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Melamine-Formaldehyde Curing Acceleration by TiO₂-based Silver-White Pigments Catalysis

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ABSTRACT

The preparation of Melamine-formaldehyde (MF) resins was found to be catalyzed by TiO₂-mica silver white pigments, the presence of small proportions of these advancing considerably the resin during its preparation under the same conditions. These pigments are composed mainly of TiO₂-mica, as ascertained by X-ray diffraction (XRD), with the TiO₂ being mainly in its rutile phase but presenting also some traces of the anatase phase. FT-IR and ¹³C NMR inferred clearly the presence of a catalytic effect of the TiO₂-mica and appeared to indicate that the catalytic effect involved mainly the –NH₂ groups of melamine and on formaldehyde. According to the peak reaction temperature measured by DSC, the highest catalytic activity of TiO₂ on MF curing appears to be achieved at a 2% addition level by weight. Different possible explanations of this effect have been proposed, the most likely one being the catalytic effect caused by TiO₂-promoted coordination complexes, the effect of acceleration being due to the Ti charge being stronger than that of H⁺, and the complex formed being unstable, thus not inhibiting the progress of the reaction.

KEYWORDS: silver white pigments, TiO₂, catalysis, polycondensation advancement, melamine-formaldehyde resins

INTRODUCTION

Pearlescent pigments are the main group of special effect pigments. They show pearl nacreous effect due to an angle dependent optical feature. The dominant class of these pigments consists of mica coated with thin layer of metal oxides. Pearl effect pigments based on titanium dioxide-coated muscovite mica are one of the most important members in this category. Different colors of titanium dioxide- mica pigments can be produced according to the TiO₂ coating layer thickness which is typically in the range of 50-300 nm

on all sides of the mica flakes. For a silver white pearl effect pigment, a coating layer with the thickness of 50 nm is needed.^{1,2}

One of the main applications of pearl effect pigments is in the printing industry, particularly in decorative printing. Flexography and Gravure printing are methods which may use special effect pigments in their ink composition. Decorative paper printing, widely used in the furniture and decoration industries, is a major application of the Gravure method.³

Décor papers are made from alpha cellulose-rich pulp and are characterized as technically advanced and highly engineered specialty papers. These alpha cellulose-based papers are known as the exclusive base print papers for producing the decorative films in gravure printing processes. Nowadays are widely used in laminated board production because of their resistance to photo-yellowing. These decorative papers are impregnated with thermosetting synthetic resins such as urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins and are converted into a technologically sensitive cellulosic composite, i.e. melamine impregnated paper or decorative foils, through the impregnation process. The decorative foils are also extensively used as coating materials for lamination on wood based panels in furniture and decoration sectors.⁴

Metals behave as hydrogen ions in accelerating the initial attack of the formaldehyde to the phenolic nuclei in formaldehyde based resins⁵⁻⁹. Indeed, they act as Lewis acids due to having vacant orbitals and the property of accepting a pair of nonbonding electrons. Apart this primary effect, the relative stability of the intermediate complexes formed determines if the reaction is accelerated, retarded or even stopped. For example bivalent metal ion always accelerate to a greater or lesser extent the reaction, while some trivalent metal ions, such as Cr^{+3} , greatly slow down the reaction due to the second effect above. Titanium ion (Ti^{+4}) is one of the most important metal ions of this sort. However, there is no literature on the effect of tetravalent ions on resins. The crosslinking reaction of melamine-formaldehyde resins occurs under acid conditions, typically by adding an acid-generating hardening catalyst. It is possible to imagine that titanium dioxide in the composition of pearl pigments could also exhibit such a catalytic activity and accelerate the polymerization reaction of the resin. Thus, the work presented here addresses this issue and is intended to provide additional insights on the mechanism of metal ions catalytic activity in the field of resin advancement and resin curing.

EXPERIMENTAL

An industrial, pure melamine-formaldehyde resin (MF) (Pars Neopan Company, Nashtaroud, Iran) for paper impregnation of 51% resin solids content was used. The MF resin had pH 8.9, specific gravity of 1.216 g cm^{-3} at 20°C and viscosity of 14.5 (Ford cup Nr 4). The melamine-formaldehyde-resin behavior was studied both without and with the addition of shiny pigments at different percentages. Notably, the silver white pearl pigments used in this study were extracted from the gravure printed decorative paper, and their catalytic role in a melamine-formaldehyde resin was studied by a set of laboratory diagnostic methods, these being:

- X-ray Powder Diffraction (XRD) test by an XPERT PRO PMD (Malvern Panalytical, Malvern, UK).
- pH tested with a Metrohm pH meter (Metrohm, Zofingen, Switzerland).

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- FT-IR test by a NICOLET-IF-10e spectrophotometer (Thermo Fisher Scientific, Geneva, Switzerland)
- ¹³C-NMR test by a Brüker 400MHz spectrophotometer (Brüker, Billerica, Massachusetts, USA)
- DSC test with a heat flux 214 Polyma DSC 21400A-0634-L (Netzsch, Selb, Germany).

Pigment extraction from raw metallic decorative paper

Pieces of metallic decorative paper of 10x10 cm² were floated in a container filled with distilled water. After about ten minute immersion, the pigments detached from the paper and settled down in the container. The container was then placed under conditions devoid of any dust or contamination, the water was evaporated and the precipitated pigments carefully collected.

X-Ray diffraction

Characterization of the extracted pigments was achieved by X-ray diffraction of a small pigments sample. The XRD pattern was obtained using an X'pert Pro MPD PANalytical diffractometer equipped with a Cu X-ray source (wavelength = 1.542 Å) under the following conditions: 30 mA flow intensity, 40 kV voltages, 2θ: 4-80° and with a 0.02° resolution. The results showed that the titanium dioxide-covered mica constituted the essential part of the pigments (Fig. 1).

pH Test

A one gram melamine-formaldehyde resin sample was placed in each of 4 different small test tubes and 0 to 3 weight percent of pearl pigments were added to them. The test tubes contents were mixed properly, and the pH of the samples was measured at 25°C.

Infra Red (IR) Spectrometry

One-gram melamine-formaldehyde resin samples with 0, 1, 2, and 3 percent weight/weight of titanium dioxide-mica, as a catalyst, were added separately to four aluminum containers of 4.5x1.5 cm dimensions. All of these samples were then heated in an oven at 120°C for 2 hours. After pill preparation IR spectra were then done of the samples so treated. Moreover, in order to obtain better results, the comparative IR test graphs of the four samples were drawn (Fig. 2).

Differential Scanning Calorimetry (DSC)

One gram of melamine-formaldehyde resin with 0, 1, 2, and 3 percent weight/weight of titanium dioxide-mica was added separately to each of 4 glass beakers. After homogenizing each sample, 10 milligrams of each sample were placed in an aluminum container with porous caps and compressed well to minimize the empty spaces between the components. The samples were then heated from 30° to 240°C at a heating rate of 10 °C/min under nitrogen.

The Differential Scanning Calorimetry results are shown in Fig.3.

