

CHAPTER 5: CHARACTERIZATION OF COPOLYMERS AS COATING MATERIALS

Coating performance tests serve a number of purposes. They are important for quality control in production, to satisfy the requirements of users' specifications and finally as a tool for research and development.

Durability of coating can be defined as its ability to endure and to remain unchanged by exposure to unfavorable conditions. Test methods are usually designed to accelerate the derivative processes to which the coatings are exposed. The performance of coatings can be assessed by visual inspection but more quantitative approach is required for objective evaluation. Reproducibility is also an important issue. Thus, it is very necessary to establish good test methods. Organizations such as American Standard Testing Method (ASTM) have established standardized methods for testing coatings that are generally useful in understanding the performance and failure of coating. However, there is no fully reliable testing to evaluate the application and appearance of coated products although much progress has been made in recent years in introducing testing instrumentations.

Many important properties of coating materials are difficult to define in scientific units. Due to the complexity of coating materials, most of the tests utilized are empirical, that are based, not on theoretical consideration, but on visual inspection. Most of the properties are seldom single physical characteristics, but resultants of several factors, as for instance in hardness measurements, adhesion and flexibility has important influence on the measured property [138].

The coating system that performs well in a known environment is not always a clear cut decision. The service environment, type of substrate, abrasive resistance and durability are all factors that should be noted before a coating system is adopted. For instance, resistance to indentation and scratching is very important, as poor scratch resistance is definitely a limiting factor for service life of a coating.

This chapter reports the testings that evaluate the palm oil-based resins discussed in the earlier chapters as coating materials on mild steel panels. Before any resin is coated on the panel, the mild steel panels for the coatings need to be treated. Curing time or drying time for coatings is reported in Section (5.2.1). Testings such as adhesion test, pencil hardness test, chemical resistance and solvent rub tests were performed and reported in the next sections. The results of coating tests are discussed in each section.

5.1 Preparation on mild steel panels and coating application

It is important that all steel test panels used should be of uniform quality, undeformed and uniform thickness. The surface should be cleaned by a method that is reproducible. Metal surfaces are usually contaminated with oil and should be perfectly cleaned and freed of any greases and oily materials because such surfaces can have very low tension [139].

There are many methods to clean the surface of steel panels. In this research, panels are prepared according to IS (Indian Standard Methods of Test for Readymade Paints and Enamels 1964). Mild steel panels of 7 cm x 20 cm were used for evaluating the coating performances. A clean cotton cloth is soaked into xylene and used for removing grease or oil from the surface of the panel. Thereafter, the surface was abraded with sandpaper No.

400 to remove loose rust scale and was smoothed by sandpaper No. 600. The surface of the test panel was wiped again with a wet cotton cloth soaked in xylene until fresh portions of the cloth show no discoloration. The prepared test panels were stored in desiccators before using.

To produce uniform films and reproducible thickness, a pool of coating material was poured across the end of the Sheen coater (model S 971096) on the panel and then drawn uniformly along the length of the panel. Films of 50 μm and 100 μm wet film thickness were coated on the panels and left to dry at room temperature for 2 days before testing. After the coating is completely dried, the thickness of the films was measured using a thickness meter (Sheen- Ecotest Plus B FN2, type 121-17-00).

5.2 Tests on coatings properties

In this work, a number of test types were performed on MMC samples produced in Chapter 4. These tests include drying time, adhesion test, pencil hardness, water immersion, acid, alkali and salt resistances, and solvent rub test. To ensure the results for each formulation, each test was repeated more than two times.

5.2.1 Solid content

Because high solid content is desirable for coating binders, the solid content of samples was calculated by equation [2.7] in Section (2.6) and the results are represented in Table 5.1. From the results, decreasing the oil length and increasing the MMA, the solid content of the samples increased.

Table 5.1 : Solid content of copolymers (MMC) and PMMA for coating application

Sample	AL1	AL2	AL3	AM1	AM2	AM3	AS1	AS2	AS3	PMMA
Solid content (%)	12.0	17.1	23.8	13.0	18.5	25.3	21.0	24.5	28.3	31.7

5.2.2 Drying time test

The three stages of film formation in the drying of coatings are determined by using the testing method stated in ASTM D1640-83. This test method describes the determination of several stages and the rate of dry-film formation of organic coatings.

In order to determine set-to-touch time, the coated films are lightly touched with the tip of a clean finger and immediately placed against a clean piece of clear glass. Pressure of the fingertip against the coated part is made in such a manner that not greater than that required to transfer a mark of the coating from 3 to 5 mm in cross section.

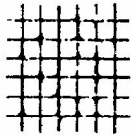
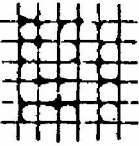
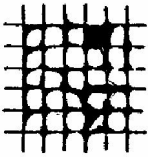
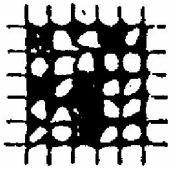
The film is considered dry-to-touch when film no longer sticks to finger and does not rub up when the finger is lightly moved across the surface.

