

Full Length Research Paper

Copolymerization of methylol urea with vegetable oil: Effect of using different types of vegetable oil on some physical properties of the copolymer composite

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The effect of using different types of vegetable oil (VO) namely soybean oil (SO), cotton seed oil (CO), moringa seed oil (MO) and neem seed oil (NO) on some physical properties of methylol urea/vegetable oil (MUR/VO) composite was investigated. Pure methylol urea (MUR) was blended with SO, CO, MO and NO to give methylol urea/soybean oil copolymer composite (MSO), methylol urea/cotton seed oil copolymer composite (MCO), methylol urea/moringa seed oil (MMO) copolymer composite and methylol urea/neem seed oil (MNO) copolymer composite. Some physical properties (viscosity, density, refractive index, moisture uptake, melting point and elongation at break) and formaldehyde emission obtained from the different types of vegetable oil were evaluated. It was observed that all the parameters studied varied from one type of vegetable oil to another showing that the type of vegetable oil used has a remarkable influence on the physical properties of MUR/VO. While the melting point, turbidity, elongation at break and dry time showed an increase in value with respect to MUR, all other parameters showed a decrease in value with respect to MUR resin. MUR/MNO copolymer composite gave the lowest values in terms of moisture uptake (0.87%), melting point (160°C) and formaldehyde emission (0.03 PPM) while maintaining the highest value in terms of elongation at break (150%). This suggests that the three drawbacks of poor water resistant, hardness/brittleness and formaldehyde emission associated with MUR can in this respect be addressed by using MNO. However, the long drying period exhibited by MNO advised that an appropriate drier is needed to speed up its rate of cure. The result from this study will add value to NO while helping to optimize the processes of MUR/VO blending for use in the coating industry.

Key words: Amino resin, vegetable oils, blending, paint binder.

INTRODUCTION

The coating industry is facing challenges and under pressure to meet environmental standard especially regarding the emission of volatile organic solvents (VOCs) from surface coatings. Whether these challenges are driven by environmental requirements, performance, quality or lower cost, we know one thing for certain that these challenges are real and only through research and innovations can the coating industry survive. The coating chemists recognize that these challenges and researches are on going all over the world to provide new paint

binders and paint formulations to support the changing face of the industry. Generally, the goal for environmental compliance is reduction of VOCs either through the use of higher-solid systems, compliant solvents or water (Osemeahon and Barminas, 2007). Amino resins are thermosetting polymers that are largely used in many industrial applications. Urea formaldehyde (UF) accounts for over 80% of amino resins while melamine makes up for most of the rest (Conner, 1996; Pizzi et al., 2001). The principal attraction of UF resin is the water solubility before cure which allows easy application to many materials; colourless, for unlimited colourability with dye and pigments, low cost, outstanding hardness and heat resistance (Pizzi et al., 2001). Despite possessing many

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attractive features, the acceptance of UF resin as a universal material in many engineering areas especially in the coating industry is impeded by some of the inherent qualities such as brittleness, poor water resistance and formaldehyde emission (Conner, 1996; Lowel, 1990). It is a known fact that in addition to desirable qualities, each polymer typically has shortcomings. Thus, there is the need to blend different types of polymer together in order to achieve a particular objective. Blending of polymers is a powerful tool which can modify their characteristics, reduce production costs, increase the value of products and broaden the range of applications of polymer materials (Lu et al., 2008). Blending or copolymerization of polymers also combines the advantages of one polymer specie with another while offsetting their shortcomings in a synergetic manner to create a higher performance class of polymer.

In our earlier experiment (Barminas and Osemeahon, 2010), we reported the successful copolymerization of methylol urea with vegetable oil. In that experiment, two problems were observed. Firstly, the dry time of MUR/SO was too long (180 min), and secondly only 25% inclusion of SO in MUR was achieved. The long dry time of MUR/SO disqualified it as a binder for the coating industry and the low fraction (25%) of the vegetable oil in MUR/SO also limits the success of the copolymer composite in terms of its water resistance, reduction of hardness/brittleness and formaldehyde emission. These shortcomings advised the need to optimize the copolymerization reaction between MUR and vegetable oil. In this work, we set out to investigate the effect of using different types of vegetable oil on some physical properties of methylol urea/vegetable oil copolymer composite.