¹³C NMR

0, 1, 2, and 3 percent weight/weight of titanium dioxide-mica were added to 4 small test tubes each containing 1 gram of melamine-formaldehyde resin. The contents of the testing tubes were mixed well, then Chloroform-D solvent was used for the samples dilution, and the ¹³C NMR spectrum was done for each sample. The chemical shifts were calculated with respect to (CH₃)₃Si(CH₂)₃SO₃Na dissolved in D₂O for NMR shift control. The spectra were taken at 62.90 MHz, for a number of transients (ca. 1000). All the spectra were run with a relaxation delay of 5 s, and the chemical shifts were accurate to 1 ppm.

RESULTS AND DISCUSSION

The pigments separated from the decorative paper were identified by XRD (Fig. 1). This showed the characteristic pattern of TiO₂ XRD spectrum with **2θ** values at 27.5°, 36.1°, 54.3° which most likely belong to the crystalline structure of rutile TiO₂. In addition, the strong sharp peak appeared at **2θ** value of 26.7° and some smaller peaks at 8.7°, 17.6° and 45.4° along with the other weak peaks could also be ascribed to mica. No clear diffraction peaks of anatase phase were detected in the XRD pattern. This indicates that the silver white pigments used in the printing ink of décor paper are predominantly composed of rutile TiO₂ and mica^{10, 11}. However, there may exist a complex double peak at 2θ = 54°/55° with an intensity lower than that of rutile peak and some small peaks within the **2θ** values of 30°-35° attributable to anatase phase that are probably masked by the rutile TiO₂ and mica peaks, respectively^{12, 13, 15}. The intensity of the 2θ = 26.7° peak is high and the width of the (101) plane becomes narrow^{12, 14, 15}. The sharpness of the peak indicates that the pigment possess a good crystalline nature with a dominant phase of rutile TiO₂¹⁶⁻¹⁸.

The pH decreased but progressively less as the pigment percentage increased in the melamine-formaldehyde resin as compared to the pigment-free resin (Table 1).

As we can observe in the IR spectrums (Fig. 2), as the amount of the pigment in the MF resin increases, the intensity of the peaks decreases, because of the growing percentage of the IR electromagnetic ray transmission, which indicates the interfering role of the pigment as a mineral in the IR ray transmission. Of interest is the shift of the primary amine peak from 1662 cm⁻¹ for the pure MF resin to ever lower values, respectively down to 1635 cm⁻¹ for 3% TiO₂ addition. This would appear to indicate that the primary amine group of melamine is somehow the main group involved in the mechanism of TiO₂ acceleration, while the secondary amine does not appear to change.

In the DSC test, each sample was heated in the 30 to 240°C temperature range at 10 °C/min heating rate. According to Fig. 3 and Fig. 4, as the TiO₂-mica percentage increases in the MF resin, endothermic peak reaction temperature decreases confirming that the curing reaction was accelerated by TiO₂. However, the lowest endothermic peak reaction temperature appeared in the thermogram of the resin containing 2% of titanium dioxide-mica. As can be seen in Table 2, the start and end temperatures of the endothermic peak of the MF resin without any TiO₂-mica is 94.5 °C and 111.9 °C respectively, and the temperature of the climax of the peak in this state is 102.4° C. Next, by the inclusion of 1 wt.% of titania-mica in the curing process of the melamine-formaldehyde resin, the temperatures of the start, end, and climax of the peak reach 97.7°, 111.3°, and 101.0° C, respectively. In the thermogram of the resin containing 2 wt.% pigments, the temperatures of the start, end, and climax of the peak reach 36.6°, 72.5°, and 63.4°C, and finally, by adding 3 weight percent of titania-mica to the resin, the temperatures of the start, end, and climax of the peak reach 35.7°, 85.5°, and 76.2°C. According to the peak reaction temperature measured by DSC, the highest catalytic activity of TiO₂ on MF curing is achieved at 2% addition level.

More accurate DSC thermograms are shown in the supplementary material (Figs 1-4) Supplementary material). The peak temperature on the first part of the peak of the 3% sample was higher than the peak temperature of 2% sample (76.2°C versus 63.4°C), while both peaks (peak of the 2% sample and first part of the peak of the 3% sample) began to appear at almost the same onset temperature of around 36°C probably implying the stronger catalytic activity of the rutile phase at 2 % pigment level. However, if

comparing the heat flow (darkened area) (supplementary material) of these two thermograms, it is found that in the 2 % sample, the total heat flow is -345.9 j/g, whereas the total heat flow in the 3 % sample even counting both parts of the endothermic peak at this pigment level will give $-139.4 \text{ j/g} + (-123.4) \text{ j/g} = -262.8 \text{ j/g}$ demonstrating a lower activation energy demand for the reaction at this level. This may be a contradiction with the findings of DSC on the catalytic activity of rutile comparing the 2 % versus the 3% addition levels based on the peak reaction temperature.

In the case of the DSC, there is again a peak shift similar to the FT-IR results. Two small peaks in the thermogram of the 2% case at around the temperature of 130°C seem not only to have shifted down to around 100°C but also have appeared stronger in the thermogram of 3% level (Supplementary material). Instead the first peak in the 3% level has become noticeably smaller than the same peak in the 2% level and slightly wider as well (Supplementary material). Possibly this could be attributed to the formation and interference of the intermediates with the reaction advancement as a result of pigments addition to the resin.

The endothermic peaks are the peaks that indicate that both added water and the water generated by the polycondensation reaction do evaporate. The exotherm peaks are most likely masked in the same region by the huge endothermic peaks. However, there are some small exothermic peaks after 101°C in the DSC of 3% TiO₂ between 120 and 140°C that are the peaks probably due to the rearrangement of methylene-ether bridges (-CH₂OCH₂-) to methylene bridges (-CH₂-). The shoulder at around 90°C in the 3% TiO₂ is also indication of a hidden exotherm.

The graph in Fig. 4 and the Results presented in Table 3 show the behavior of the melamine-formaldehyde resin curing in the 4 aforementioned states (using 0 to 3 percent of TiO₂-mica) comparatively. The minimum start, end, and climax of the peak temperatures, which are related to sample 2, are quite recognizable in this graph. It is worth mentioning that in sample 4, the resin plays a catalytic role in the cooking process (using 3-percent titan-mica) compared to sample 1, but according to the peak reaction temperature, the effect is less strong compared to sample 3, and this occurs probably because the TiO₂-mica disturbance begins in the resin cooking process. In brief, the optimal amount of TiO₂-mica to be used as a catalyst in the MF resin polymerization process is 2 wt%, and as this amount increases, the catalytic role of TiO₂-mica appears to decline.

The ¹³C NMR spectrum interpretations of the MF reacted with TiO₂-mica and the MF that has not reacted to TiO₂ are as below (Figs. 5abcd, 6abcd):

- There is a definite catalytic effect of the reaction very evident from the spectra in the 140 to 175 ppm range, starting from 2% TiO₂ addition. This is shown by the widening of the peaks indicating the formation of oligomers of much higher molecular weight. Thus the reaction has advanced more. This occurs for all the three 1%, 2% and 3% TiO₂-mica cases in relation to the untreated MF and is an indication that the TiO₂-mica reaction have advanced further.