The third testing for drying is to determine the dry-hard-time. Dry-hard-time is reached when the drying and curing, have proceeded sufficiently. With the end of thumb resting on the test film and the forefinger supporting the test panel, a maximum downward pressure (without twisting) of the thumb on the film is applied. The contacted area is lightly polished with a soft cloth. The film is considered dry to hard when any spot left by the thumb is completely removed by the polishing operation. Times were measured in seconds by using stopwatch. After the coating is completely dried, the thickness of the film is measured by using thickness meter. The dried coatings have an average thickness of 30 ± 3 μm .

5.2.3 Adhesion measurement

Adhesion test was designed to assess the adherent strength of the film according to ASTM D3359-93. A criss-cross lattice pattern with six cuts in each direction was made with space of 1 mm and 20 mm long.

Table 5.2 : Classification of adhesion test results

Classification	Surface of cross-cut area from which flaking has occurred. (Example for six paralleled cuts)	Remarks
5B	None	The edges of the cuts are completely smooth; none of the squares of the lattice is detached. Good and acceptable
4B		Small flakes of the coating are detached at intersections; less than 5% of the area is affected. Good and acceptable.
3B		Small flakes of the coating are detached along edges and at intersection of cuts. The area affected is 5 to 15 % of the lattice. Good and acceptable
2B		The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35% of the lattice. Not acceptable.
1B		The coating has flaked along the edges of cuts in large ribbons and whole squares have detached. The area affected is 35 to 65% of the lattice. Not acceptable.
0B	Greater than 65%	Flaking and detachment worse than Grade 1B. Not acceptable.

After making the required cuts, the film was brushed lightly with a soft brush to remove any detached chips of coatings. A piece, about 75 mm long, of pressure-sensitive tape was separated and placed over the grid and smoothed into place by finger. The tape is rubbed

firmly with eraser to ensure sufficient contact with the film. The tape was removed after 90 s in an angle close to 180°. The grid area was inspected by visual inspection for removal of any coating from the substrate. The adhesion is rated according to the scale displayed in Table 5.2 adapted from ASTM D3359-93. The best adhesion performance is indicated by 5B (0% of area removed) while the worst performance is 0B (> 65% of area removed).

5.2.4 Pencil hardness test

The scratch hardness was estimated by pencil hardness test. The test procedure was done using a Sheen Pencil Hardness Kit according to ASTM D3363-92a with a set of calibrated wood pencils with scale of hardness 6B (softest) to 6H (hardest).

6B - 5B - 4B - 3B - 2B - B - HB - F - H - 2H - 3H - 4H - 5H - 6H

Softer

Harder

The pencil was shaved to remove approximately 5-6 mm wood to expose about 3 mm length of pencil lead. The sharpened pencil was rubbed with an abrasive paper at angle of 90° to obtain a flat, smooth and circular cross section. A new sharpened pencil lead was used for each test. The pencil test used constant pressure and variable hardness of the test tool as its fundamental principle. The pencil was moved over the surface using the pencil tester at an angle of 45°. The schematic diagram of the pencil tester and test conducted is shown in Figure 5.1.

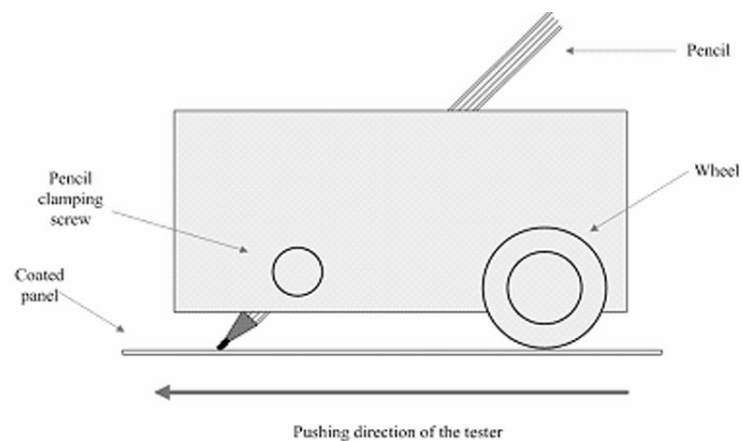


Figure 5.1 : Schematic diagram of a Sheen pencil hardness tester kit

Usually a mid range pencil was chosen, e.g. 2H. The pencil tester was put onto its end face and the pencil was inserted until its point touches the flat surface. The clamping screw was tightened and the pencil was held firmly in the tester at a 45° angle. The coated panel was located on a stable and flat level with the coated surface side upward. The tester was placed gently on the panel and was pushed forward (away from the operator) by 6-12 mm in a fixed continuous movement. The coating was examined for any indentation or notch. If there is no indentation or scratching, the test is repeated using a harder pencil, e.g. 3H. If the surface is scratch or indented, then the test was repeated with a softer pencil e.g. H. The process was repeated until a pair of pencil is found, one which indents the coating, the other which is not able to make indent the coating. The determination was repeated at least twice for each panel coated.