MATERIALS AND METHODS

Materials

Urea, formaldehyde, sodium dihydrogen phosphate, sulphuric acid, sodium hydroxide pellets and sucrose were reagent grade products from the British Drug House (BDH). Soybean oil, moringa seed oil, neem seed oil and cotton seed oil were obtained from Yola market, Nigeria. All materials were used as received.

Resin synthesis

Trimethylol urea was prepared by the method described by Chen et al. (2001). One mole (6.0 g) of urea was reacted with three moles (24.3 ml) of 37% (w/v) formaldehyde using 0.2 g of sodium dihydrogen phosphate as catalyst. The pH of the solution was adjusted to 6 by using 0.5 M H₂SO₄ and 1.0 M NaOH solutions. The solution was then heated in a thermostatically controlled water bath at 70°C. The reaction was allowed to proceed for 2 h after which the sample was removed and kept at room temperature (30°C).

Preparation of MUR/VO copolymer composite and films

Copolymer composite and film of MUR/VO and MUR were obtained as reported by Mirmohseni and Hassanzadeh (2001). In brief, 100

ml of MUR was added to 25 ml of VO to form MUR/VO copolymer composite. The mixture was stirred and left for 24 h at room temperature (30°C) and then poured into a glass Petri dish for casting. The composite was also allowed to cure and set for seven days at 30°C. The above procedure was performed for the different types of vegetable oil studied. The physical properties of these films were then investigated.

Determination of viscosity

Viscosity of MUR and MUR/VO resins were carried out as earlier reported (Barminas and Osemeahon, 2010). A 100 ml Phywe made graduated glass macrosyringe (Phywem, Gottingen, Germany) was utilized for the measurement. The apparatus was standardized with a 20% (w/v) sucrose solution whose viscosity is 2.0 mPa.s at 30°C (Lewis, 1987). The viscosity of the resin was evaluated in relation to that of the standard sucrose solution at 30°C. Five different readings were taken for each sample and the average value calculated.

Determination of density, turbidity, melting point and refractive index

The above properties were determined according to standard methods (AOAC, 2000). The density of each of the resins was determined by taking the weight of a known volume of resin inside a density bottle using metler Model, AT400 (GmbH, Greifensee, Switzerland) weighing balance. Five readings were taken for each sample and average value calculated. The turbidity of the resin samples was determined by using Hanna microprocessor turbidity meter Model, H193703 (Villafranca Padovana, Italy). The melting points of the different film samples were determined by using Galenkamp melting apparatus Model, MFB600-010F (Loughborough, UK). The refractive indices of the resin samples were determined with Abbe refractometer (Bellinglam and Stanley, Tunbridge well kent, UK). Five readings were taken for each sample and average value calculated for each of the aforementioned parameters.

Determination of moisture uptake

The moisture uptakes of the different resin film were determined gravimetrically (Osemeahon and Barminas, 2007). Known weight of the sample was introduced into a desiccator containing a saturated solution of sodium chloride. The increase in weight (wet weight) of the sample was monitored until a constant weight was obtained. The difference between the wet and dry weight of each sample was then recorded as the moisture intake by resin. Triplicate determinations were made for each sample and the average value recorded.

Determination of formaldehyde emission

Formaldehyde emission test was performed by using the standard 2 h desiccator method (Kim, 2001). The evaluation of the absorbed formaldehyde by the 25.0 ml water was obtained from standard calibration curves derived from refractometric technique using Abbe refractometer. In brief, the prepared resin was aged for 2 days. At the end of this period, the resin was poured into a mold made from aluminum foil with a dimension of 69.6 x 126.5 mm and thickness of 1.2 mm. The mold and its content was then allowed to equilibrate for 24 h in the laboratory after which it was then placed inside a desiccator along with 25 ml of water, which absorbed the formaldehyde emitted. The set up was allowed to stay for 2 h after

