Enhancing the Properties of Mahang *(Macaranga* spp.)

Wood through Acrylic Treatment in Combination with Crosslinker

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Abstract

Macaranga spp. (mahang) was treated with methyl methacrylate (MMA) in combination with a crosslinker trimethylolpropane trimethacrylate (TMPTMA). Polymerisation was carried out by catalyst heat treatment. A fairly consistent acrylic retention was found in the wood when treated with or without crosslinker. Polymerisation of MMA is at maximum with 1% crosslinker and beyond this concentration the polymerisation decreased. The dimensional stability in terms of anti-swelling efficiency (ASE) was determined and found to be improved on treatment. Water absorption was also found to be decreased considerably for treated wood. Mechanical strength of the treated wood in terms of modulus of rupture (MOR), compressive stress and hardness were improved, but the stiffness (modulus of elasticity) did not change. In terms of specific strength (strength to density ratio), the treated material is less stiffer and less strength in lateral direction compared to untreated wood.   However, the specific compressive strength perpendicular to the grain and hardness of the treated material were superior compared with the untreated.

Keywords: Mahang, Methyl methacrylate, Crosslinker, Anti-swelling efficiency

1. Introduction

Mahang (*Macaranga* spp.) is a light density hardwood from a pioneer tree species which emerge large quantity in logged-over forest in Southeast Asia (Helmer *et al*., 2000). It has a   potential as resources to augment the depleting supply of logs from natural and plantation forests. Due to its poor properties in nature, it is still underutilized, but this wood can have value added by being made into wood suitable for different applications like flooring, panelling and furniture through proper treatment such as chemical modification.

Wood properties can be modified through treatment either with or without changing the chemical nature of the wood (Norimoto and Gril, 1993). Considerable work has been done on the modification of wood by impregnation with suitable polymers depending upon the end uses (Hill, 2006). Treatment with vinyl type monomer followed by curing (radiation or calatlyst) significantly improved the moisture resistance, hardness of wood (Meyer, 1984). Vinyl monomers have also proven effective in imparting dimensional of oil palm wood (Ibrahim, 1989). This treatment does not change the chemical nature of the wood and is known as wood-polymer composite (WPC) (Hill, 2006). WPC shows improvement in both physical and mechanical properties over untreated wood (Rowell and Konkol, 1987). Impregnation of rubberwood with styrene in combination with a crosslinker glycidyl methacrylate improved the dimensional stability, strength and stiffness of the wood (Devi *et al.,* 2003). The impregnation of wood with acrylic or vinyl type monomer showed less dimensional stability in the presence of moisture. This was due to the confinement of the monomer in the cell lumen instead of the cell wall (Rowell and Youngs, 1981). Attempt has also been made to impregnate acrylic polymer into softwood and hardwood but the dimensional stability imparted was low (Ashaari *et al.,* 1990a). A greater dimensional stability was achieved when treated with aqueous dimethylodihydroxythleneurea (DMDHEU), a glyoxal urea adduct, but this treatment significantly reduced the strength and stiffness of wood (Ashaari *et al*., 1990b).

Methyl methacrylate (MMA) is one of the least expensive and most readily monomers and is used alone or in combination with other monomers to crosslink the polymer system. Ng *et al.* (1999) stated that dimensional stability of MMA-treated wood can be further enhanced through incorporation of crosslinking agent to the treating solution. Crosslinking agents generally accelerate polymerization reaction rate and improve the properties of WPC (Kenaga, 1970). Geraldes *et al.* (2004) did a series of studies on acrylates crosslinking agents capable to impart a more effective croos-linking on Poly(MMA) matrix. They found out that trimethylene propane trimethylacrylate (TMPTMA) and diethylene glycol diacrylate (DEGDMA) presented higher reactivity or compatibility with the polymer. Modification of mahang with MMA is expected to enhance its properties and may expand the usage of this material especially in the manufacturing of laminated products such as flooring, panelling and furniture components.

The purpose of this study was to modify the low density wood of *Macaranga* spp. (mahang) with acrylate in combination with crosslinker (TMPTMA), and examine the effect of the treatment on dimensional stability and strength properties of the modified wood.