5.2.5 Water immersion testing

Immersion in water can affect coating and cause deterioration of the coating. Recognizing the resistance to water immersion in coating materials can be helpful in predicting its service life. The factors that may affect failure for water immersion test are deficiency in coating itself, inadequate surface preparation and contamination of the

substrate [140]. The method of water immersion test is according to ASTM D1647-89. The aim of this test is to check the resistance of the coating against prolonged exposure to moisture. The test is carried out at room temperature according to reported procedure [141]. The dried panels were immersed in a beaker containing distilled water for 18 h. After 18 h, the panels were taken out, air-dried and inspected for any defects, like whitening, shrinkage, film softened, loss of gloss and lift off.

5.2.6 Acid resistance test

Acid resistance test was carried out according to reported procedure described by K.P Somani et al. [142]. Aqueous solution of acid hydrochloric 0.1 M (HCl) was prepared in a beaker and warmed up to 80°C. The coated panels were placed, with the edge about 5 cm on the bottom of the beaker and the top of the panel resting by the side. Each panel was tested in a separate beaker. The coated panels were immersed in the solution for 1h at 80°C during the testing period. At the end of the examination time, each panel was removed from the solution. The panel was then dried at room temperature for 24 h before checking for any deterioration.

5.2.7 Alkali resistance test

Alkali resistance test was performed by using sodium hydroxide 0.1 M (NaOH) and following the same procedure as that of the acid resistance test.

5.2.8 Salt water resistance test

This test was performed to assess the coating resistance to marine conditions. In this work the testing method for salt water immersion test was adapted from K.P. Somani et al.

[142]. Sodium chloride solution 5% was prepared in a beaker and heated up to 80°C. The rest of the procedure was done according to the Section (5.2.5) and Section (5.2.6).

5.2.9 Solvent resistance test (Solvent rub)

Rubbing with a cloth soaked in suitable solvent is one method to determine resistance of coated panel to solvent. Solvent resistance can be influenced by film thickness, humidity, temperature and air movement (ASTM D5402-93). The solvent resistance testing was carried out according to ASTM D5402-93. An area of 150 mm long and 25 mm width was marked using a pencil on the coated surface. Thickness of the dried film of the coating in the selected area was measured before solvent test. A cotton cloth was folded into a pad of double thickness and soaked into the specified solvent. The index finger was placed at the center of the pad at an angle of 45° to the test surface while holding excess cloth with the thumb and remaining fingers of the same hand. The rectangular test area was rubbed with moderate speed in forward and backward motion.

One forward and backward motion was counted as one double rub. Each double rub should be completed at the rate of approximately 1s. The test area was continuously rubbed for a total of 25 double rubs in the rectangular test area. The area was immediately checked for any visual changes in appearance, comparing to an adjacent unrubbed area. The film thickness of the rubbed area was measured again after solvent test and two thicknesses were compared. The cloth was visually inspected for any indication of coating removal. Solvent rub test was performed by using acetone, ethyl acetate and methyl ethyl ketone.

5.3 Results and discussion

As mentioned in Chapter 4 three kinds of macromers were used in synthesizing the copolymers. These macromers differ by the oleic acid content where AlkOA28 has lowest oleic acid content (28%), AlkOA40 contains 40% oleic acid and finally AlkOA65 has the highest percentage of oleic acid (65%).

The MMC samples were synthesized with varying MMA/macromer ratio and oleic acid content in macromers compositions and the influence of these two factors on the coating characteristics is studied. To improve some of the coating properties, BA monomer was utilized as a comonomer and the effect of BA monomer was also evaluated. It is expected that these factors will give significant changes in the performance of the finished coatings. The results of the coatings performance by examined MMC and MMBC samples will be discussed in next sections i.e. 5.3.1 to 5.3.7 and 5.4.1 to 5.4.7 respectively.

5.3.1 Coatings appearance

Overall each film shows appearance in term of clarity and shininess. With increment of MMA/macromer ratio, shininess of the coatings seems to remain the same. However, a slight tinge of yellowness is observed in AL samples. Of course the yellowing could be covered using pigments in the formulation of the coatings.

The coating appearance observed above can be explained along these lines. The macromers were synthesized by fatty acid method. Alkyds cooked from this procedure are expected to be more viscous with lighter color than those cooked by conventional method [143]. Phthalic anhydride, oleic acid and glycerol were used for synthesis of the macromers. Polyesterification of just phthalic anhydride and glycerol gives a very clear product. However as oleic acid is included, the end product, i.e. macromers show a slight tinge yellowness due to the nature of the oleic acid itself. Percentage of the oleic acid

determines the properties of the macromers with oil like properties (the highest oleic acid content) locating at one extreme and resin like properties (with the lowest oleic acid content) locating the other end. AlkOA65 shows oil like properties and AlkOA28 shows resin like properties. It can be expected that as the oleic acid content in the macromer formulation increases, the color and gloss retention decrease or vice versa. Moreover, the percentage of the MMA monomer in copolymer composition plays important role in appearance of the films, as more MMA content would cause to be shinier.

