

Synthesis and Characterization of an Emulsion Paint Binder from a Copolymer Composite of Trimethylol Urea/Polyethylene

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Abstract: To improve the the potentials of an emulsion paint binder production from urea formaldehyde, trimethylol urea (TMU) was synthesized and copolymerized by blending at varying concentrations (0 – 50%) with dissolved polyethylene (PE) waste. The blends were subjected to such tests as formaldehyde emission, moisture uptake and elongation at break, among others. Formaldehyde emission and moisture uptake of the blends decreases while the elongation at break increases with increase in the amount of PE. These basically show an improvement in the challenging properties of urea formaldehyde resins, that limits its utility as a binder in an emulsion paint formulation. Infrared spectra show the incorporation of the PE in the TMU, as the blends spectra intermeddle the spectra of PE and TMU. TMU/PE composite produced in this work therefore is more environmental friendly as an emulsion paint binder, and has improved such limiting properties as brittleness and high moisture uptake, compared to the pure TMU. The work also potentiates PE waste recycling.

Key words: Urea formaldehyde, Polyethylene, Copolymer composite, Paint binder.

1. Introduction

The life of a paint is that of the binder from which it is made [1]. Binders also called film-formers, stabilize the structural integrity of paint, as it cohesively holds other particles in the paint, and adhesively hold the paint to the substrate.

Emulsion (water based) paints and oil paints are the two classes of paint based on the solvent or dispersant i.e. water and organic solvents respectively. And the organic solvents are generally referred to as volatile organic compounds (VOCs). Typical oil paints have excellent characteristics, such as heat resistance, high strength, good resistance to corrosion, weather, water and chemicals, good adhesion, full gloss and flexibility [2]. Emulsion paints are typically inferior to the oil paints considering many of these properties, however the use of water as the thinner or dispersant presents emulsion paints to be cheaper, non-flammable, and environmental friendlier than the oil paint, and also as workable alternative in the quest to omit VOCs in paint formulation. The emission of VOCs from surface coatings has been under strict regulations by empowered regulatory agencies, with the intents to meet some safe environmental standards [3]. This presents the major challenge in the coating industry, while volumes of works have therefore been focused on the production of emulsion paints with characteristics that can competitively challenge those of the oil paints [4, 5].

Urea formaldehyde is a cheap, colourless water soluble thermosetting resin. It has found its major

2.2. Formation of liquid Polyethylene (PE)

Waste PE was cleaned before it was constituted into liquid by dissolving 5g of polyethylene with 50 ml of toluene into a conical flask, using a thermostatically control oil bath at about 135 °C. The mixture was stirred continuously and allowed to stay for 24hrs to achieve a homogenous solution and kept at room temperature (30 °C).

2.3. Copolymerization

This was carried out by blending serial concentrations (0-50%) of PE in TMU.

2.4. Determination of Formaldehyde Emission

Formaldehyde emission test was carried out using the standard 2 h desiccator test as described in Osemeahon and Archibong [9]. Average values of triplicate determinations were recorded.

2.5. Determination of Moisture Uptake

The resin films moisture uptake was determined gravimetrically as described in Osemeahon and Archibong [9]. Average value of triplicate determinations of each sample was recorded.

2.6. Determination of Viscosity and Gel Time

Viscosity measurements was carried out using 100 ml graduated glass macro-syringe at room temperature, as described in Osemeahon and Archibong [9]. Average value of triplicate determinations of each sample was recorded. The gel point of the resin was determined by measuring the viscosity of the resin with time until a constant viscosity profile was obtained.

2.7. Elongation at Break

The elongation at break was measured using Inston Tensile Testing Machine (Model 1026) based on ASTM D638. Five runs were carried out for each sample and the average elongation evaluated and expressed as the percentage increase in length.

2.8. Solubility in Water

Solubility of the resins in water was determined by mixing 1ml of the resin with 5ml of distilled water at room temperature (30°C).

