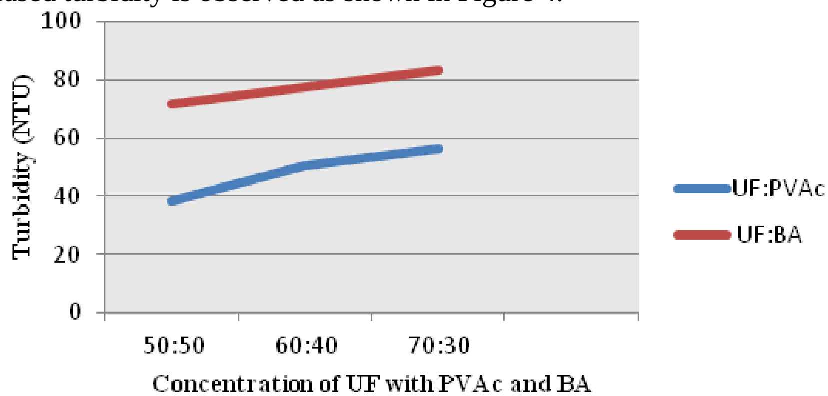

Figure 4. Effect of PVAc and BA Concentration on the Turbidity of UF

Measure of the ability of the coated surface to reflect light is called gloss. Considering the surface aesthetic or decoration, gloss is an important property[36-37]. Reflection of light and smoothness of the paint is indicated by the gloss. This property is exhibited mainly in the oil paints. The effect of PVAc and BA concentration on the refractive index of UF is shown in Table 1. It is observed that among all the compositions, higher refractive index value is observed at 70:30 (UF:BA) composition as shown in Figure 5. This is due to the increase in molecular weight and hence the interaction with the light also varied resulting in the increase of refractive index. Packing nature of resin molecules also affects the refractive index values[38].

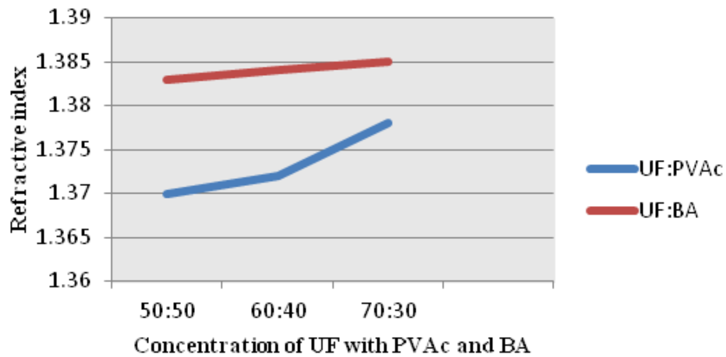

Figure 5. Effect of PVAc and BA Concentration on the refractive index of UF

Figure 6. shows the effect of PVAc and BA concentration on the moisture uptake of UF resin. It is observed that the moisture uptake of MUF decreases with increase in UF concentration. The possible reason for this development may be due to decrease in the molecular size holes in the polymer structure with increase in UF concentration[45-46]. Interaction between the UF and BA results in the increase in crosslinking, narrowing the intermolecular spacing within the matrix and hence reduction in the moisture uptake. Water uptake affects the essential properties of the polymer material such as the physical, mechanical, thermal and structural properties. In the paint-making industry, the moisture uptake of the binder is very crucial because it is responsible for blistering of paint film[42-43]. One of the major drawbacks of UF resin is poor water resistance[44]. This needs to be improved for using the UF in coating industry.