2. Materials and Method

2.1 Materials

Mahang *(Macaranga* spp.) wood was obtained from Forest Research Institute, Malaysia. The treating solution was methyl methacrylate (MMA) and trimethylolpropane trimethacrylate (TMPTMA) as crosslinking agent while benzoyl peroxide (BPO) was used as a free radical catalyst to accelerate the polymerization process. All chemicals were of analytical grade and were used as received. The solution was prepared by adding 2% BPO and 0%, 1%, 3% and 5% crosslinkers separately to MMA solution. The wood were flat sawn into samples (the width is tangential surface) of nominally 10-mm thick, 50-mm wide and 150-mm long. End-matched samples were assigned to one of five groups: 0%, 1%, 3% and 5% crosslinking agents or control . The control group was untreated.

2.2 Impregnation process

All samples were dried in an forced circulation air oven at 103 ± 2^0C to constant weight before treatment and the dimensions (V_o) and weights (W_o) were measured. The samples were then impregnated with the MMA solutions separately using a Bethel cycle in a cylinder. The treating cycle consisted of a 15-min initial vacuum of 85 kPa. The cylinder was then filled with treating solutions under vacuum. When the cylinder was completely filled with the solution, a pressure of 340 kPa was applied and held for 30 min at ambient temperature. The cylinder was then vented to atmospheric pressure and the solution was withdrawn. The impregnated samples were immediately weighed and wrapped with several layers of aluminium foil to prevent evaporation of MMA. Prior to weighing (W_f), excess solution was removed by blotting. The samples were then heat in an oven maintained at 65ºC±1ºC for 2 h. Excess polymer on the surface of the treated wood was scrapped off using scrapper. This was followed by drying in an oven at 103 ± 2^0C to constant weight. Oven dry weight (W_{to}) and volume were measured (V_{to}) before the were conditioned to equilibrium condition at 65±5% relative humidity maintained at 25±2°C.

2.3 Determination of polymer content

The treated samples were evaluated for percentage of monomer in the sample (% M), percentage of polymer content in the sample (% P), and percent conversion of monomer into polymer (% C). They were calculated using the following Equations (Duran and Meyer, 1972):

$\% \text{ M} = 100 \ (W_m / W_o)$ [1]

$\% \text{ P} = 100 \ (W_p / W_o)$ [2]

$\% \text{ C} = 100 \ (W_p / W_m)$ [3]

% Change in dimension (ΔD) $= 100 \ [(V_o - V_{to}) / V_o]$ [4]

where,

W_m (weight of monomer, g) $= (W_f - W_{od}) / \ W_{od}$ [5]

W_p weight of polymer, g $= (W_{to} - W_{od}) / \ W_{od}$ [6]

W_o = oven dried weight of untreated wood sample, g

2.4 Evaluation of dimensional stability

Dimensional stabilization was quantified by comparing the volumetric swelling coefficients and water absorption of treated and control specimens. The swelling process were done through 30-min vacuum followed by soaking in distilled water for 24 h (Ashaari *et al.,* 1990a*)* and exposing in water vapour at 95% relative humidity (Rowell and Youngs, 1981). In this case, the exposure time is taken to be completed when the untreated samples reached constant weight. This took approximately 35 days. For this test, oven-dried wafers measuring 20 mm x 20 mm in cross sections and 10 mm were used. The weight and volume of samples before and after swelling process were measured. The volumertic

swelling coefficient (S), reduction in water absorption (R) and antiswelling efficiency (ASE) were calculated using the following equations.

$$S\ (\%) = \quad 100\ (V_w - V_d)\ /\ V_d \qquad\qquad [7]$$

$$R\ (\%) \quad = 100\ (M_c - M_t)\ /\ M_c \qquad\qquad [8]$$

$$ASE\ (\%) = 100\ (S_c - S_t)\ /\ S_c \qquad\qquad [9]$$

Where,

V_w = volume after humidity conditioning or soaking in water, mm^3

V_d = volume of oven dry, mm^3

M_c = moisture content untreated,%

M_t = moisture content treated, %

S_c = untreated volumetric swelling coefficient, mm^3

S_t = treated volumetric swelling coefficient, mm^3

2.5 Evaluation of mechanical properties

2.5.1 Static bending test

Static bending test was performed according to procedure specified in British Standard BS 373: 1957 (BSI 1957) with a modification of the specimen size (10-mm thick, 20-mm wide and 250-mm long). The specimens were tested under a static load with the crosshead speed of 5.0 mm/min. The test was carried out on 50 kN Instron universal testing machine. Load deflection curves were recorded. Mechanical properties calculated from the load deflection curves included modulus of rapture (MOR) and modulus of elasticity (MOE).