5.3.2 Drying time test

Results of set-to-touch, dry-to-touch and dry-hard time experiments for the MMC samples are tabulated in Table 5.3. From Table 5.3, it is very clear that coatings based on formulation of AlkOA28 macromer achieves the shortest drying time, followed by AlkOA40 and AlkOA65. Copolymers with lower oleic acid content could dry faster compared to the copolymers with the highest oleic acid content which take longer time to dry. Copolymers with more oleic acid content have more side chains in the copolymer structure and more side chains result in more soft segments in molecular structure and hence slowing down the rate of drying time.

From Table 5.3, the changes in drying times of the coatings are not only dependent on oleic acid content but also on MMA/macromer ratios. The set-to-touch, dry-to-touch and dry-hard times decrease as the MMA/macromer ratio increases for all the three series of copolymers. With increasing MMA ratio, as the solvent evaporates from the film, the viscosity increases and free volume decreases and consequently lead to decrease in drying time. On the other hand, one the effective factors in drying time is increase in molecular weight, whereby shorter time is required to form the coherent film or to reach the drying stage [144]. In addition, with increasing the average functionality, the concentration of

functional groups will be high, and a dried film will be formed in a shorter time [145], as copolymers synthesized by using AlkOA28 macromer due to having higher functionality of macromer compared to the rest of the macromers show faster drying. It is also important to note that in all the three groups of coating samples in this study were dried by physical drying without any need to be cured at high temperature or usage of drying agent.

Table 5.3 : Set-to-touch, Dry-to-touch and Dry-hard time observed for MMC samples (All unit of time in seconds)

Sample	Test	Set-to-touch time		Dry-to-touch time		Dry-hard time	
	Thickness MMA/macromer	50 μ m	100 μ m	50 μ m	100 μ m	50 μ m	100 μ m
		AL series prepared with AlkOA65					
AL1	50/50	37	63	135	480	654	1050
AL2	65/35	30	50	92	114	210	550
AL3	80/20	28	38	65	81	200	503
AM series prepared with AlkOA40							
AM1	50/50	30	40	120	128	450	590
AM2	65/35	27	35	60	106	200	482
AM3	80/20	22	26	54	78	188	420
AS series prepared with AlkOA28							
AS1	50/50	23	37	81	78	150	302
AS2	65/35	20	32	37	72	141	300
AS3	80/20	17	28	34	70	135	292

5.3.3 Adhesion measurement of methacrylate copolymers (MMC)

Overall, a value of 3B and higher would be taken as acceptable adhesion in coatings field. The results of adhesion tests for the MMC copolymers are displayed in Table 5.4. All the samples exhibit fairly good adhesion performance on mild steel panel. One of the effective factors of adhesion can be attributed to the presence of pendant hydroxyl groups

in the samples. Adhesion of coatings to the surface is promoted by developing hydrogen bond interactions between groups on the resin molecules and oxide and hydroxide groups on the surface of the steel [139]. In our system, samples with lower molecular weight and higher amount of the oleic acid as a flexible side chain have shown also better adhesion of coat with steel. Moreover, lower viscosity due to lower molecular weight could also result in better penetration of the liquid into pores and crevices of the substrate [139].

Table 5.4 : Results of adhesion measurement, pencil hardness and water immersion tests on MMC samples

Samples	Test	Adhesion test		Pencil hardness		Water resistance	
	Thickness	50 μm	100 μm	50 μm	100 μm	50 μm	100 μm
	MMA/macromer						
AL series prepared with AlkOA65							
AL1	50/50	5B	5B	4B	6B	4	4
AL2	65/35	5B	5B	HB	HB	4	4
AL3	80/20	4B	4B	H	F	3	4
AM series prepared with AlkOA40							
AM1	50/50	5B	4B	H	2H	3	4
AM2	65/35	5B	4B	2H	3H	3	3
AM3	80/20	4B	4B	4H	3H	1	1
AS series prepared with AlkOA28							
AS1	50/50	5B	4B	6H	6H	1	1
AS2	65/35	5B	4B	3H	3H	1	1
AS3	80/20	4B	3B	2H	2H	1	1

Note-Water resistance behaviour: 1, unaffected; 2, slightly whitening; 3, heavily whitening; 4, slightly shrinkage; 5, film soften; 6, film lift out

5.3.4 Pencil hardness test

The scratch hardness was estimated by pencil hardness test. The hardness was expressed in term of the designation of the hardest pencil that failed to scratch the film.

Table 5.4 demonstrates the results of pencil hardness tests on the samples. The results reveal that the hardness of the film is improved as the oleic acid content of macromer decreases. AS series shows resin like properties due to the existence of higher content of rigid aromatic moiety (phenyl groups) in polymer chain and as expected it displays better mechanical properties.

The variation MMA/macromer ratio also show significant contribution on the hardness of coatings as MMA/macromer ratio increases hardness also increases. The macromer portion comprise of the soft segment with low T_g , while MMA portion comprise the hard segments. Hard segments give the mechanical strength whereas soft segments give high extensibility and resiliency. However, an exception occurs for the AS series where increasing of the MMA/macromer ratio causes to the pencil hardness to decrease. This exception may be due to the fact that increasing in PA and MMA up to a certain limit may lead to increase in the brittleness of the film which in turn decreases the hardness of film. This variation in hardness and flexibility can be proved by DMA results. From Table 4.7 in Chapter 4, it is found that the loss modulus in the AS series increases with increasing MMA content. Overall, it can be concluded that flexibility of the AS1 is much more than AS2 followed by AS3. AS1 and AM3 exhibited the best scratch hardness compared to the rest of samples. It is also found that increment of the thickness of the coatings has not affected much on the hardness of the coatings.