- Again in the 140 to 175 ppm range it appears the shoulder of trisubstituted and multisubstituted triazine in the 3% TiO₂ case. This indicates that the system is even more advanced in its reaction as tridimensionally branched oligomers have started to form and they are relatively abundant in the reaction system. This confirms that increasing the percentage TiO₂ catalyzes the reaction.
- Again in the 140 to 175 ppm range it appears at 3% TiO₂-mica that there are two peaks of unsubstituted triazine, indicating that one of them shows that the unreacted melamine molecule is in two different environments. One is as the previous spectra just unreacted melamine, but the other peak is an intermediate formed by the linkage of unreacted melamine with TiO₂, thus an intermediate complex intervening in the catalysis of the reaction. This confirms what deduced in IR spectrometry from the progressive shift of the primary amine groups peak as the percentage of TiO₂-mica progressively increases. This means that the mechanism of catalysis involves the primary amine group of melamine, this group being bound to TiO₂ in some intermediate form of the mechanism.
- In the 0 to 85 ppm range there are several less evident indications of the TiO₂ catalytic effect. First the peak at 69.9 ppm indicates that the –N(CH₂OH)₂ practically disappear when 3% TiO₂ is present. Equally the small amount of unreacted urea at 82 ppm present in the 1% and 2% TiO₂ cases is almost certainly generated by the rearrangements of the –CH₂OCH₂– methylene ether bridges to methylene –CH₂– bridges. This must be so because the 82 ppm peak does not exist at 0% TiO₂, thus is the TiO₂ induced catalysis that leads rapidly to the rearrangement of the –CH₂OCH₂– methylene ether bridges with liberation of the formaldehyde seen at 82 ppm for the 1% and 2% TiO₂ cases. That this is what occurs is further supported by the disappearance of the –CH₂OCH₂– methylene ether bridges peak at 67.9 ppm in the 3% TiO₂ case.
- The peak at 68.9 ppm shifts slowly to lower ppm as the percentage of TiO₂ increases, to eventually be found at 68.3 ppm for the 3% TiO₂ case. It is difficult to assign this peak to a particular group but it does not appear to be particularly affected by the catalysis.
- The three peaks at 60, 62 and 64 ppm are plain –NH-CH₂OH groups under different environments, belonging to the melamine-formaldehyde resin. The peaks at 49 and 47 ppm are peaks belonging to methylene bridges –CH₂– between melamine molecules, one to a linear –NH-CH₂-NH- and one to a branched –N(-CH₂)-CH₂-NH- environment. Their intensity is small not because their proportion is low but simply as in this shifts region the intensity of the peaks is always much smaller.

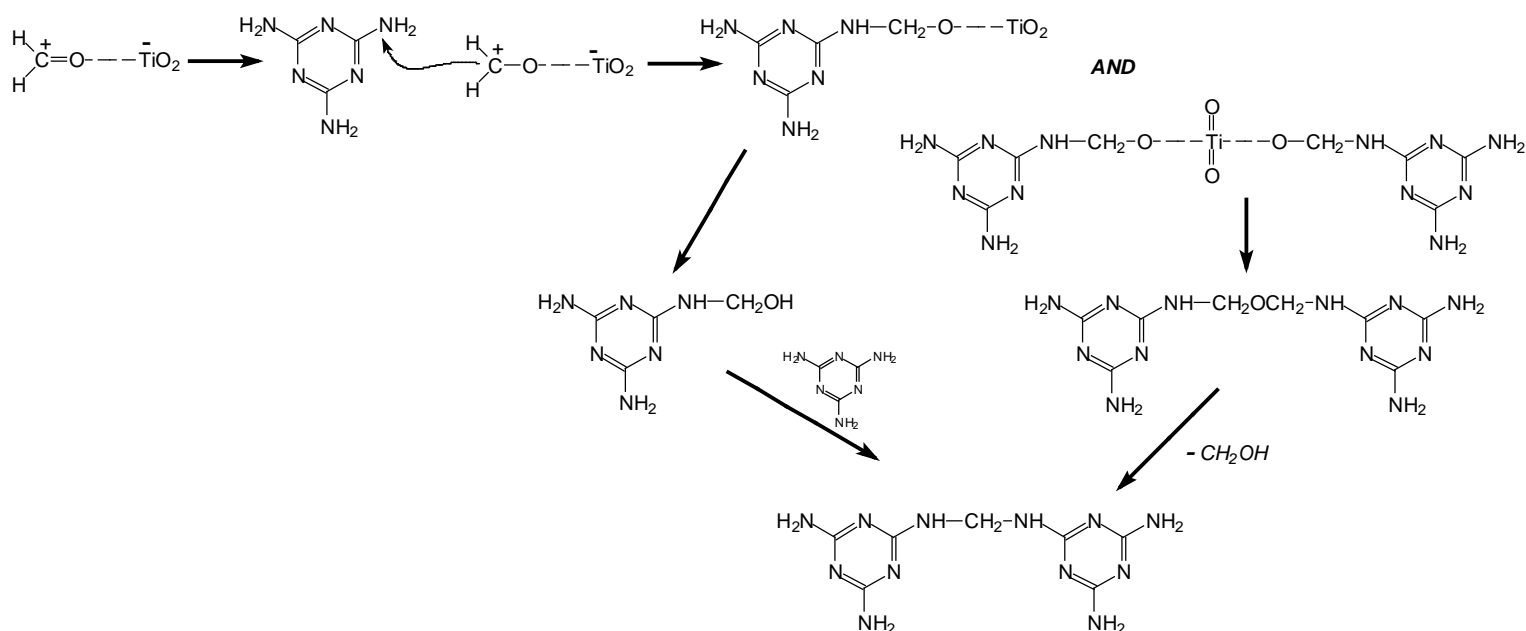
It remains to discuss what type of mechanism may cause the acceleration catalysis of MF resins by TiO₂. The effect is noticeable and could be due to a variety of causes. Thus, there are several possible explanations for this effect. Thus, firstly, Ti is known to form coordination complexes with carbonyl groups (as an aldehyde to pass the C=O to a C–OH, with the intermediate CH₂–O–TiO₂, thus an effect of acceleration due to the Ti charge being stronger than that of H⁺. This effect is well known in PF resins, for example⁵⁻⁹. In this case, one should assume that the Ti in TiO₂ behaves as a divalent ion. With this approach, TiO₂ might even complex more than one molecule of formaldehyde at the same time, possibly rapidly increasing the number of aldehyde molecules added onto the same or to different NH₂ groups, also explaining the acceleration of the rate of reaction. It is interesting to calculate that the amine FT-IR shift does not really change if the TiO₂ complexes directly with such a group, but it definitely shifts to slightly

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lower levels if the TiO_2 complexes with the methylol group linked to the amine ($-\text{NH}-\text{CH}_2\text{OH}$). However, as it is the amine group that appears linked (see IR and NMR) the most likely mechanism is as outlined for other metallic ions catalysis in phenol-formaldehyde resins^{5,9,19}. Thus, as shown in **Scheme 1**.