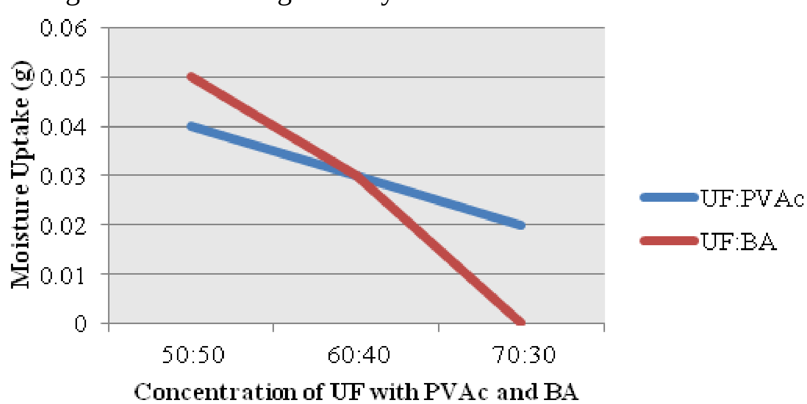

Figure 6. Effect of PVAc and BA Concentration on the moisture uptake of UF

Effect of PVAc and BA concentration on the solid content of UF resin. It can be observed that the solid content of UF resin increases with increase in the percentage composition as shown in Figure 7.

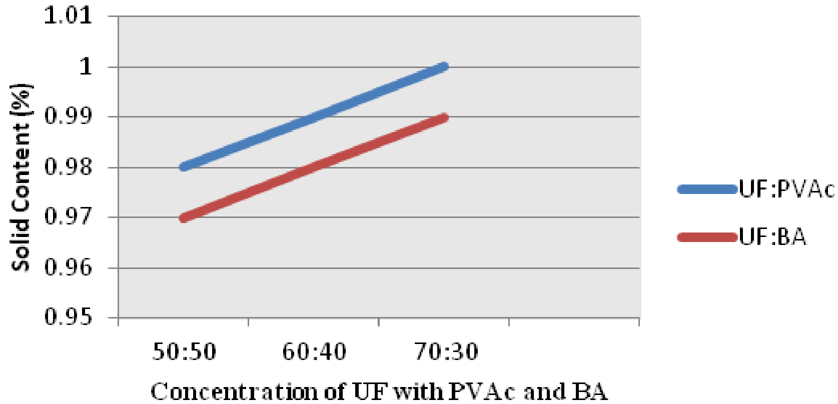

Figure 7. Effect of PVAc and BA Concentration on the solid content of UF

Figure 8. shows the effect of PVAc and BA concentration on the formaldehyde emission of UF. As the percentage concentration of UF increases, formaldehyde value is decreased. The reduction is maximum i.e. 0.75% at 70:30 composition of (UF: PVAc). This reduction might be due to the presence of PVAc behaving as obstacle in the matrix of UF resin and hence causing the difficulty for the reactive groups of urea and formaldehyde to come close and interact. It is necessary to determine the formaldehyde emission values before it is used as a paint coating[39]. Formaldehyde emission occurs because of hydrolysis of UF resin causing the sick building syndrome. Latex paints are known to have high emission of formaldehyde[40-41].