2.5.2 Compression perpendicular to grain test

The tests were carried out according to British Standard BS 373:1957 (BSI 1957) with small specimens size (10-mm thick, 20-mm wide and 20-mm long). The crosshead speed of this test was 0.5 mm/min. The properties computed were compressive stress at proportional limit (CSPL) and compressive stress at compression of 2.50mm (CSmax).

2.5.3 Hardness test (Janka indentation test)

The size of test blocks was 10 mm x 40 mm x 60 mm. The test was carried out by probing 11.3-mm diameter sphere onto the wide surface of the specimens. Load at which the ball had penetrated to one half its diameter was recorded (BSI 1957)

2.6 Experimental design

Statistical analyses were performed on physical and mechanical property values to detect any changes in the treated material compared to untreated group. A complete randomized design with 4 levels of treatment and untreated was conducted where the treatment means were separated by using Tukey at $p < 0.05$.

3. Results and Discussion

3.1 Polymerization of MMA in mahang wood

The trends of monomer and polymer loadings in mahang wood with various concentrations of crosslinking agent are shown in Figure 2. A consistent loading of MMA monomer (254-265%) in the wood when treated with or without crosslinking agent. The higher monomer uptake by the wood is very much attributed to the porosity and permeability of the material. It is known that mahang is a very low density and permeable wood. In terms of polymerisation, MMA with 1% TMPTMA crosslinker gave the highest polymer loading (230%) with 87% monomer converted to polymer, while wood treated without crosslinking agent had the lowest loading (186%) with only 74% conversion when curing at 65^0C. The results suggest that the crosslinking agent had successfully generate higher crosslinked matrix of Poly(MMA). Earlier research found that 1% TMPTMA can generate 96.6% crosslinked matrix of   PMMA at 87.8^0C (Geraldes *et al.,* 2004). However, with the increasing concentration of TMPTMA in the treating solution, the polymer loading decreases. This is shown by the polymer loading values in 3% and 5% TMPTMA which were 216% and 197% respectively (Table 1). The additional amount of the crosslinking agent will depress the increasing molecular weight of linear Poly(MMA) (Meyer, 1984).

The location of polymers in the samples was investigated using a scanning electron microscope. As shown in Figures 1 and 2, polymer is seen occupying the cell lumen and vessels of the wood. In the case of acrylic treatment with 1% crosslinker (Figure 2), higher percentage of cell lumens and vessels were filled with polymers than in sample treated without crosslinking agent (Figure 1), indicating that the TMPTMA had successfully generated higher crosslinked matrix of polymer.

3.2 Properties of Mahang-MMA composite

Table 1 summarises the analysis of variance (ANOVA) on properties of untreated and MMA-treated mahang. The descriptive statistics of the properties is given in Table 2. Group means with the same letter are not significantly different. Percent increment of property values exhibited in the table is compared to untreated values. The ANOVA shows that except for modulus of elasticity (MOE), all the properties tested significantly differ among the treatment groups.

3.2.1 Effect on physical properties

The density of mahang wood increased significantly by approximately 200% from 288 kgm^{-3} (untreated) to about 829 – 910 kgm^{-3}. This variation in density was affected by the polymer loading. Samples with the highest polymer loading (with 1% crosslinker) had the highest density (910 kgm^{-3}) and those with the lowest polymer loading had the lowest density (829 kgm^{-3}). When immersed in water for 24 h, the anti-swelling efficiency (ASE) of the wood ranged from of 48-51% with no significant difference was noticed among the treatments. It has been reported oil palm wood treated with MMA without crosslinking agents had an ASE of 46% (Ibrahim, 1989). When exposed to water vapour (95%) up to 35 days, the modified wood without crosslinker had lower ASE value (21.9%) compared to those with crosslinker (36.3 – 41.6%). There is no difference in ASE of the modified wood with different concentration of crosslinker. After that, the dimensional stability is expected to behave similar to untreated wood (Hill, 2006). This poly(MMA) is simply bulked the cell lumens and vessels of the wood. There is no significant changes in dimension of the wood after treatment suggesting that no monomer penetrated the cell wall (Table 2). The cell wall is freely to swell and polymers are just act as barrier to reduce the moisture uptake (Calleton *et al.*, 1970; Noah and Foudjet, 1988 and Ibach and Ellis, 2005). In this study, MMA treatment with or without crosslinker showed very effective in reducing water or moisture uptake. In 24 h soaking in water, the R values were in the range of 92-94%, while in longer time exposure to water vapour, the values were 50-64%.