2.9. Density, Turbidity, Melting Point and Refractive Index Determination

Density was measured by taking the weight of a known volume of resin inside a density bottle using metler (Model, AT400) weighing balance. Average value of five readings was taken for each sample. Turbidity of the resin samples was measured using Hanna microprocessor turbidity meter (Model, H193703). Melting points of the film samples was determined by using Galenkamp melting point apparatus (Model, MFB600-010F). The refractive indices of the resin samples were determined with Abbe refractometer. The above properties were determined according to standard method [10].

2. 10. FTIR Analysis

The infra-red (IR) analysis of TMU, PE and TMU/PE blend was carried out using infra-red spectrophotometer (Buck Scientific Inc, CT USA, Model M500) between 600 to 4000cm⁻¹.

3. Result and Discussion

3.1. FTIR Spectra

Fig. 1 presents the IR spectra of the resins. A is a spectra of pure Tri-methylol urea (TMU), B is the spectra

of the blend (TMU/PE) and C is the spectra of polyethylene resin (PE). For TMU (A), the broad band from 3700-3200 cm^{-1} can be attributed to absorption by OH, H bonded OH stretching vibration and NH, while the small narrow picks can be attributed to non-bonding OH stretching vibrations. The peaks at 3000-2700 cm^{-1} can be associated with sp^3 C-H stretching vibration, while the sharp peak at 2280-2240 cm^{-1} can be associated with aliphatic nitriles on the Condensed UF polymer. Peaks between 1650-1150 cm^{-1} can be progressively associated the stretching carbonyls (C=O), alkyl substituted ether (C-O-C at the methylene ether bridges), primary amine (NH) bending and tertiary amine bending vibrations. Within 750-720 cm^{-1} , peaks can be associated with methylene $-(\text{CH}_2)-$ rocking vibrations. For PE (C), the peak at 2935-2845 cm^{-1} can be associated with methylene C-H asym/sym stretching vibration (along the PE chain). Within 1485-1445 cm^{-1} , peaks can be associated with methylene C-H bend, while at 750-720 cm^{-1} , peaks can be associated with methylene $-(\text{CH}_2)-$ rocking vibrations [11]. The blend (B) presents intermediate spectra compared to TMU and PE. Compared to the TMU, the broad band attributed to OH, H bonded OH stretching vibration and NH, has significantly diminished. This shows a reduction in the OH groups in the blend hence the reduced hydrophilicity. Also, the reduced alkyl substituted ether (C-O-C) spectra indicates indicated the UF resin condensation hindrance on incorporation of PE, which may reduce the emission of formaldehyde [1]. The methylene $-(\text{CH}_2)-$ rocking vibrations peak is also sharper in the blend and this signals hydrophobicity.

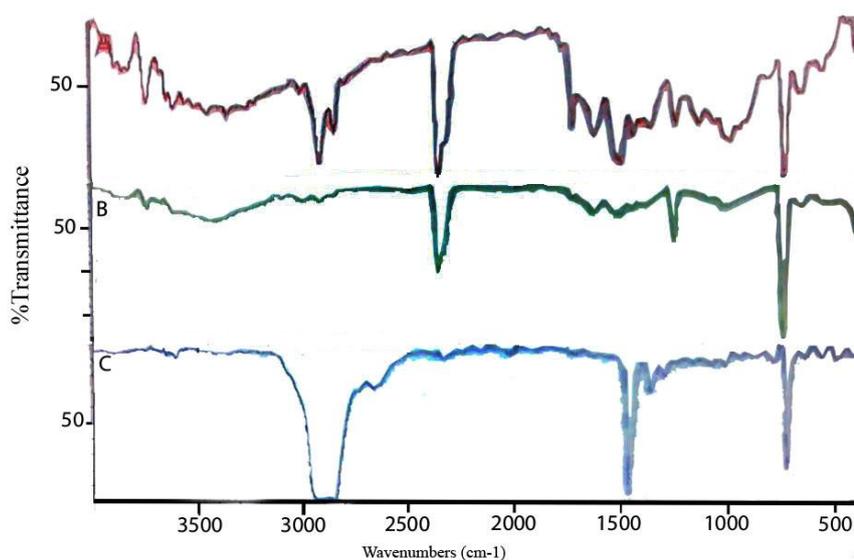


Fig. 1. IR Spectra of the copolymer composite (i.e. blend), TMU and PE
A= Trimethylol Urea (TMU), B= TMU/PE (Blend), C= Polyethylene (PE)