5.3.5 Water resistance

The results of water resistance of the coated films are shown in Table 5.4. The water resistance improves with coatings having lower content of oleic acid in macromer composition and higher MMA percentage in copolymer composition.

From the results, AS series is unaffected by immersion in water for 18 h. As for AM series and AL series, water immersion cause whitening of films and slight shrinkage. Referring to the Chapter 3, Section (3.3), AlkOA28 comprises higher percentage of PA whereby, this aromatic moieties should theoretically provide lower rate of molecular permeability, resulting in better hydrolytic stability [146]. A few of the coated samples with thickness 100 μm show lower resistance to water immersion test.

Figure 5.2 illustrates coated panels of AS1 sample after one hour and one year exposure in the open lab. bench (under hot and humid conditions).

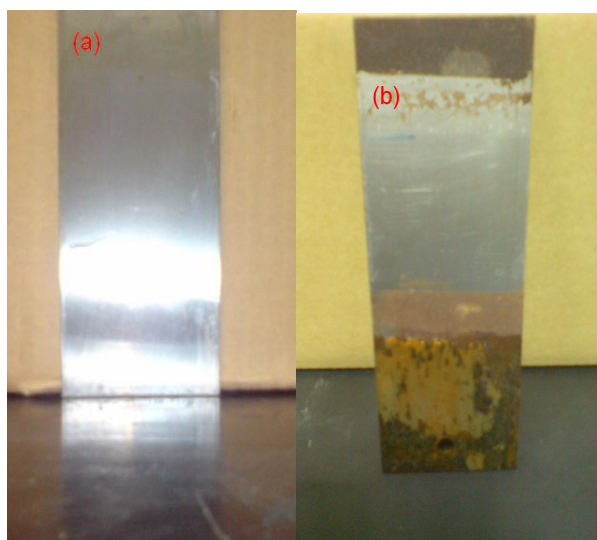


Figure 5.2 : Coating performance: Coated panels of AS1 sample after one hour (a), after one year exposure in the open lab. bench (under hot and humid conditions) (b)

5.3.6 Acid, alkali and salt resistances

The results shown in Table 5.5 are based on the effect of acid, alkali and salt solutions on the coatings. The represented results indicate that the coatings have good resistance against acid solution and amount of oleic acid and also ratios of MMA/macromer not show any variation on the acid resistance.

Moreover, the results reveal that higher content of MMA monomer improves alkali resistance and also the films deteriorate to some extent when more macromer content was used. Films with thinner thickness show better results. Overall, AS series of copolymers shows better results for alkali resistance.

Hydrolysis of ester bonds in polyester resins is very common under basic conditions [146, 147]. The parameters affecting onto the hydrolysis resistance of ester bonds was studied by Turpin [54]. He expressed that steric hindrance plays important roles in hydrolysis reaction. According to his study as long alkyl substitution as possible at the alpha and beta carbons on either side of the ester group improves hydrolysis resistance. Thus copolymerization of the macromer with MMA has increased the resistance to alkaline hydrolysis presumably the methyl groups on C=C in MMA units stabilize the ester groups toward hydrolysis due to steric hindrance and hydrophobicity of methyl group moiety. For this reason the methacrylate esters are more resistance to chemical attack than the acrylate ester resin [148, 149]. Moreover the ester groups of the alkyd are along the main chains, while those on PMMA are as side chains. Thus hydrolysis of the ester groups along the main chain would lead to chain scissions, causing the polymer films to loss their mechanical strength. The hydrolysis of ester groups along the side chains in PMMA would not lead to deterioration of the polymer films. These several reasons account for the chemical resistance of this kind of polymer.

In addition, it has been found that salt resistance of samples are excellent compared to acid and alkali resistances. It can be therefore concluded that salt does not have effect on the films. In fact strong adhesion may also prevents ions passing through the coating [150]. From these experiments it can be concluded that macromer composition and also MMA/macromer ratios do not demonstrate any effect on deterioration of the films.

Table 5.5 : The results of acid, alkali and salt resistance for three series MMC samples

Samples	Test	0.1 M HCl		0.1 M NaOH		5% NaCl	
	Thickness Macromer/MMA	50 μm	100 μm	50 μm	100 μm	50 μm	100 μm
AL copolymer series prepared with AlkOA65							
AL1	50/50	2	3	6	6	1	1
AL2	65/35	2	3	6	6	1	1
AL3	80/20	2	3	3	3	1	1
AM copolymer series prepared with AlkOA40							
AM1	50/50	2	3	6	6	1	1
AM2	65/35	2	3	6	6	1	1
AM3	80/20	2	3	2	2	1	1
AS copolymer series prepared with AlkOA28							
AS1	50/50	2	3	3	3	1	1
AS2	65/35	2	3	2	2	1	1
AS3	80/20	2	2	2	2	1	1

Note-Chemical resistance behaviour: 1, unaffected; 2, slightly whitening; 3, heavily whitening; 4, slightly shrinkage; 5, film soften; 6, film lift out

5.3.7 Solvent rub test

Table 5.6 displays the results of solvent rub tests. By increasing the oleic acid content in the macromer compositions, films show more resistance to acetone while decreasing the oleic acid content in macromer composition and increasing MMA in copolymer composition causes to increment of resistance to ethyl acetate.