3.2.2 Effect on mechanical properties

A significant increment was found for MOR, compressive stress and hardness values of modified mahang. No difference in MOE was found between the modified wood and the untreated wood, although 11 - 23% improvement for MMA-treated wood. The result suggests that regardless of the presence of TMPTMA in the treatment, the polymer content alone affects the mechanical properties except for MOE. The insignificant change in MOE suggests that the polymer itself was not elastic enough which could enhance the elasticity of the wood. Schneider *et al.* (2003) also reported the same for basswood when treated with MMA. For MOR, the increment was between 23 to 55% from the original value of 57.27 Nmm^{-2}. Among the MMA-treated material, those with the highest polymer content, i.e., treatment with the addition of 1% TMPTMA had the highest MOR value (88.87 Nmm^{-2}). The same was also noted for compressive stress. CSPL and CSmax values for the treated material were markedly increased, i.e., by between 576 -1384% and by 632 – 1188%, respectively. The MMA treatment also significantly increased the hardness of mahang. The increasing rates vary between 219% and 386% and the highest value was recorded for treated wood without TMPTMA (6.07 kN). Majority of the treated samples failed before the sphere fully penetrates the surface of the test blocks. This shows that *in situ* polymerisation of MMA tends to produce more brittle material.

Specific strength is the ratio of mechanical values over density. It is known that mechanical properties of wood are directly proportional to density (Haygreen and Bowyer, 1982). The analysis was done to investigate whether the weight gain due to the treatment would compensate the increment in mechanical properties. Results in Table 3 show that the treated board had much lower specific MOE values (8.60-8.95 Nm^3/kgmm^2) and MOR (0.084-0.098 Nm^3/kgmm^2) compared to 22.7 Nm^3/kgmm^2 and 0.199 Nm^3/kgmm^2, respectively in untreated material. This indicates that at an equal density level, the treated wood is 60% less stiffer and can only sustain 49% of its original lateral load. However, the specific stress perpendicular to the grain 3-4 folds than that of untreated. For hardness, the specific value was about similar or slightly higher compared to the untreated material.

4. Conclusions

The study shows that MMA loading in mahang wood was fairly consistent when treated with or without crosslinking agent (TMPTMA) using a bethel process. The highest degree of polymerisation was attained with the addition of 1% crosslinker and beyond this concentration the polymerisation decreased. The density of the modified wood increased markedly and it is very much associated with the polymer contents. The dimensional stability of the modified wood with or without crosslinker when soaked in water for 24 h was similar. However, in water vapour, treatment with crosslinker imparted higher dimensional stability. The stability of the material was not affected by the contents of the crosslinking agent. Polymer loading significantly affects the strength and hardness of the wood but did not change the stiffness. As regards to specific strength, the results show that at equal density level, the treated material is less stiffer and sustained lesser lateral load than that of untreated wood. Nevertheless, the specific compressive strength perpendicular to the grain and hardness were greater in treated mahang compared to untreated.

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Table 1. Summary of ANOVA on properties of MMA-treated mahang

Source of variation	%P	ASE	CSPL	CSmax	Hardness	MOE	MOR
Treatments	-	-	**	**	**	ns	**
Concentrations of TMPTMA	**	**	**	**	ns	ns	**

** = significantly different at $p<0.05$, ns = not significantly different

Table 2. Physical properties of MMA-treated mahang

TMPMTA concentrations (%)	0%	1%	3%	5%
Polymer (%)	187.5b	229.6a	216.4ab	197.2ab
	$N=5$	$N=5$	$N=5$	$N=5$
ΔD (%)	-3.9	-1.85	-3.33	-2.41
Density (kgm^{-3})	829b±80.0	910a±70.0	903a±79.3	844ab ±16.2
Increment, %	188	216	214	193
	$N=5$	$N=5$	$N=5$	$N=5$
Reduction in absorption (R_1, %)	94.36a±0.51 $N=10$	93.95a±1.930 $N=10$	94.29a±1.03 $N=10$	92.0a±3.19 $N=10$
ASE_1, %	48.49a±8.92 $N=10$	50.82a±9.61 $N=10$	49.64a±8.66 $N=10$	48.24a±11.38 $N=10$
Reduction in absorption (R_2, %)	60.05a±10.52 $N=12$	59.21a±11.51 $N=12$	63.35a±6.48 $N=12$	49.38b±5.44 $N=12$
ASE_2, %	21.94b±2. 63 $N=12$	41.53a±4.7 $N=12$	36.28a±3.55 $N=12$	41.63a±6.71 $N=12$