3.2. Effect of PE Concentration on the Density of TMU/PE Copolymer Composite

As shown in Fig. 2, there was an initial drop in density on the incorporation of PE, followed by a rapid rise in density with increase in PE concentration. The initial phenomenon can be attributed to an insignificant rise in the molecular weight of the blend as the volume increases. Further addition can be said to increase PE to the amount that can homogeneously blend with the TMU, hence the possibility of covalent or intermolecular bonds formations leading to a rise in the molecular weight of the blend [9]. The density of a binder influences such properties as the dispersion and stability of pigment and can be used to determine the critical pigment volume concentration, spreading capacity and consistency of the paint [1].

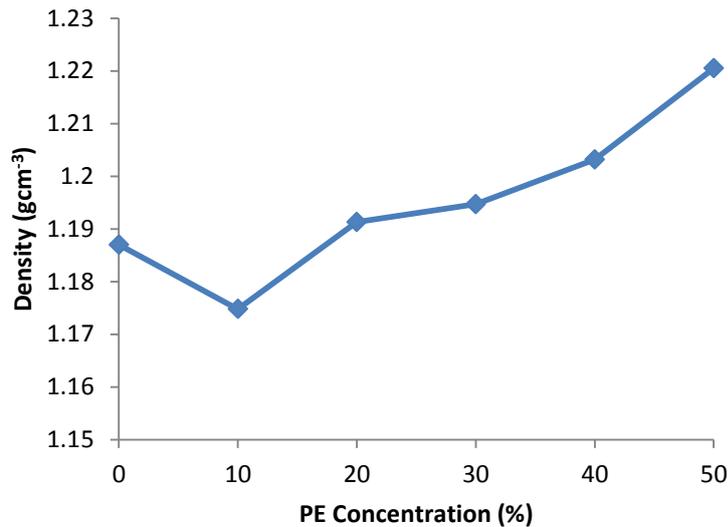


Fig. 2. Effect of PE concentration on the density of TMU/PE copolymer composite

3.3. Effect of PE Concentration on the Refractive Index of TMU/PE Copolymer Composite

Fig. 3 shows the gradual rise in refractive index of TMU/PE with PE loading. This result may be due to increasing discontinuities in the molecular structure of the blend, and the differences in the level of specific interaction between the two polymers thereby creating light scattering [12, 13]. This may also be attributed to a possible rise in crosslinking density as the concentration of the PE increases [9]. Gloss which is a qualitative property of paint has been reported to be a function of refractive index [14]. And the binder plays a vital role in the exhibition of this property.

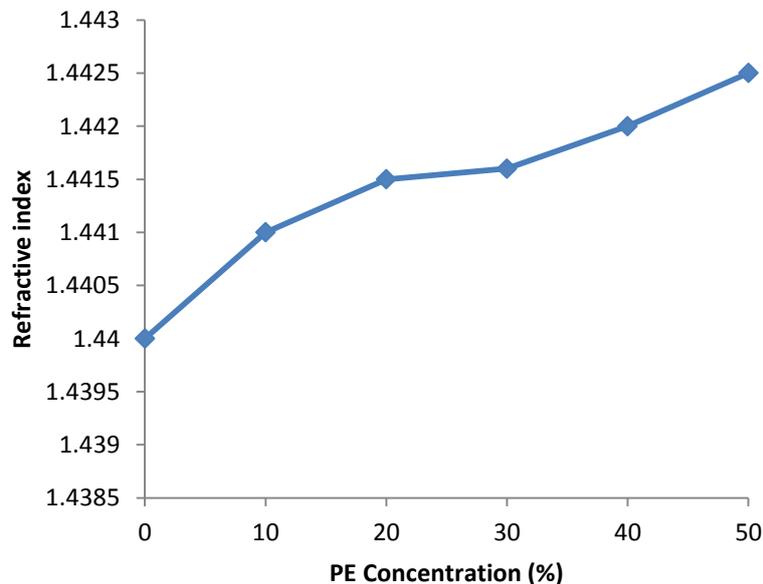


Fig. 3. Effect of PE concentration on the refractive index of TMU/PE copolymer composite