Generally, solvent resistance depends primarily on polarity of polymer and solvent, and polymers containing sites for hydrogen bonding are most affected by polar solvent. Dielectric constant (as criterion for polarity) for acetone, methyl ethyl ketone and ethyl acetate are 20.6, 18.5 and 6.02 respectively. Non polar polymers show solvent resistance to acetone and other polar solvents and polymers containing sites for hydrogen bonding are

most affected by polar solvent. The molecular weight and crosslink density of polymer networks are also directly related to its resistance to solvent attack. Crosslinking is the ultimate structural factor in preventing a polymer from dissolving in a solvent, although this cannot eliminate the effects of polarity and hydrogen bonding [150]. In this respect, it was found that the most of the copolymers have poor solvent resistance due to the abundant polar ester groups in their structures. AL1 and AM1 showed good resistance to acetone and only lost gloss, which may be due to the existence of higher percentage of oleic acid as a non polar moiety in copolymer structures.

Table 5.6 : Results of solvent rub tests on MMC samples

Samples	Test	Acetone		Methyl ethyl Ketone		Ethyl acetate	
		Thickness	50 μm	100 μm	50 μm	100 μm	50 μm
MMA/macromer							
AL series prepared with AlkOA65							
AL1	50/50	L.G	L.G	L.G	L.G	R	R
AL2	65/35	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
AL3	80/20	S.R L.G	S.R L.G	S.R L.G	S.R L.G	L.G	L.G
AM series prepared with AlkOA40							
AM1	50/50	L.G	L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
AM2	65/35	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
AM3	80/20	S.R L.G	S.R L.G	S.R L.G	S.R L.G	L.G	L.G
AS series prepared with AlkOA28							
AS1	50/50	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
AS2	65/35	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
AS3	80/20	S.R L.G	S.R L.G	S.R L.G	S.R L.G	L.G	L.G

Note- S.R and L.G refer to Slight Removal of the films and Loss of Gloss respectively, P refers to the Pass and R remove

5.4 Effect of butyl acrylate monomer on coatings properties of MMBC samples

The BA monomer (10 wt.%) was used to improve coatings properties of copolymer samples. It should be noted that ASB series were synthesized using two different percentages of BA i.e. 5 wt.% and 10 wt.% of BA. All coated panels were prepared 2 weeks prior to performing the coating tests on the coated panels under room temperature.

5.4.1 Coatings appearance

The appearance of films did not show much difference compared to the MMC samples, i.e. most of the coated panels were shiny and colorless.

5.4.2 Solid content of MMBC samples

The solid content of samples is calculated using equation [2.7] in Section (2.6) and is presented in Table 5.7. The result shows the same trend as that obtained by unmodified the copolymer samples (MMC), but with higher solid contents. Increasing of the amount of BA monomer, the solid content also increases.

Table 5.7 : Solid content of the copolymers containing BA, MMBC samples

Sample	AL1B	AL2B	AL3B	AM1B	AM2B	AM3B	AS1B (5%)	AS2B (5%)	AS3B (5%)	AS1B (10%)	AS2B (10%)	AS3B (10%)
Solid Content(%)	13.3	21.6	30.0	15.3	22.0	29.5	21.5	30.3	31.1	22.9	31.7	32.6

5.4.3 Drying times of MMBC samples

The results of drying times, including set-to-touch, dry-to-touch and dry-hard time, are tabulated in Table 5.8. In these series of experiments, all of the samples took longer time for drying compared to the MMC samples.

By introducing a small percentage of the BA monomer, more side chains due to existence of butoxy groups and consequently more soft segments will be present in copolymer structure and hence slowing down the rate of drying time. The trends of the drying times between the all samples are the same with the MMC samples which discussed in Section (5.3.2).

Table 5.8 : Set-to-touch, Dry-to-touch and Dry-hard time observed for MMBC samples (All unit of time is seconds)

Sample	Test	Set-to-touch time		Dry-to-touch time		Dry-hard time	
	Thickness	50 μm	100 μm	50 μm	100 μm	50 μm	100 μm
	MMA/macromer						
ALB series prepared with AlkOA65							
AL1B	50/50	After one week, samples were sticky and undried					
AL2B	65/35	70	90	130	220	1600	2910
AL3B	80/20	40	48	95	110	800	2700
AMB series prepared with AlkOA40							
AM1B	50/50	55	82	220	268	1240	2605
AM2B	65/35	45	69	117	210	990	2420
AM3B	80/20	37	40	90	100	520	2160
ASB(10%) series using (10 wt.%) BA monomer with AlkOA28							
AS1B(10%)	50/50	47	60	175	240	1200	2450
AS2B(10%)	65/35	40	50	120	200	730	2400
AS3B(10%)	80/20	35	50	75	90	600	1100
ASB(5%) series using (5 wt.%) BA monomer with AlkOA28							
AS1B(5%)	50/50	42	50	160	200	730	910
AS2B(5%)	65/35	38	45	120	185	550	750
AS3B(5%)	80/20	30	42	60	75	420	630

5.4.4 Adhesion measurement of MMBC samples

The results of adhesion properties of MMBC samples are shown in Table 5.9. Comparing the results from this table with those of Table 5.4, it can be concluded that

adhesion property of MMBC samples improves with introduction of BA monomer because the side chains of BA monomer can increase flexibility of sample and subsequently increment of adhesive characteristic.