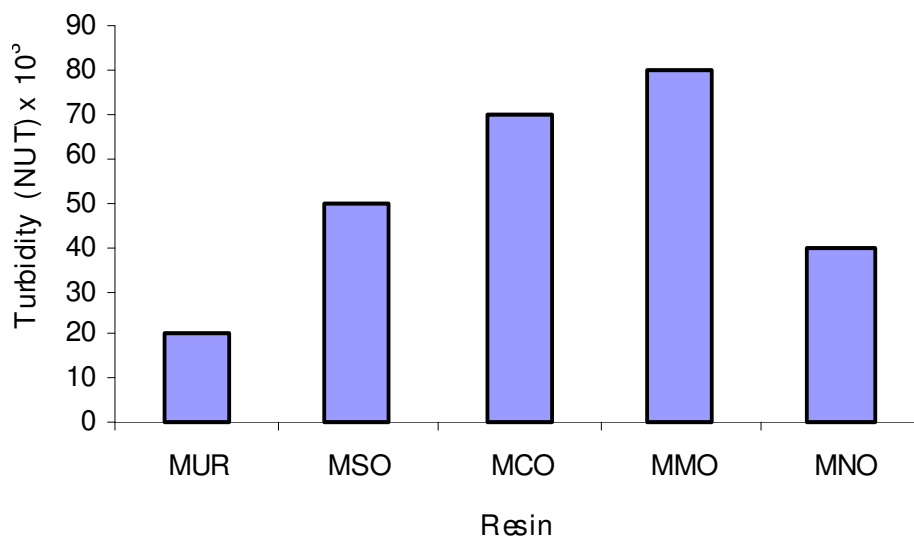


Figure 1. Effect of using different types of vegetable oil on the turbidity of MUR/VO.

which the 25 ml water was removed and analyzed for formaldehyde content. Triplicate determinations were made for each sample and mean value recorded.

Tensile test

Tensile property (elongation at break) was measured as described by Wang and Gen (2002) using Instron Testing Machine Model 1026 (USA). Resin films of dimension 50 mm long, 10 mm wide and 0.15 mm thick were brought to rupture at a clamp rate of 20 mm/min and a full load of 20 kg. Five runs were performed for each sample and the average elongation evaluated and expressed as the percentage increase in length.

RESULTS AND DISCUSSION

Turbidity

In the coating industry, the optical property of the binder such as turbidity is an important factor to the coating chemist, because it is related to the gloss property of the paint. Figure 1 shows the effect of using different vegetable oils on the turbidity of methylol urea/vegetable oil (MUR/VO) copolymer composite. A relatively high increase in turbidity is observed in MUR/VO with respect to the pure MUR resin. The difference between MUR and MUR/VO can be attributed to the presence of VO in MUR/VO composite. Differences among the different MUR/VO copolymer composites are due to differences in molecular weight, orientation and crystallinity among the different MUR/VO composites (Sekaran et al., 2001).

High turbidity of MUR/VO composite translates into better incorporation of the vegetable oil into the methylol urea polymer resin. This will lead to higher molecular weight and hence affect both physical and chemical

properties of the resulting MUR/VO copolymer composite. Thus, MNO can be said to have the highest level of interaction with MUR and MMO the least.

Viscosity

The viscosity of a binder is an important factor to the coating industry. This is because the viscosity of the binder controls many of the processing and application properties such as flow rates, leveling and sagging, thermal and mechanical properties, dry rate of paint film and adhesion of the coating to the substrate (Updograft, 1990; Osemeahon and Barminas, 2007). Because of the presence of functional groups in the polymeric backbone, inter-polymeric specific interactions have long been known to result in unusual behaviour and material properties that are dramatically different from those of the nonfunctional polymers (Qi et al., 2002). These interactions include ion-ioncoulombic interaction, hydrogen bonding and transition metal complexation. Specific interaction between polymers causes aggregation or complexation of the component polymer chains, resulting in solution viscosity variation (Qi et al., 2002). Figure 2 shows the effect of using different types of vegetable oil on MUR/VO copolymer composite. It can be observed that the viscosity of the different MUR/VO differs and that of the pure MUR lower than any of the MUR/VO composites. The difference between the pure MUR and MUR/VO is due to increase in molecular weight in the presence of vegetable oil in MUR/VO composite. While the differences recorded between the different MUR/VO copolymer composites can be attributed to differences in specific interaction between MUR and the different types of vegetable oil (Qi et al., 2002).