3.4. Effect of PE Concentration on the Moisture Uptake of TMU/PE Copolymer Composite

Fig. 4 shows a reduction in moisture uptake of TMU/PE with increase in PE concentration. TMU is hydrophilic while PE is hydrophobic. This behavior therefore can be associated with the decrease in the amount of TMU with increase in PE content in the blend [1]. A possible interaction between TMU and PE can also reduce the OH groups in the copolymer resin, thereby reducing its affinity for water molecules [1, 15]. Moisture uptake in polymeric materials is very crucial on both physical and structural levels. In synthetic resins used as binders, it is responsible for blistering, alligatoring, brooming etc, of paint film, affecting its mechanical properties in a way that might lead to the paint's failure.

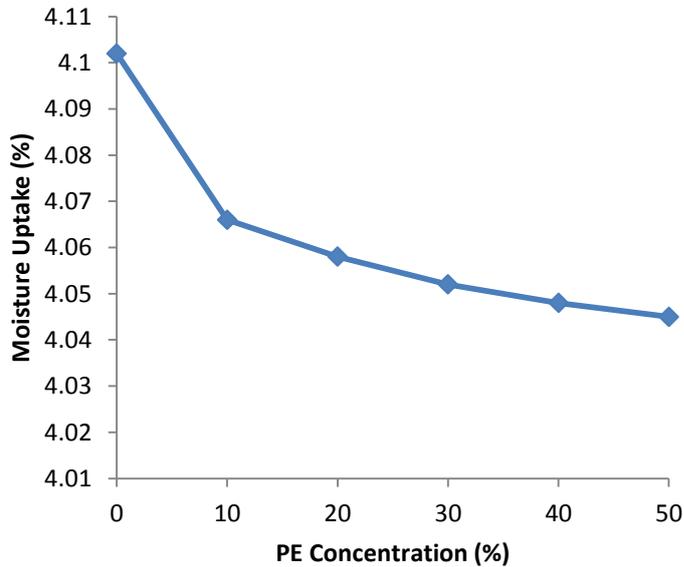


Fig. 4. Effect of PE concentration on the moisture uptake of TMU/PE copolymer composite

3.5. Effect of PE Concentration on the Viscosity of TMU/PE Copolymer Composite

As shown in Fig. 5, the viscosity of the blend increases with increasing PE concentration. This may be attributed to increase in molecular weight and degree of polymerization due to crosslinking interactions between the resins' macromolecules [16]. The rise in viscosity may also be attributed to increasing internal friction in the blend with increase in the amount of PE [16]. Being the base component, the viscosity of the binder is very important in the effects of such paint factors as; sagging, leveling, flow rate, adhesion, etc [17].

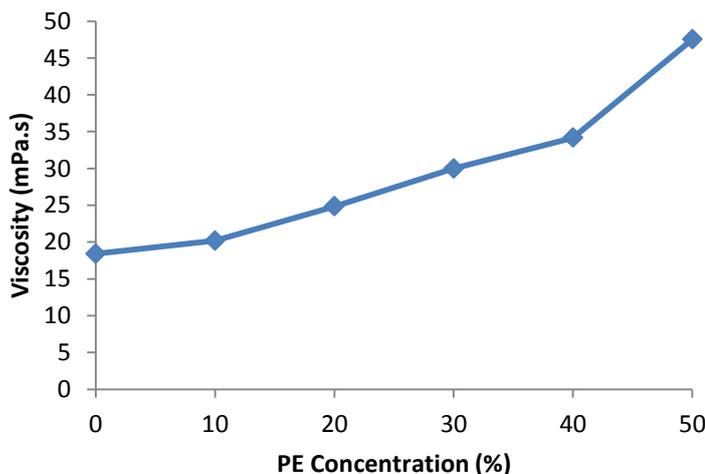


Fig. 5. Effect of PE concentration on the viscosity of TMU/PE copolymer composite

3.6. Effect of PE Concentration on the Gel-time of TMU/PE Copolymer Composite

As shown Fig. 6, the gel time decreases with increase in the concentration of PE in TMU/PE. The decrease can be due to increasing rate of condensation in the blend as the amount of PE increases [18]. Gelation which is the time required for a polymeric substance to reach infinite viscosity has also been marked to be point at which a polymer substance attain an infinitely large molecular weight [19]. Operationally, gel time can be used to determine the dry time of a binder, hence an optimum operational condition for the paint formulated.