However, exception occurs for ALB series where using BA monomer results in decrement of adhesion properties. This exception may be due to the fact that BA monomer introduces soft segments from its butoxy groups. Also the oleic acid, as another kind of soft segment in AlkOA65, is higher in this series.

Table 5.9 : Results of adhesion measurement, pencil hardness and water resistance tests for MMBC samples

Samples	Test	Adhesion test		Pencil hardness		Water resistance	
	Thickness	50 μ m	100 μ m	50 μ m	100 μ m	50 μ m	100 μ m
	MMA/macromer						
ALB series prepared with AlkOA65							
AL1B	50/50	1B	1B	6B	6B	3	3
AL2B	65/35	2B	2B	2B	2B	2	3
AL3B	80/20	2B	2B	F	HB	2	2
AMB series prepared with AlkOA40							
AM1B	50/50	5B	5B	3H	2H	3	3
AM2B	65/35	5B	5B	3H	3H	1	1
AM3B	80/20	5B	5B	5H	4H	1	1
ASB series using (10 wt.%) BA monomer with AlkOA28							
AS1B(10%)	50/50	5B	5B	6H	6H	1	2
AS2B(10%)	65/35	5B	5B	6H	4H	1	1
AS3B(10%)	80/20	5B	5B	6H	4H	1	1
ASB series using (5 wt.%) BA monomer with AlkOA28							
AS1B(5%)	50/50	5B	5B	6H	6H	1	2
AS2B(5%)	65/35	5B	5B	6H	5H	1	1
AS3B(5%)	80/20	5B	5B	5H	5H	1	1

Note-Water resistance behaviour: 1, unaffected; 2, slightly whitening; 3, heavily whitening; 4, slightly shrinkage; 5, film soften; 6, film lift out

Therefore, a much higher percentage of soft segments are presented, which in turn decreases the adhesion of film as a result of formation of very soft films. It is also noted that with increasing the MMA content in ALB series, adhesion increases due to decrement of soft segments of oleic acid in copolymer composition.

5.4.5 Pencil hardness test for MMBC samples

The scratch hardness of MMBC samples are shown in Table 5.9. The ASB and AMB series of samples exhibited better results in pencil hardness. As has been discussed in Chapter 4, Section (4.5.1), the MMA content in the copolymers formulation plays an important role in the brittleness of copolymer synthesized due to the existence of the methyl group in the MMA moiety. Thus more MMA used in the copolymer formulation results in less flexibility. As mentioned before by introducing BA monomer, flexible side groups and subsequently extensibility and resiliency increase. Understanding of this proposition will be much clearer by comparing the results obtained in the ASB(10%) series and ASB(5%) series with AS series and also in the AMB series with AM series. For the ALB series, the BA monomer causes decrement in pencil hardness, as noted in section (5.4.4). This exception may be due to the existence of soft segments of the butyl groups and oleate branches in AlkOA65 structure.

5.4.6 Water resistance for MMBC samples

The MMBC samples were tested for water resistance and the results are shown in Table 5.9. From the results, the water resistances of some of the samples improve to some extent. These results may be due to the presence of the butyl group as non polar group, which decreases the permeability of water molecules into the copolymer structure.

Figure 5.3 shows coated panel of AS3B(5%) sample after 8 months under hot and humid conditions.



Figure 5.3 : Coated panel of AS3B(5%) sample after 8 months exposure in the open lab. bench (under hot and humid conditions)

5.4.7 Acid, alkali and salt resistances for MMBC samples

The results of the acid, alkali and salt resistance tests carried out on MMBC samples are presented in Table 5.10. The results show that introducing BA monomer has negative effect on the samples and this effect worsens when the copolymers contain the higher amount of macromer. The presence of flexible side chains in both macromer and BA monomer structures results in more side chains, and more softness, thus less resistance to acid.

It is also observed that, using BA monomer show not much effect on alkali resistance and seems to cause the samples to deteriorate in salt solution. This deterioration becomes worst when the film composition of the coatings has higher percentage of macromer. The butoxy chains, as soft segments, allow ions to pass through the coating. However, with incorporation of 5% BA in AS3B(5%) sample, salt resistance and alkali resistance remained unchanged compared to the AS3 sample.