[1]Means followed by the same letter are not significantly different ($p < 0.05$), ± are standard deviations

ASE_1 and R_1 = determined by soaking after vacuumed for 24 h, ASE_2 and R_2 = determined by humidity conditioning, N= Number of samples

Table 3. Mechanical properties of MMA-treated mahang compared with untreated wood

TMPMTA concentrations (%)	Control	0%	1%	3%	5%
Polymer (%)		187.5b	229.6a	216.4ab	197.2ab
MOR (Nmm^{-2})	57.27c±4.5	79.34ab±15.04	88.87a±1.1	79.60ab±8.16	70.64b±6.3
Increment, %		39	55	39	23
MOE (Nmm^{-2})	6540a±740	7424a±909	7886a±640	8040a±567	7259a±569
Increment, %		14	21	23	11
CSPL (Nmm^{-2})	2.80d±0.53	23.98c±4.35	41.57a±2.35	32.60b±3.92	18.93c±0.78
Increment,%		632	1188	1025	710
CSmax (Nmm^{-2})	5.65c±1.0	41.36b±6.17	72.75a±6.7	63.58a±11.55	45.79b±6.86
Increment,%		386	219	279	350
Hardness (kN)	1.25b±0.21	6.07a±1.97	3.99a±1.49	4.74a±1.03	5.63a±0.93
Increment,%		386	219	279	350

[1]Means followed by the same letter are not significantly different ($p < 0.05$), ± are standard deviations

Table 4. Specific strength of MMA-treated mahang compared with untreated

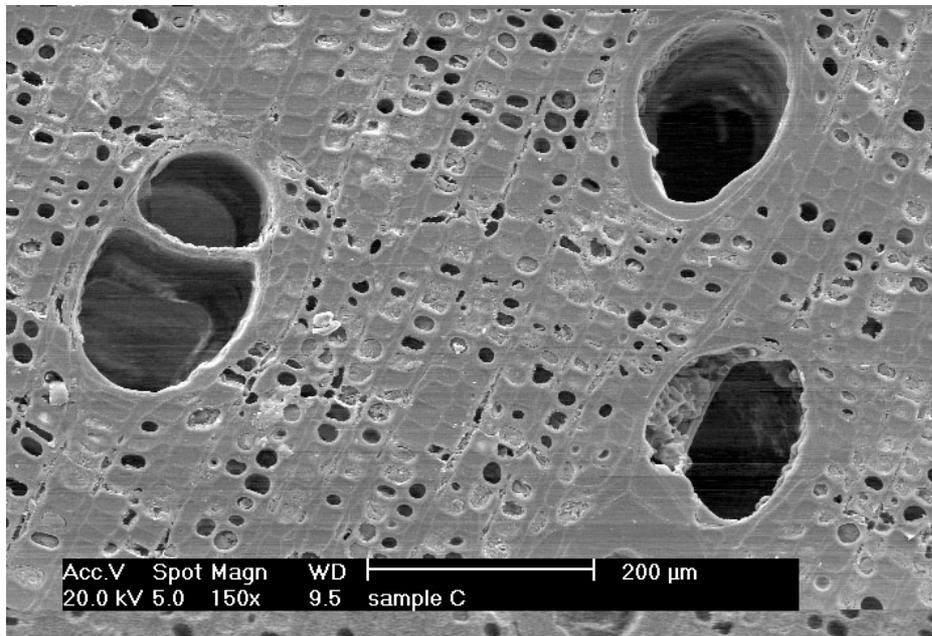| TMPMTA concentrations (%)	MOE (Nmm^{-2}/kgm^{-3})	MOR (Nmm^{-2}/kgm^{-3})	CSPL (Nmm^{-2}/kgm^{-3})	CSmax (Nmm^{-2}/kgm^{-3})	Hardness N/kgm^{-3}
Control	22.7	0.199	0.010	0.020	4.34
0.0	8.95	0.096	0.029	0.050	7.32
1.0	8.67	0.098	0.046	0.080	4.38
3.0	8.90	0.088	0.036	0.070	5.25
5.0	8.60	0.084	0.022	0.054	6.67