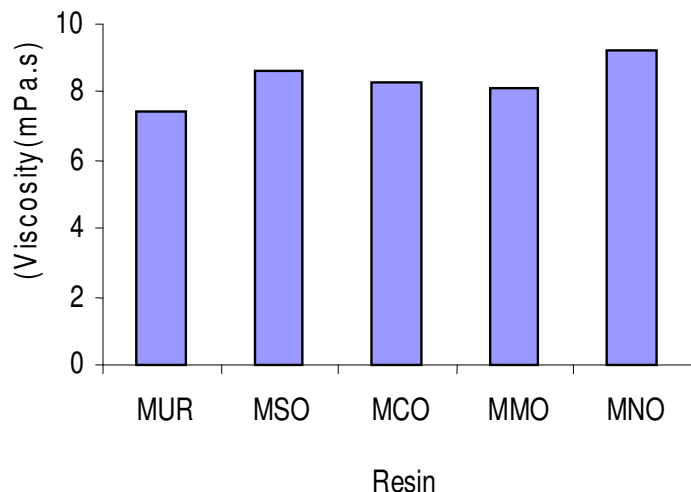


Figure 2. Effect of using different types of vegetable oil on the viscosity of MUR/VO.

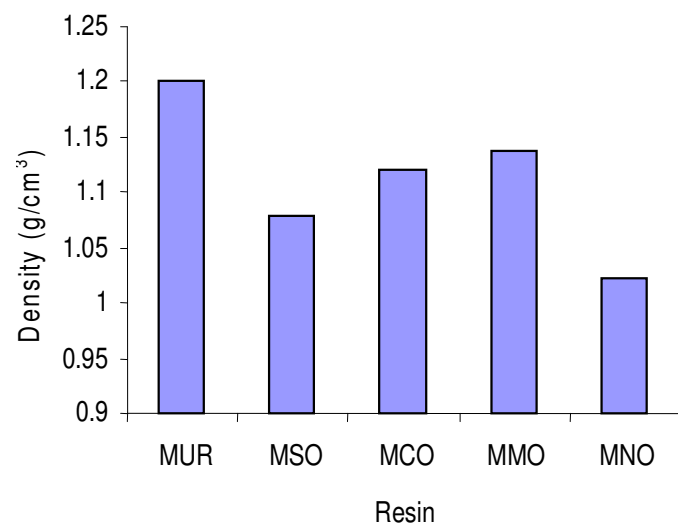


Figure 3. Effect of using different types of vegetable oil on the density of MUR/VO.

Differences in available free-volume are also implicated here. The free-volume of a material is the summation of the spaces or holes that exist between molecules of a material resulting from the impact of one molecule or molecular segment striking another. These holes open and close as the molecules vibrate. If the holes are large enough and last long enough, the molecular segments can move into them leading to low viscosity (Clauson et al., 2007).

Density

The density of a paint binder is an important factor to the coating industry because it influences many of both the

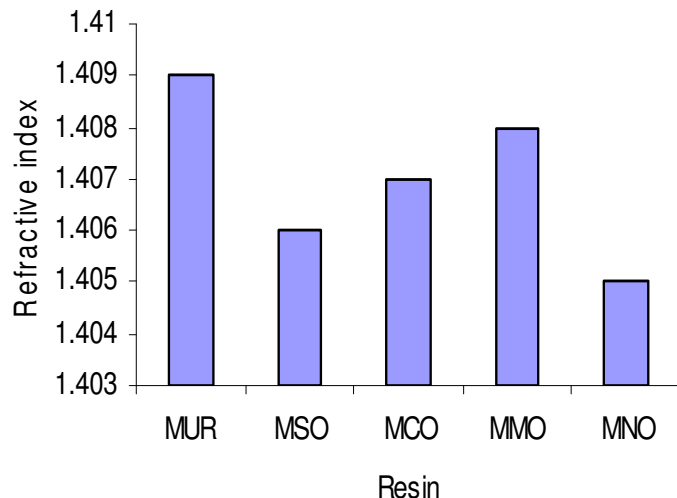


Figure 4. Effect of using different types of vegetable oil on the refractive index of MUR/VO.

processing and application factors. These factors include pigment dispersion, brushability of paint, flow, leveling and sagging (Lowel, 1990). Figure 3 shows the effect of using different types of vegetable oil on the density of MUR/VO. It is observed that the density of MUR dropped on blending with any of the vegetable oils. Also, differences are observed among the different MUR/VO copolymer composites. These trends may be due to differences in the molecular features and morphology between the pure MUR and the composites on one hand and among the different blends on the other hand. This influences the packing nature of the resin molecules (Sekaran et al., 2001).