**Scheme 1**

The second possibility is the McMurry reaction, where catalysis by Ti joins two carbonyl groups by elimination of the two oxygens, thus from $\text{H}_2\text{C}=\text{O} + \text{O}=\text{CH}_2$ passing to $-\text{CH}_2=\text{CH}_2-$. What would happen, then, is not the formation of just $-\text{CH}_2=\text{CH}_2-$ but the reaction of the $-\text{NH}_2$ group of melamine with the C of two formaldehyde molecules and the formation of a $-\text{NH}-\text{CH}=\text{CH}-\text{NH}-$ or $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-$ bridge between two molecules of melamine and, thus, two formaldehydes at the time bridging instantly, again explaining the catalysis of the reaction. This is possible but improbable as the McMurray reaction needs more drastic reaction conditions of what used here.

The third possibility is that if TiO_2 forms a stable complex, then the initial attack of the aldehyde on the melamine will be fast, but after that, all will remain blocked⁵⁻⁹. It has been proven that this is not the case as the reaction accelerates. It means that if complexes are formed, the rate of exchange in solution is very rapid¹⁹ as the complex is not stable (and the TiO_2 complexes cannot be very stable, otherwise they could not function as catalysts in a number of organic chemistry reactions) and, thus, only the effect of the initial fast attack remains, hence, the acceleration in rate⁵⁻⁹.

Lastly a further explanation might well be valid, thus that once blocked the reaction of the aldehyde with the melamine the bridges forming in the resin are instead through the Ti itself if the complexes formed are stable. First, as $-\text{NH}-\text{CH}_2\text{O}-\text{Ti}-\text{OCH}_2-\text{NH}-$ with the other two valences of the Ti having been linked in the same way to other $-\text{NH}-\text{CH}_2-\text{O}-$ groups, thus, forms a tridimensional knot. This too would explain the strong acceleration. It may be possible that several of these mechanisms might be at work, although to a different extent.

CONCLUSIONS

Melamine-formaldehyde (MF) resins appeared to be catalyzed during their synthesis by TiO₂-mica silver white pigments, the presence of small proportions of these (1%-3% by weight on resin solids content)) appeared to markedly advance the resin during its preparation under comparative conditions. TiO₂-mica, as ascertained by X-ray diffraction (XRD), presented the TiO₂ mostly composed of its rutile phase but also presenting some traces of the anatase phase. FT-IR and ¹³C NMR analysis inferred clearly the presence of a catalytic effect of the TiO₂-mica and appeared to indicate that the catalytic effect involved mainly the –NH₂ groups of melamine and on formaldehyde. According to the peak reaction temperature measured by DSC, the highest catalytic activity of TiO₂ on MF curing appears to be achieved at a 2% addition level by weight. Different possible explanations of this effect have been proposed, the most likely one being the catalytic effect caused by TiO₂-promoted coordination complexes, the effect of acceleration being due to the Ti charge being stronger than that of H⁺, and the complex formed being unstable, thus not inhibiting the progress of the reaction.

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Table 1. Influence of pigment content on PH of MF resin

Pigment content	pH
0	8.95
1%	8.22
2%	8.15
3%	7.90

Table 2. FT-IR bands assignments of Cured MF spectrum, Neat and pigmented resins

Functional Groups	Vibration Mode	Pure MF	MF + 1% Pigment	MF + 2% Pigment	MF + 3% Pigment
N-H (Secondary amine)	Stretching	3398	3359	3388	3431
C-H Asym. (Methylene)	Stretching	2950	2940	2934	2922
N-H (Primary amine)	Bending	1662	1645	1636	1625
N-H (Secondary amine)	Bending	1530	1530	1530	1520
C-N (Aromatic)	Stretching	1325	1326	1327	1330
C-N (Ring) C-O-C Asym (CH ₂ -O-CH ₂)	Stretching	1158	1164	1161	Not appeared
C-O (CH ₂ OH) C-O-C Sym (CH ₂ -O-CH ₂)	Stretching	1004	995	994	1033
Triazine Ring	-	815	809	810	810

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Table 3. Onset, End set and Peak Temperatures of the MF curing reaction measured by DSC at 10 °C/ min heating rate

Pigment content	Onset temperature °C	End set °C	Endothermic ΔH (J/g)	Peak Temperature °C
0	94.5	111.9	-526.2	102.4
1%	97.7	111.3	-496.7	101.0
2%	36.6	72.5	-345.9	63.4
3%	35.7	85.6	-139.4	76.2

FIGURE LEGENDS

Figure 1. XRD Patterns of TiO₂-Mica

Figure 2. FTIR spectra of MF resin at different pigment content (0-3%)

Figure 3. DSC spectra of MF resin at different pigment content (0-3%)

Figure 4. Effect of the pigment content on the peak temperature of MF resin

Figure 5. ¹³C NMR detail of the 154-176 ppm range of (a) MF resin alone, (b) MF resin + 1% TiO₂-mica catalyst, (c) MF resin + 2% TiO₂-mica catalyst, and (d) MF resin + 3% TiO₂-mica catalyst,

Figure 6. ¹³C NMR detail of the 53-91 ppm range of (a) MF resin alone, (b) MF resin + 1% TiO₂-mica catalyst, (c) MF resin + 2% TiO₂-mica catalyst, and (d) MF resin + 3% TiO₂-mica catalyst,

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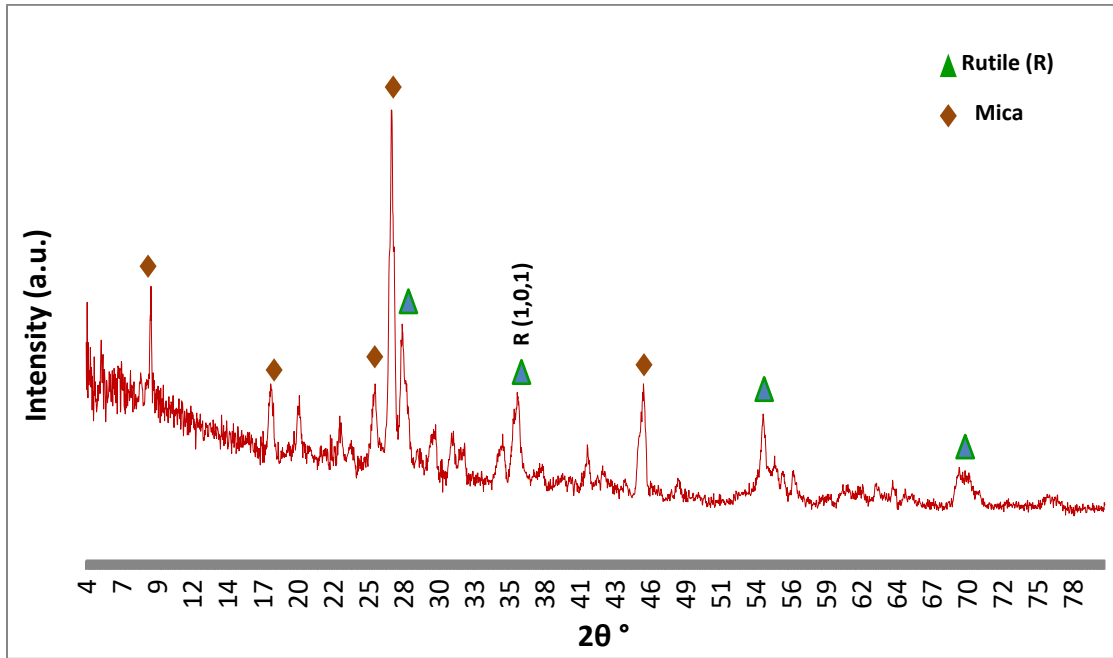