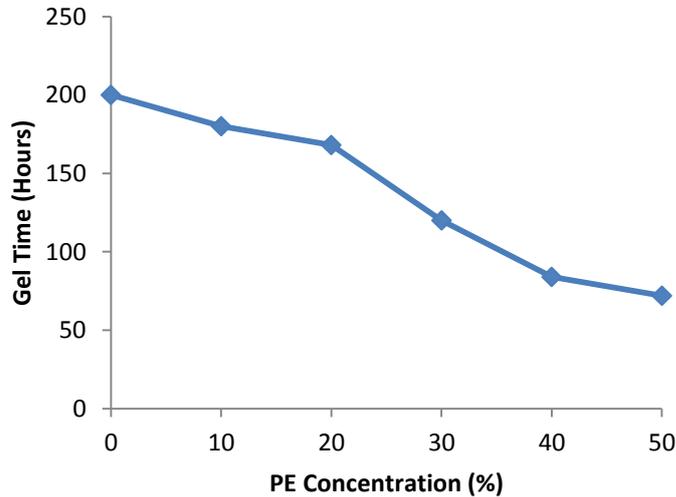


Fig. 6. Effect of PE concentration on the gel-time of TMU/PE copolymer composite

3.7. Effect of PE Concentration on the Melting Point of TMU/PE Copolymer Composite

Fig. 7 shows decrease in the melting point of the blends as the amount of PE incorporated increases. Decreasing melting point signals decreasing hardness and increasing flexibility of the blend compared to the pure TMU. This phenomenon can be attributed to PE serving either or combined purposes including; a flexible spacer, crosslink modifier and/or urea formaldehyde resin condensation inhibitor [1]. Rigidity and flexibility which can be determine form the thermal property of paint's binder is a critical factor in their processing and application.

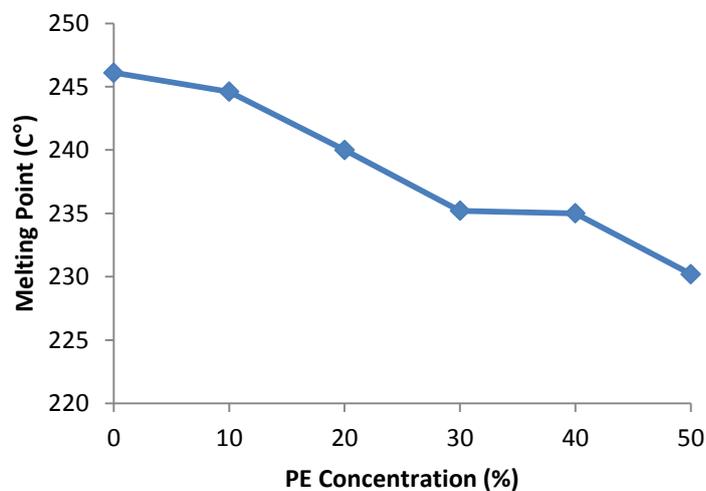


Fig.7. Effect of PE concentration on the melting point of TMU/PE copolymer composite

3.8. Effect of PE Concentration on the Formaldehyde Emission of TMU/PE Copolymer Composite

As presented in Fig. 8, formaldehyde emission decreases in the blend with increase in the concentration of PE. This can be attributed to reduction in the amount of urea formaldehyde in the composite as PE is added. The reduction in the formaldehyde emission may also be attributed to a possible interaction between TMU and PE resins, which may hinder the condensation reactions in the urea formaldehyde resin, hence hindering the release of formaldehyde from the reaction [1]. The emission of formaldehyde during cure is one of the major disadvantages of urea formaldehyde resin which consequently lead to the restrictions on its utility by regulatory organization [20].