Table 5.10 : Acid, alkali and salt resistances for MMBC samples

Samples	Test	0.1 HCl		0.1M NaOH		5% NaCl	
	Thickness	50 μ m	100 μ m	50 μ m	100 μ m	50 μ m	100 μ m
	MMA/macromer						
ALB series prepared with AlkOA65							
AL1B	50/50	6	6	6	6	6	6
AL2B	65/35	3	3	6	6	6	6
AL3B	80/20	3	3	3	3	4	4
AMB series prepared with AlkOA40							
AM1B	50/50	4	4	6	6	4	4
AM2B	65/35	2	3	6	6	4	4
AM3B	80/20	2	3	2	2	2	2
ASB series using 10 wt.% BA monomer with AlkOA28							
AS1B(10%)	50/50	3	3	3	3	2	2
AS2B(10%)	65/35	2	3	3	3	2	2
AS3B(10%)	80/20	2	2	2	2	1	1
ASB series using 5 wt.% BA monomer with AlkOA28							
AS1B(5%)	50/50	3	3	3	3	1	1
AS2B(5%)	65/35	2	3	3	3	1	1
AS3B(5%)	80/20	2	2	2	2	1	1

Note- Chemical resistance behaviour: 1, unaffected; 2, slightly whitening; 3, heavily whitening; 4, slightly shrinkage; 5, film soften; 6, film lift out

5.4.8 Solvent rub test for MMBC samples

Comparing Table 5.6 and Table 5.11, it can be found that AS1B(10%) and AS1B(5%) show better results compared to the AS1 with acetone while AL2B, AL3B, AM3B, AS3B(10%) and AS3B(5%) exhibited worse results to ethyl acetate compared to the AM3 and AS3 samples.

Table 5.11 : Results of solvent resistance test on copolymers coatings (MMBC)

Samples	Test	Acetone		Methyl ethyl Ketone		Ethyl acetate	
		50 μm	100 μm	50 μm	100 μm	50 μm	100 μm
MMA/macromer							
ALB series prepared with AlkOA65							
AL1B	50/50	L.G	L.G	L.G	L.G	R	R
AL2B	65/35	S.R L.G	S.R L.G	S.R L.G	S.R L.G	R	R
AL3B	80/20	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
AMB series prepared with AlkOA40							
AM1B	50/50	L.G	L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
AM2B	65/35	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
AM3B	80/20	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
ASB (10 wt.%) series prepared with AlkOA28							
AS1B(10%)	50/50	L.G	L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
AS2B(10%)	65/35	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
AS3B(10%)	80/20	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
ASB(5 wt.%) series prepared with AlkOA28							
AS1B(5%)	50/50	L.G	L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
AS2B(5%)	65/35	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G
AS3B(5%)	80/20	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G	S.R L.G

Note- S.R and L.G refer to Slight Removal of the films and Loss of Gloss respectively, P refers to the Pass and R remove

This is probably due to the presence of oleic acid in macromer structure and existence of butoxy chain in BA monomer as non polar moieties and consequently low intermolecular instructions with polar solvents and higher intermolecular instructions with non polar solvents.

5.5 Summary

The study on physico-mechanical properties and chemical resistance of palm oleic acid-based coatings materials demonstrated many interesting properties of the films. Overall, the physico-mechanical and chemical resistance of the coatings were improved with increment of the MMA content. The AS samples exhibited far superior coating properties followed by AM and finally the AL series. Another factor that can contribute to the superior coating properties is use lower percentage of oleic acid in macromer formulation.

The physico-mechanical properties of this kind of polymers can be attributed to the molecular structure, shown in Figure 5.4.

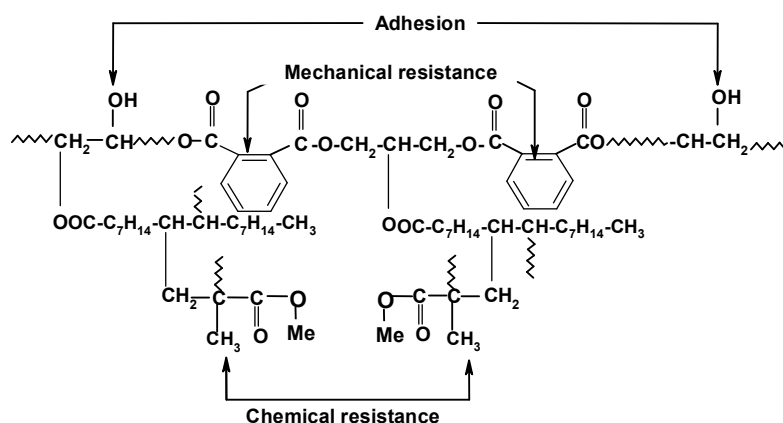


Figure 5.4 : Molecular structure of MMC samples and related reactive sites for chemical and mechanical resistances

Incorporating small amount of BA into the MMBC copolymers can improve some of the characteristics of the coated films. As expressed before, side chains of butyl groups have brought improvement in adhesion and scratch resistance for most of the coated films except of ALB series. Water resistance of some of the coated films has also improved. However, there was no effect on alkali resistance and instead led to negative effects on acid

and salt resistances, and longer drying times. It was found that the incorporation of 5% w/w of BA into AS2 and AS3 copolymers led to significant improvement as coatings materials.