Figure 1. Cross section of MMA-treated mahang wood without crosslinking agent showing cell lumen and vessels with partially and fully filled with polymer
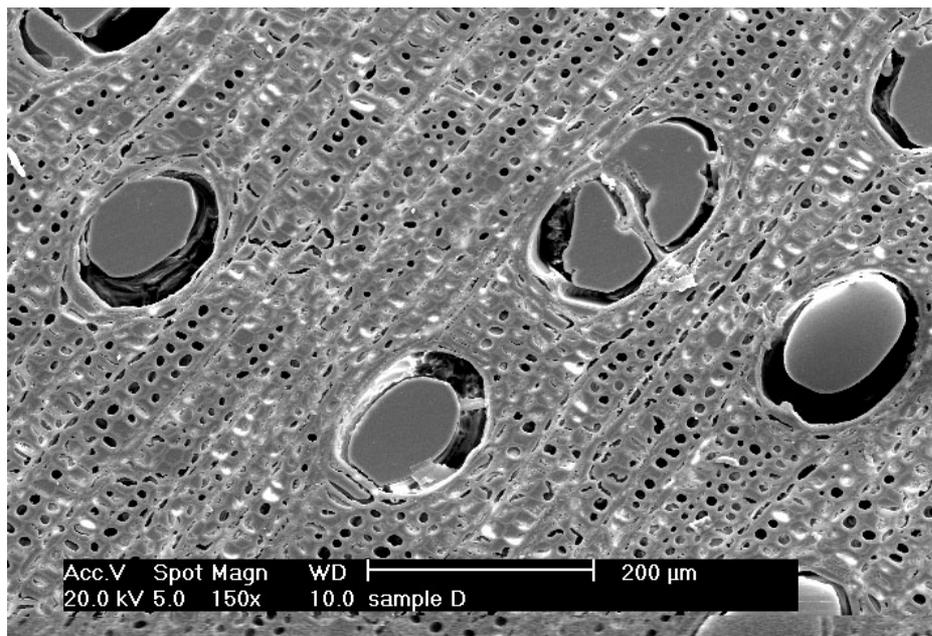

Figure 2. Cross section of MMA-treated mahang wood with 1% TMPTMA showing higher percentage of lumens and vessels filled with polymer
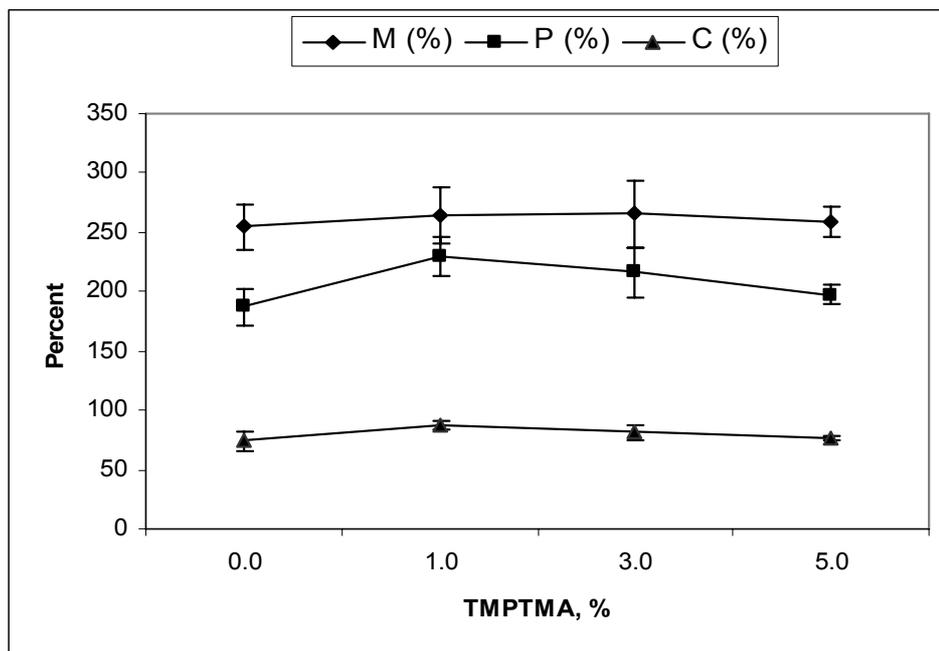
Figure 3. Effect of TMPTMA concentrations on polymerization of MMA in mahang