Fig. 1

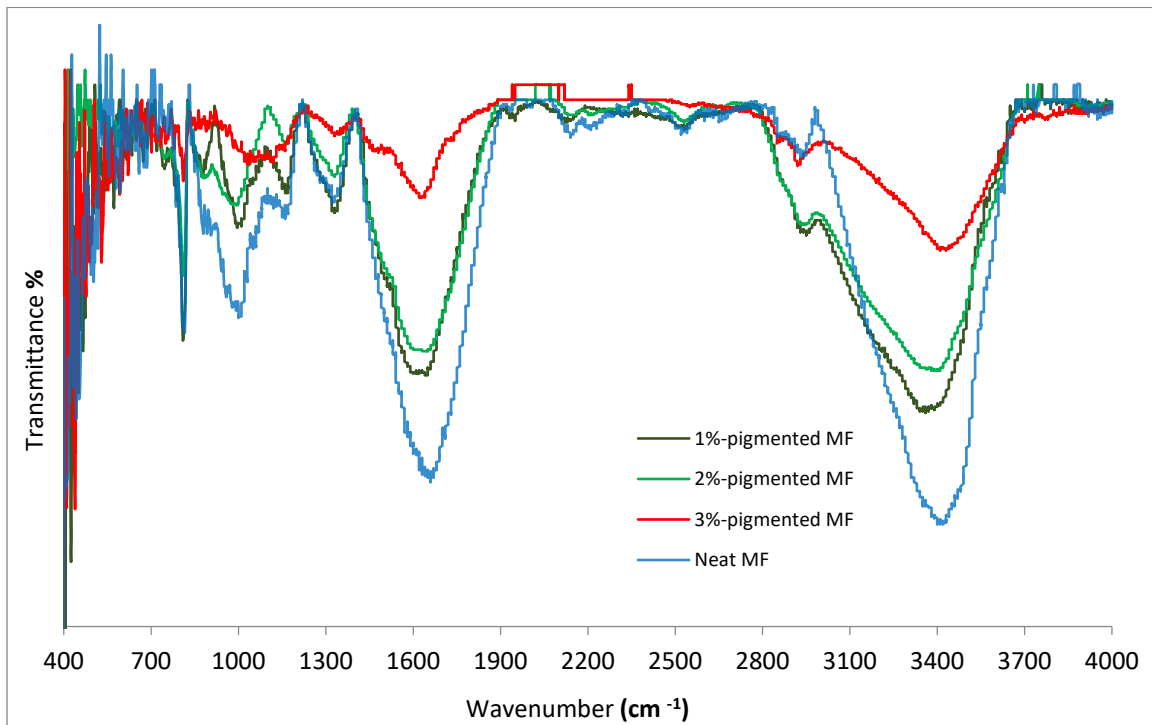


Fig. 2

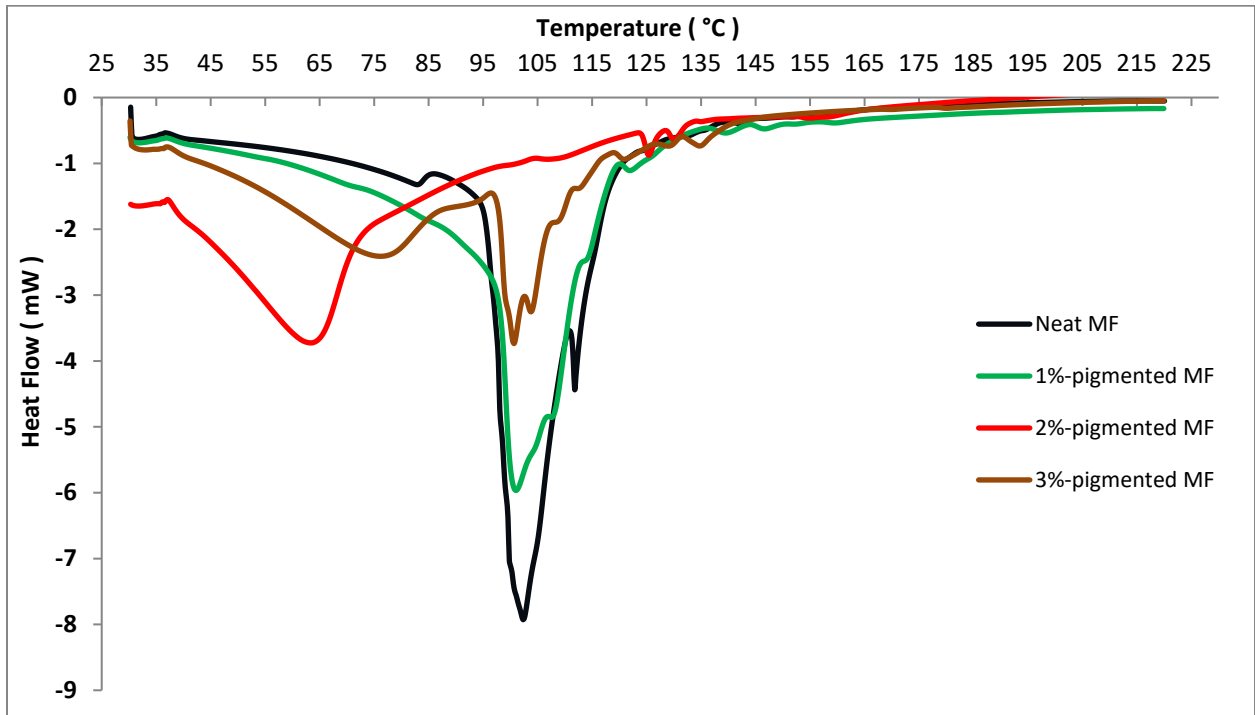


Fig. 3

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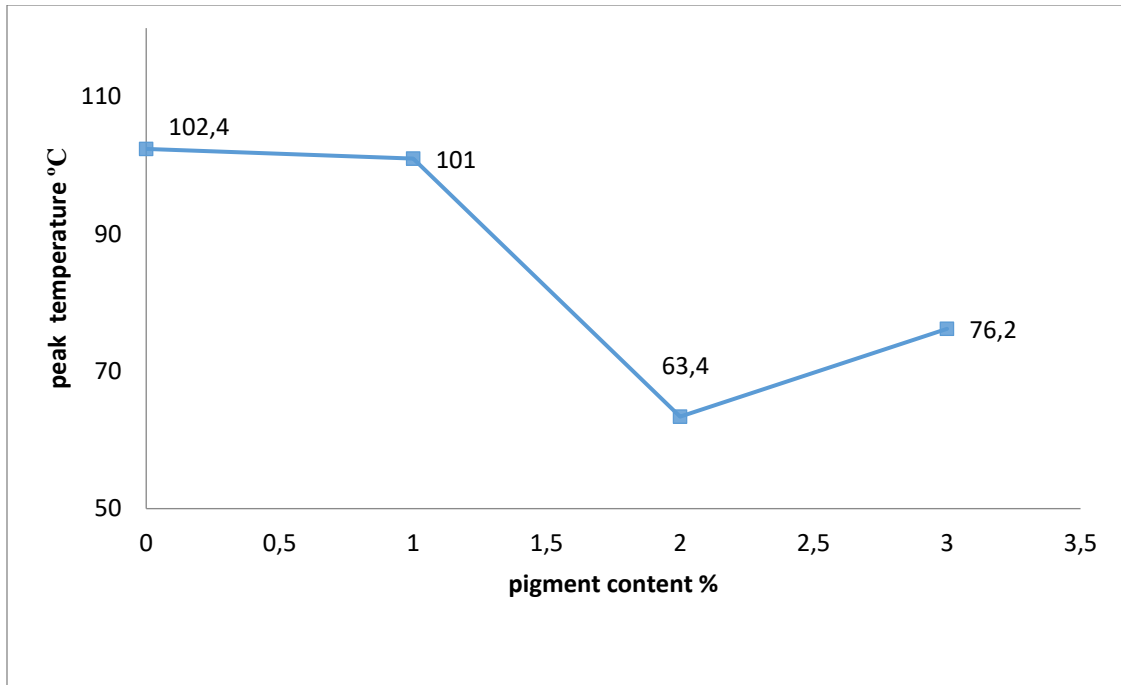