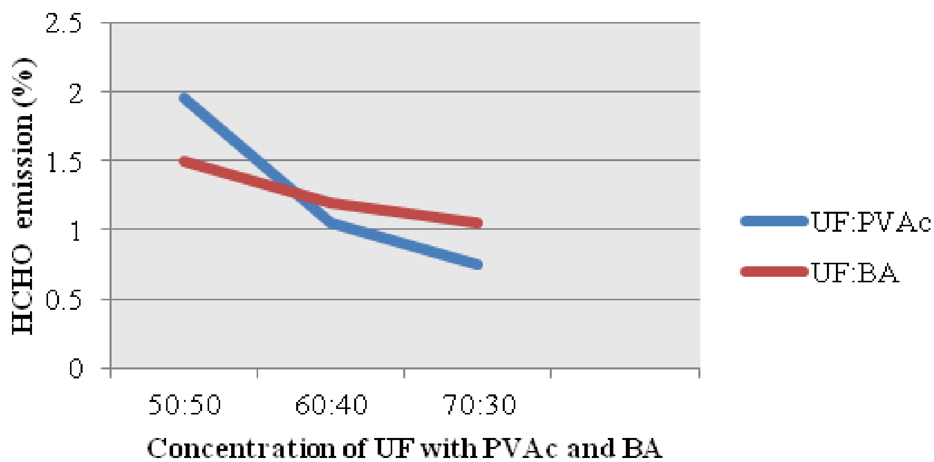

Figure 8. Effect of PVAc and BA Concentration on the HCHO emission of UF

Table 2. Appe arance and properties of Air-dried sample

Sample	Appearance	Properties
A (50:50) UF:PVAc		**White, shiny glass like, very hard layer**
B (60:40) UF:PVAc		**White, hard layer**
C (70:30) UF:PVAc		**White, powdered like**
D (50:50) UF:BA		**White, very hard layer**
D (60:40) UF:BA		**White, hard layer**
F (70:30) UF:BA		**White, powdered like**
G (100%)		**White, powdered like, easily scratch able layer**

3.9 FT-IR Analysis

FTIR spectroscopy is a very important tool which is used for the identification of functional groups. The spectra of UF, UF−PVAc and UF−BA are shown in Figures 9-11.
In the spectrum of UF (Figure. 9), the broad band stretching at 3332 cm^{-1} is due to (O−H), 1551 cm^{-1} is due to (N−H), 1241 cm^{-1} is due to (C=O), 1389 cm^{-1} is due to (–CH_2) and 1132 cm^{-1} is due to (C−O−C). All the above peaks of UF also appeared in the spectrum of UF−PVA and UF−BA resins.

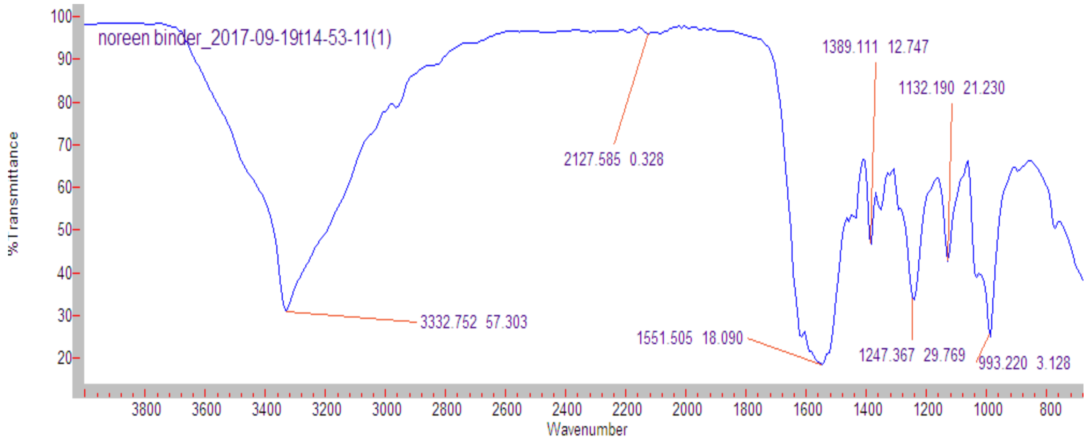

Figure 9. IR Spectra of UF

The graph of (UF−PVAc), (Figure. 10) showed the presence of –OH, N−H, $-CH_2-$, C−O−C, CO functional groups having corresponding peaks at 3336 cm^{-1}, 1632 cm^{-1}, 1372 cm^{-1}, 1242 cm^{-1} and 1126 cm^{-1} respectively.