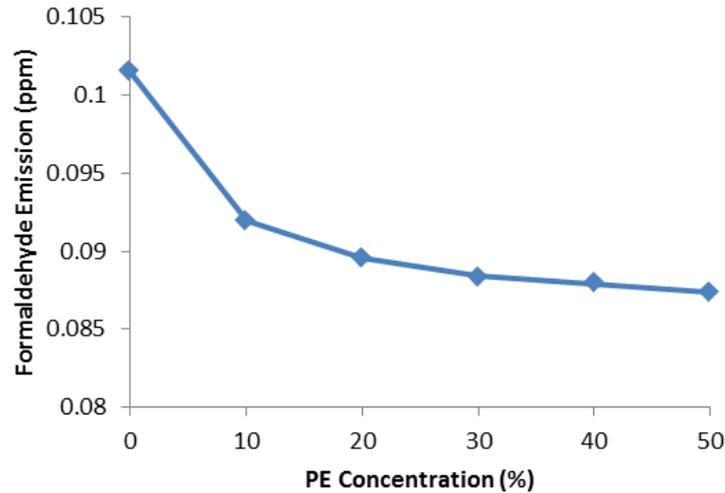


Fig. 8. Effect of PE concentration on the formaldehyde emission of TMU/PE copolymer composite

3.9. Effect of PE concentration on the elongation at break of TMU/PE copolymer composite

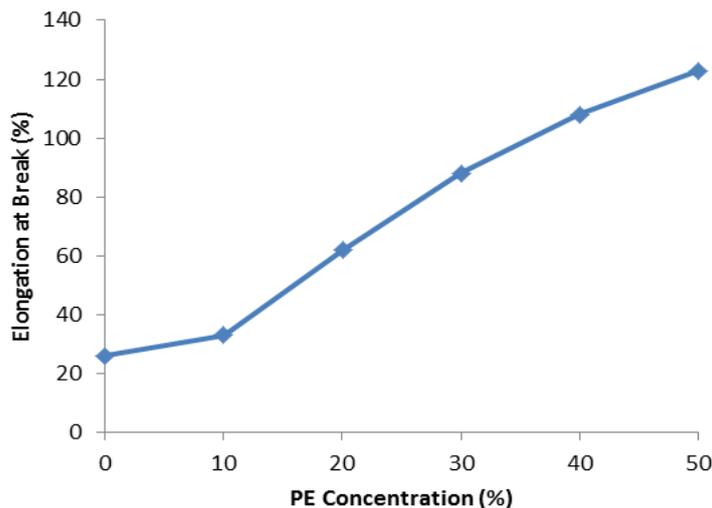


Fig. 9. Effect of PE concentration on the elongation on break of TMU/PE copolymer composite

Fig. 9 shows a gradual increase in elongation at break of the blends with increase in concentration of PE. This signals an increase in the soft segments in the blends as more PE resin is added. This also can be due the ability of the PE to enhance flexible spacing, hence increasing the free volume in the TMU/PE blend [1]. Change in the molecular weight, morphology and the crosslinking density in the copolymer with change in

PE concentration may also be responsible for the observed behaviour [17]. One of the shortcomings of UF resin is that it is too hard and brittle to be used as a binder [8]. Remedies to this will approve its use as a paint binder among other uses.

3.10. Effect of PE Concentration on the Turbidity of TMU/PE Copolymer Composite

Fig. 10 shows the effect of PE concentration on the turbidity of TMU/PE composite. Turbidity increases with increase in concentration of PE. This can be attributed to the progressive changes in crystalline orientation and morphologies responsible for light scattering. Light scattering hence turbidity, is relatively used in the determination of the average molecular weight of polymeric materials [21]. The phenomenon therefore can be associated with a gradual increase in the molecular weight of blend with the increasing incorporation of PE. Turbidity in addition to the pigment is a factor that enhances the opacity of paint films.