Fig. 4

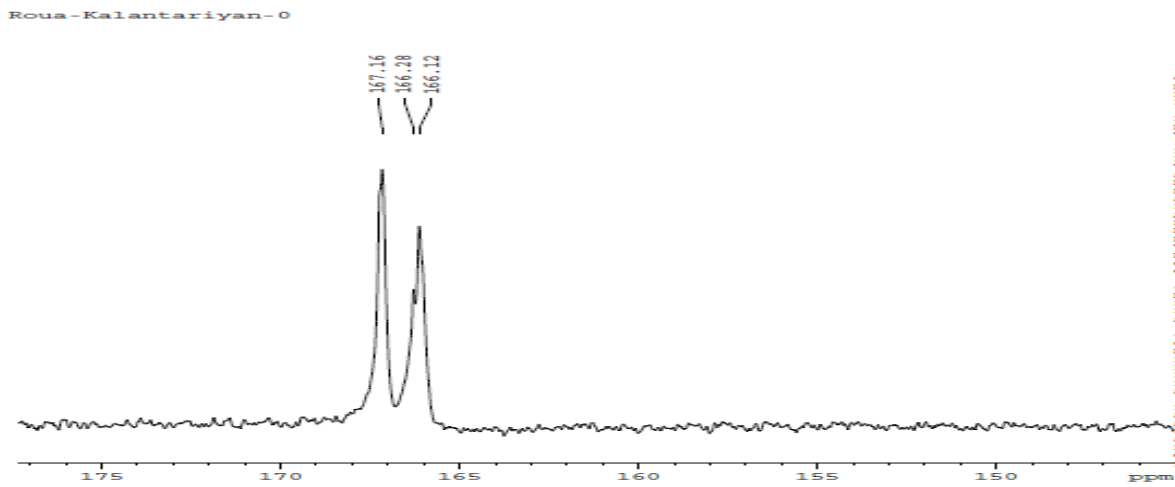


Fig. 5(a)

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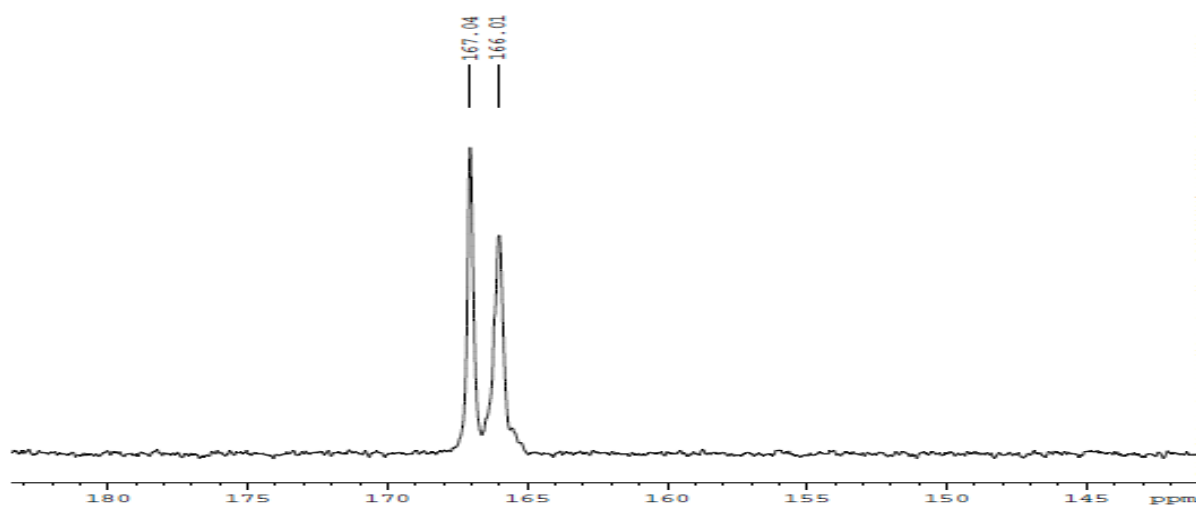


Fig 5(b)

Roya-Kalantariyan-2

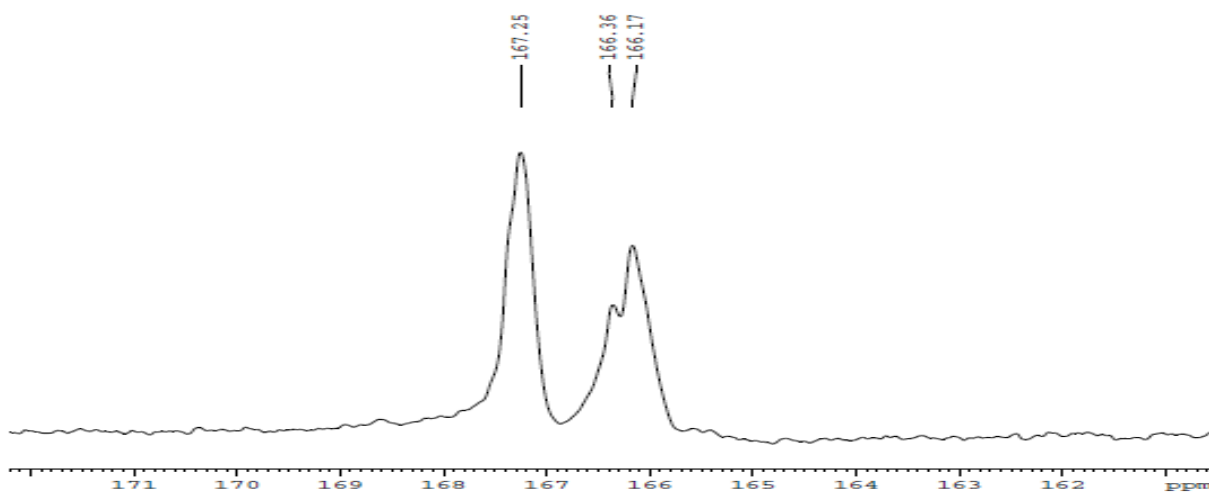


Fig 5(c)