Refractive index

One of the quality factors of many coating products is the gloss. Presently, high gloss air-drying waterborne finishes are rarely able to match the gloss levels of traditional alkyds, and if they do, the haze or distinctness of image is usually inferior (Morrison, 2007). Fundamentally, the apparent gloss is dependent on surface roughness and overall refractive index of the film. Therefore, attempt to reduce the surface roughness in emulsion paint in order to challenge the gloss of oil paint can only be achieved through the search for appropriate binder. Figure 4 shows the effect of using different types of vegetable oil on the refractive index of MUR. It is seen that the refractive index of MUR reduced differently depending on the type of vegetable oil used. This result may be due to differences in the level of specific interaction between MUR and the different oils used to produce the different MUR/VO copolymer composites (Osemehon and Barminas, 2007).

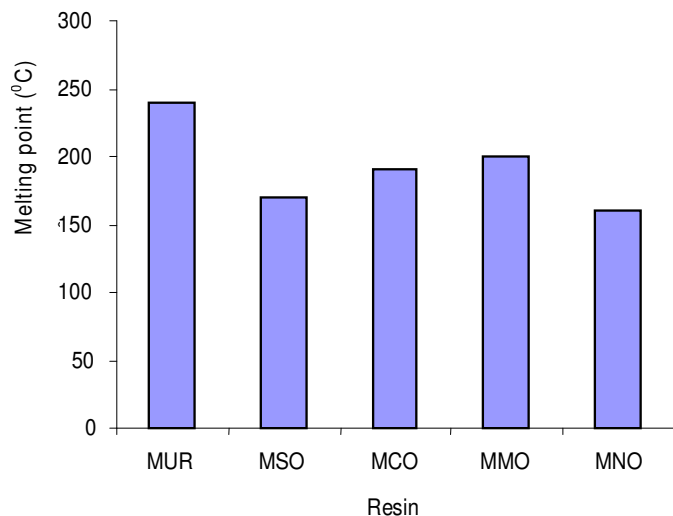


Figure 5. Effect of using different types of vegetable oil on the melting point of MUR/VO.

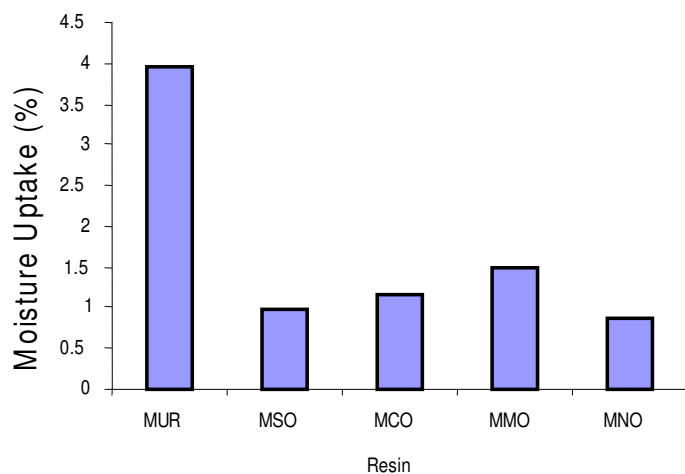


Figure 6. Effect of using different types of vegetable oil on the moisture uptake of MUR/VO.

Melting point

One of the shortcomings of urea formaldehyde resin which negates it being used as a binder for the coating industry is that it is too hard and brittle. The melting point of a polymer is related to its thermal property, its molecular weight, degree of crosslinking and the level of rigidity of the polymer (Part et al., 2001). Figure 5 indicates the effect of using different vegetable oils on the melting point of MUR. A reduction in melting point between the pure MUR and the different composites is observed. Differences in melting point among the different MUR/VO blends are also noticed. This phenomenon can be attributed to the different level of

Table 1. Effect of using different types of vegetable oil on the formaldehyde emission of MUR/VO.

Sample	Formaldehyde emission (ppm)
MUR	0.120 ± 0.003
MSO	0.060 ± 0.001
MCO	0.090 ± 0.002
MMO	0.100 ± 0.001
MNO	0.050 ± 0.002

specific interactions between MUR and the different vegetable oils. This specific interaction led to the formation of a gel-like intermolecular complex structure which gave rise to an increase in molecular mobility; hence a reduction in melting point (Qi et al., 2002).