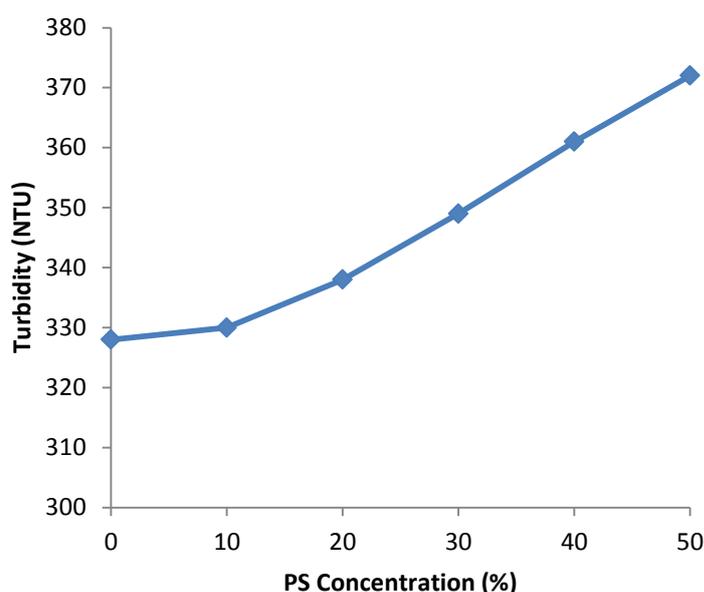


Fig. 10. Effect of PE concentration on the turbidity of TMU/PE copolymer composite

3.11. Effect of PE Concentration on the Solubility of TMU/PE Copolymer Composite

As presented in Table 1, the blends are soluble in water up to 30% PE, above which the blends form dispersions in water. This increasing hydrophobic behaviour is expected as the amount of the hydrophobic PE resin increases in the blends. In the development of amino resin for emulsion paint formulation, resin solubility or dispersability in water is an important factor in the resin's acceptability [7].

Table 1. Effect of PE concentration on the solubility of TMU/PE copolymer composite

PE concentration (%)	Solubility
0	Soluble
10	Soluble
20	Soluble
30	Partially Soluble
40	Insoluble
50	Insoluble

3.12. Comparison of Resins

Table 2. Comparison of some properties of TMU, TMU/PE and the acceptable levels for binders in the coating industry

	TMU	TMU/PE	Acceptable level in the coating industry [9]
Density (g/cm	1.1870	1.2032	1.07 (min)
Refractive index	1.4400	1.4420	1.4000 (min)
Formaldehyde emission (ppm)	0.1051	0.0879	0.1 (max)
Moisture uptake (%)	4.102	4.048	3.10 (max)
Viscosity (mpa.s)	18.40	34.16	3.11-38.00
Elongation at break (%)	80	140	125 (min)
Melting point (°C)	246.1	236.8	200 (max)

Key: TMU – Trimethylol Urea

PE – Polyethylene

TMU/PE – Trimethylol Urea/Polyethylene

Table 2 compares the blend with optimum properties (40 %) with the pure TMU, and the accepted levels for binders in the coating industry. Density, refractive index, and elongation at break has favorably raised in the blend above the minimum acceptable level in the coating industry, formaldehyde emission higher in the pure TMU has been favorably reduced in the blend below the maximum acceptable limit. Melting point and moisture uptake even though reduced in the blend compared to the pure TMU, are still higher than the acceptable levels in the industry, while the viscosity of both the blend and pure TMU are within the acceptable levels.

4. Conclusion

Composites formulated by blending varying amount of PE with TMU were analyzed for some physical properties that give vital information about their improved suitability as paint binder compared to the pure TMU. The infrared spectra of the blend reveal an obvious variation in its functionality compared to that of the pure TMU and PE resins. This work after all reported the improvements in such properties as formaldehyde emission, hardness/brittleness and poor resistance to moisture which has been identified has the demerits limiting the utility of the TMU in many applications including a binder in paint formulation, on incorporation of PE resin obtained from waste, by blending. The environmental impact of this work is its potentials in the recycling of waste PE materials, and the reduction of toxic formaldehyde emissions from the final product. Economically, the formulation of a locally sourced and cheaper emulsion paint binder with comparable properties with those of industrial standards is reported. This work therefore potentially contribute to sustainability, especially in the coating industry.

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