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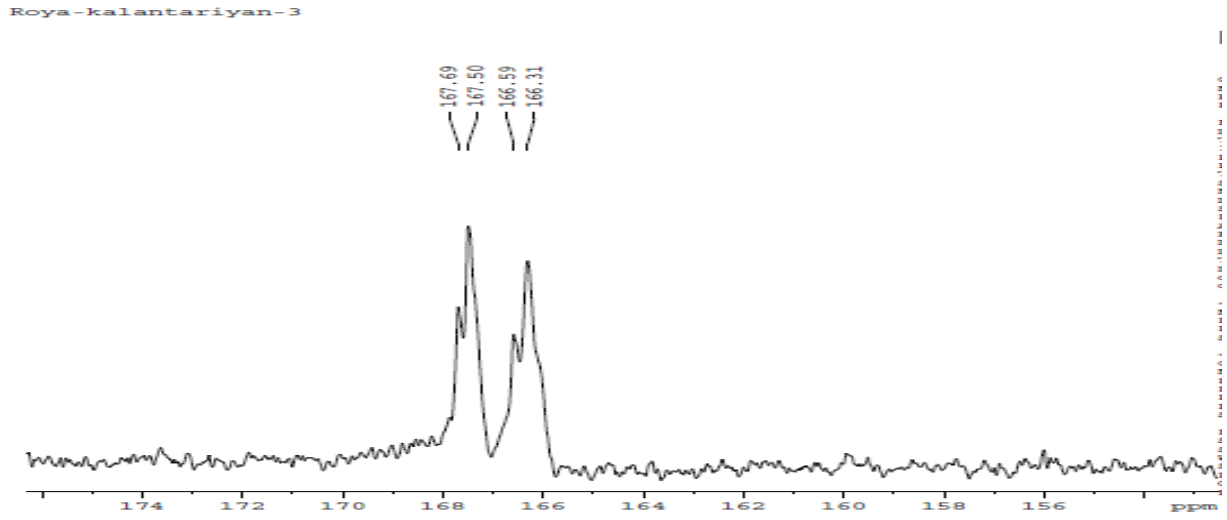


Fig 5(d)

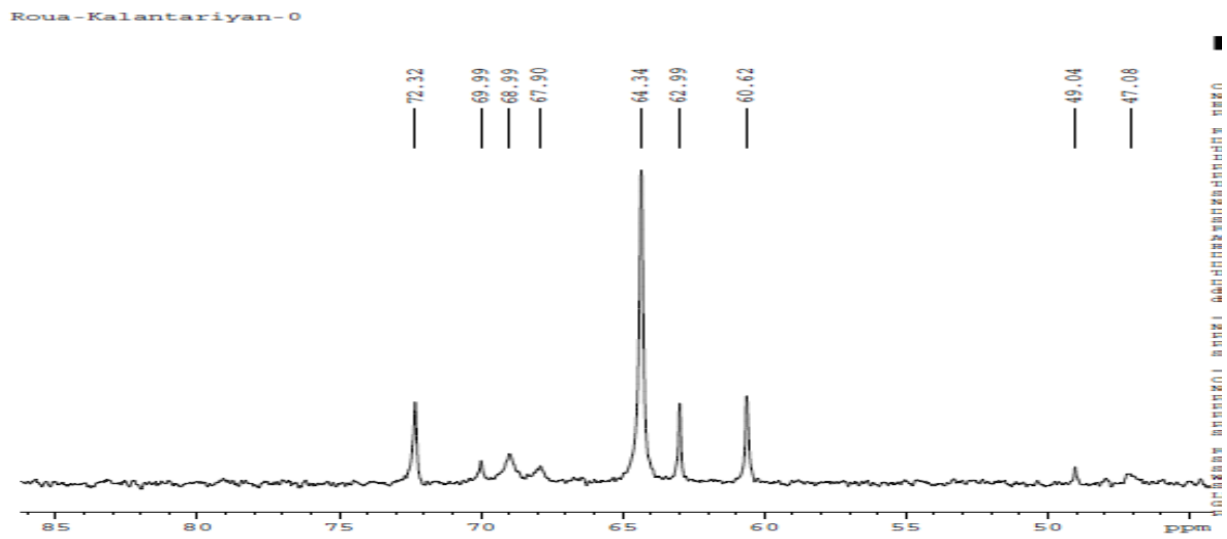


Fig.6(a)

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Roya-Kalantariyan-1

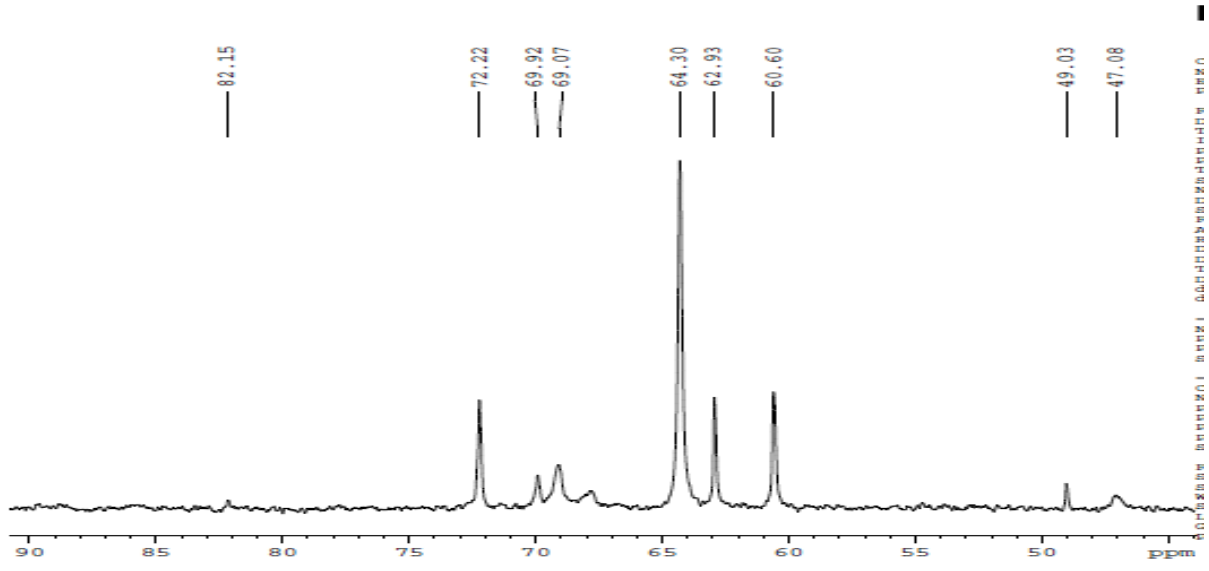


Fig.6(b)