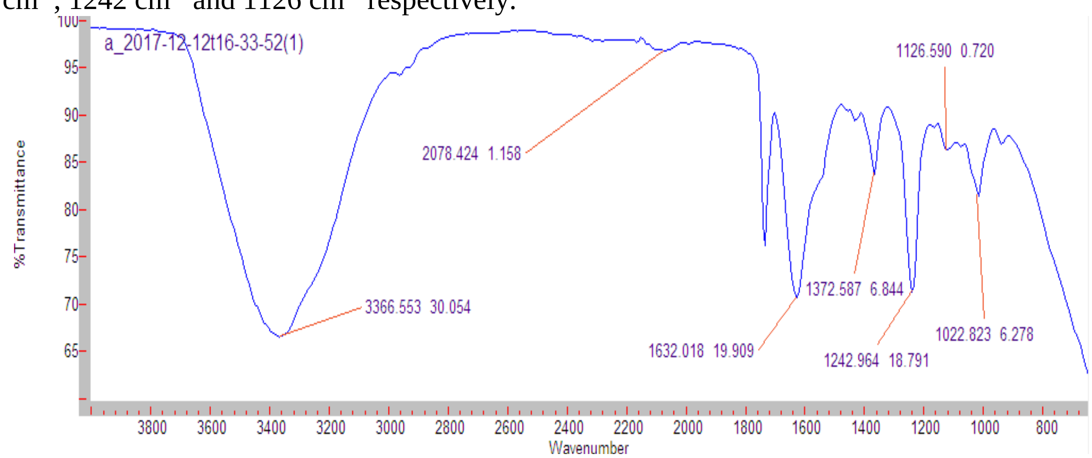

Figure 10. FT-IR Spectra of UF:PVAc

The graph of (UF−BA), (Figure. 11) showed the presence of –OH, N−H, C−O−C, CO functional groups having corresponding peaks at 3343 cm^{-1}, 1627 cm^{-1}, 1251 cm^{-1} and

1140 cm^{-1} respectively. The –OH, N−H, C−O−C and CO bands of UF shifted to the slightly different frequencies indicating the phenomenon of polycondensation, during the copolymerization reaction. These observations showed that the chemical reaction has taken place between UF with PVAc and BA.

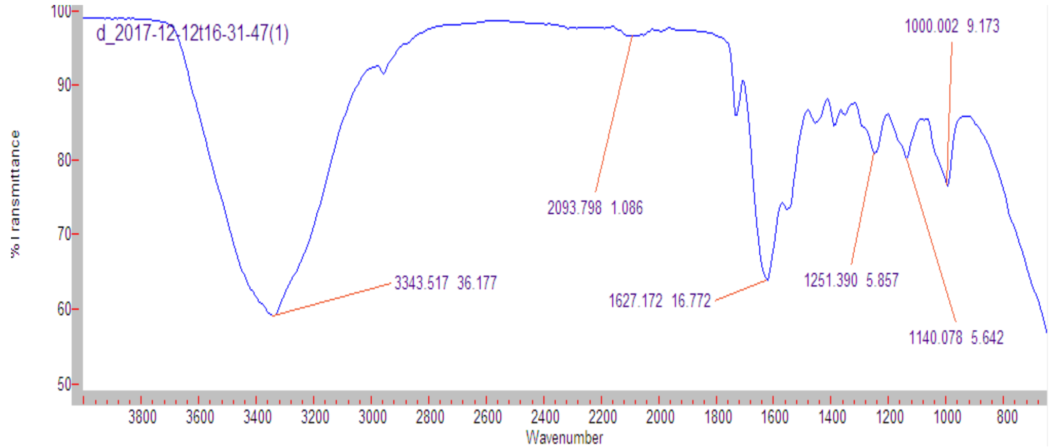

Figure 11. IR Spectra of UF: BA

CONCLUSION

Copolymerization reaction of urea formaldehyde with polyvinyl acetate and butyl acrylate was successfully carried out. The physical properties like viscosity, density, turbidity, melting point, moisture uptake, solid content, refractive index and formaldehyde emission levels were determined. The Infrared analysis confirmed that there is an interaction between UF resin and copolymerized resin. Copolymerized urea formaldehyde resin with polyvinyl acetate reduced the formaldehyde emission as compared to butyl acrylate at 70:30 (UF: PVAc) composition. Physical properties were assessed for its level by comparing with the permissible limits given by the coating industry and levels are in the safety baseline for human use indicating that the copolymer resins can be used as a binder for paint formulation.

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