Moisture uptake

Moisture uptake affects vital properties of polymer materials such as the physical, mechanical, thermal and structural properties. One of the major drawbacks of urea formaldehyde resin is poor water resistance (Conner, 1996). In the coating industry, the moisture uptake of the binder is very crucial because it is responsible for blistering and broominess of paint film (Osemeahon et al., 2009). Figure 6 shows the effect of using different types of VO on the moisture uptake of MUR/VO composite. A drastic reduction in moisture uptake is observed in all the MUR/VO copolymer composites with respect to the pure MUR. Differences in moisture uptake are also observed among the different blends. The low moisture uptake recorded in the MUR/VO composites is explained by the reduction of MUR loading in the presence of the hydrophobic vegetable oil. The differences in moisture uptake among the different blends are due to the differences in the specific interactions between MUR and the different vegetable oils; thus, the differences in free-volume, in the different composites which gave rise to differences in moisture uptake (Clauson et al., 2007).

Formaldehyde emission

The emission of formaldehyde during the cure of urea formaldehyde is a serious limiting factor against its usage in many engineering fields including the coating industry (Kim, 2001). Table 1 shows the effect of using different types of vegetable oil on the formaldehyde emission of MUR/VO. It is observed that the formaldehyde emission decreased in all the MUR/VO composites. This trend is due to the reduction of MUR content in the presence of vegetable oil in the blend (Pizzi et al., 2001). The differences observed among the different MUR/VO

Table 2. Effect of using different types of vegetable oil on the elongation at break (%) of MUR/VO.

Sample	Elongation at break (%)
MUR	115.07 ± 0.32
MSO	140.05 ± 0.08
MCO	130.62 ± 0.52
MMO	120.78 ± 0.21
MNO	150.01 ± 0.34

Table 3. Effect of using different types of vegetable oil on the dry time (h) of MUR/VO.

Sample	Dry time (h)
MUR	48
MSO	60
MCO	72
MMO	54
MNO	60

composites are due to the differences in the specific interaction between MUR and the different oils.

Tensile test

Elongation at break determines to what extent a material stretches before breaking and hence the ductility or flexibility of the material (Osemeahon and Barminas, 2007). In the coating industry, a paint binder must be able to withstand stress emanation from variation in environmental factors. Therefore in developing a paint binder from amino resin, tensile property such as elongation at break must be taken into consideration (Osemeahon and Barminas, 2007). Table 2 indicates the elongation at break of both pure MUR and MUR/VO copolymer composites. It is observed that the elongation at break increased in the presence of vegetable oil. This may be due to increase in molecular mobility emanating from the specific interactions between MUR and the oils. The differences in the elongation at break among the different blends can be explained in terms of differences in their respective interaction with MUR or inequality in the blending exercise (Lu et al., 2008) (Table 2).

Dry time

The time it takes for a paint to dry (reaction time) after application is an important factor for the paint formulator. This is because if the paint dries too fast, a surface 'skin' of partly coalesced particles may form which inhibits further evaporation and leads to irregular film formation

and hence prone to brittleness. On the other hand, if the paint film dries too slowly, the paint film may be subject to pick up dirt (Trumbo et al., 2001). The effect of using different types of vegetable oil on the dry time of MUR/VO composite is shown in Table 3. Increase in the dry time of MUR in the presence of any of the vegetable oils is observed. This is expected. The presence of oil is responsible for the slow drying exhibited by the MUR/VO copolymer blends. The differences in the inherent chemical structures of the different vegetable oils account for the differences in the dry rate among the different MUR/VO copolymer composites (Table 3).

Conclusion

This study examined the effect of using different types of vegetable oils namely MSO, MCO, MMO and MNO, on some physical properties of MUR/VO. The study revealed that using different types of vegetable oil has a remarkable influence on some physical properties of MUR/VO copolymer composite. The values of moisture uptake, refractive index, density, elongation at break, melting point, turbidity, formaldehyde emission and dry time varied from one type of vegetable oil to another. MUR/MNO copolymer composite gave the lowest values in term of moisture uptake (0.87%), melting point (160°C) and formaldehyde emission (0.03 ppm) while maintaining the highest value in terms of elongation at break (150%). This suggest that the three drawbacks of poor water resistant, hardness/brittleness and formaldehyde emission associated with MUR can in this respect be best addressed by using MNO vegetable oil. The result from this study will help in the optimization processes of MUR/VO for use in the coating industry.

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