Roya-Kalantariyan-2

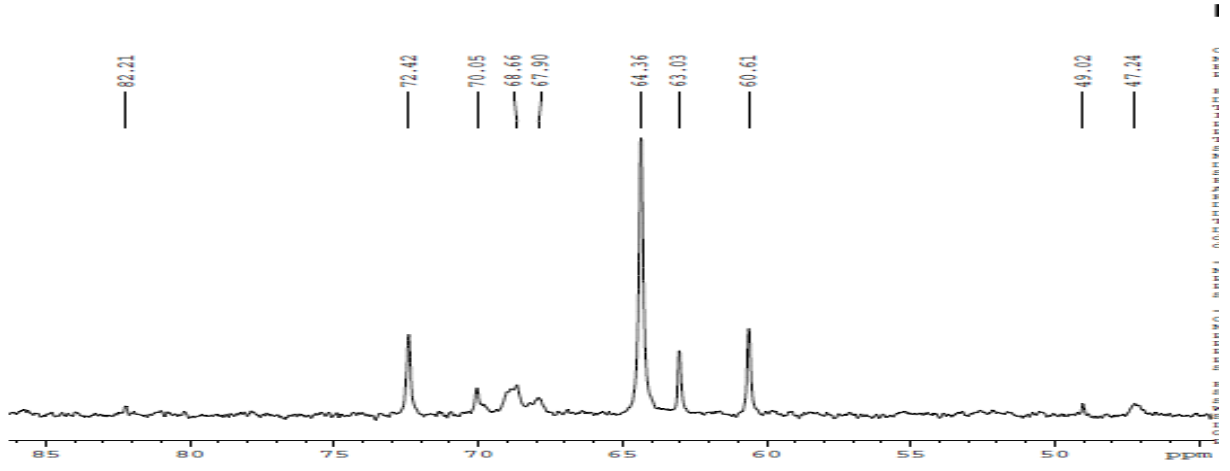


Fig.6(c)

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Roya-kalantariyan-3

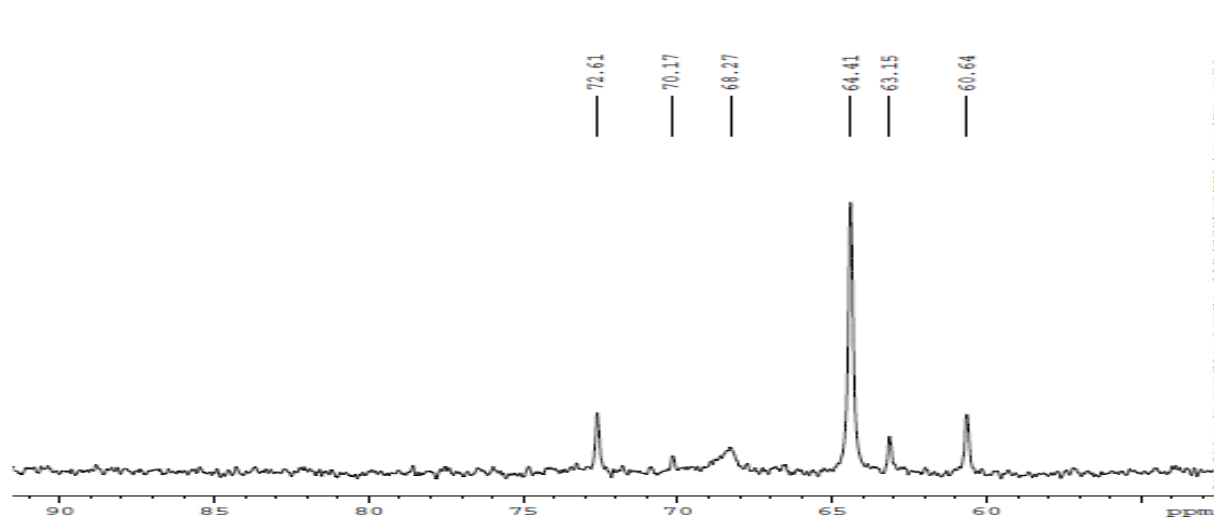
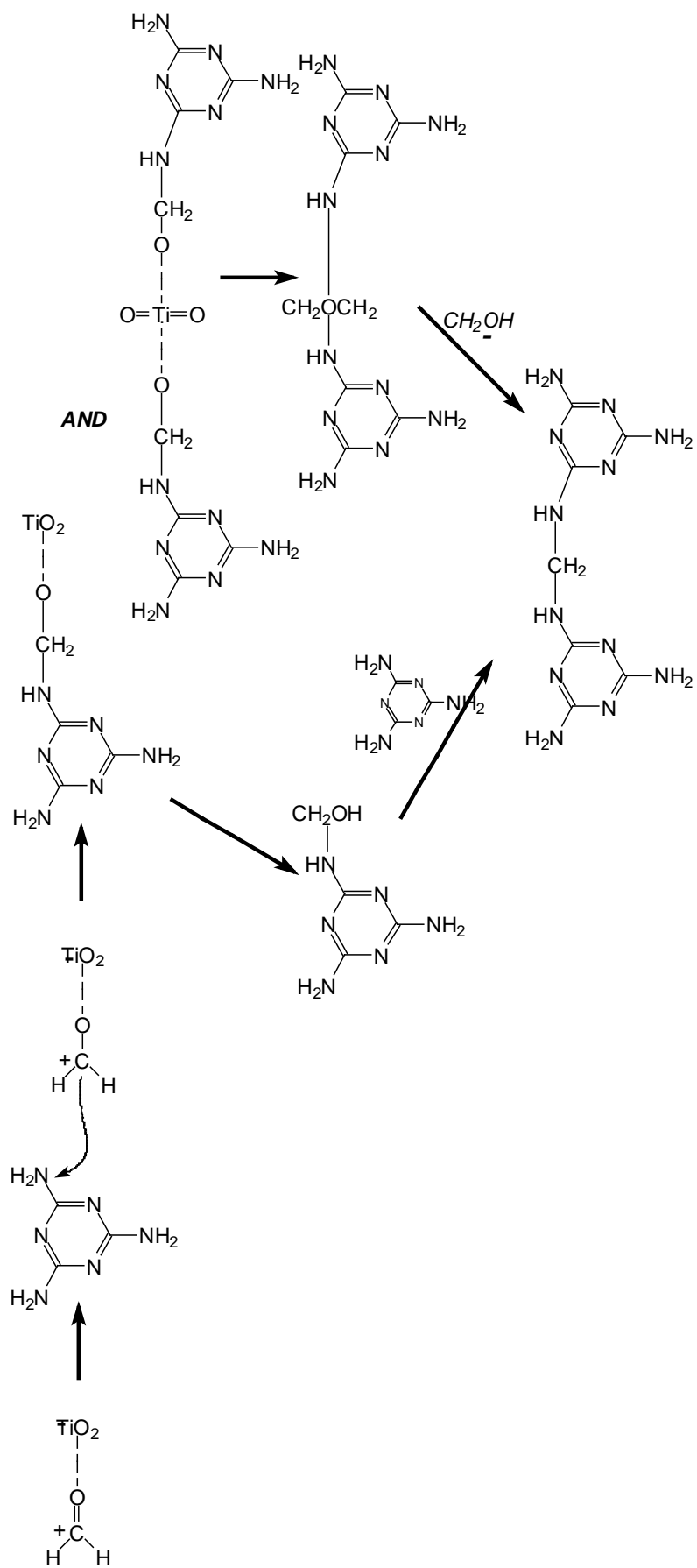


Fig.6(d)

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SCHEME 1