UV-Curing of Novel Tri-functional Melamine-phosphate Oligomer: An Effect of Coating With Polyurethane Acrylate Towards Mechanical, Thermal And Flame Retardant Properties

Pundalik Mali (✉ pundalik.mali@gmail.com)

Pratap College Amalner

Narendra Sonawane

.S.S.P. Mandal's Arts, Commerce & Science College Songir

Nilesh Pawar

Khandesh Education Society

Vikas Patil

University Institute of chemical technology

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Abstract

A novel melamine-phosphate trifunctional acrylate (MPTO) was successfully synthesized via simple cyclization of hexamethylolmelamine (HMM) with phosphorous oxychloride (POCl_3) followed by addition reaction of hydroxyethylmethacrylate (HEMA). The molecular structure of MPTO was identified by FTIR and ^1H -NMR, ^{13}C -NMR, and GC-MS spectra. The synthesized MPTO oligomer was impregnated with polyurethane acrylate to make the various formulation of UV-cured coatings. The polyurethanes-MPTO oligomers were coated on wood and galvanized steel panels. The properties of UV-cured PU-MPTO were studied by differential scanning calorimeter (DSC), while their crystallinity by X-ray diffraction analysis (XRD). The thermo-gravimetric analysis (TGA) exhibited a high char yield of 18.4% at 800 °C. Moreover, coating films show prominent flame retardancy with UL-94 V-0 rating and maximum limiting index value (LOI) values of 34.8%, which are much higher than the common polyurethane coatings. The polyurethane coatings cured with MPTO exhibited excellent mechanical properties were estimated various tests such as adhesion, pencil hardness, solvent resistance, flexibility, and corrosion test. The coating performance revealed that MPTO improves the mechanical, thermal, and flame retardant properties because their unique structure contains melamine-phosphate moiety and long aliphatic chains of an acrylate ester. These high-performance melamine-based UV-curable coatings are promising for extensive applications.

1. Introduction

The various treatments using resin or chemicals have been widely studied to enhance the properties of wood or metal surfaces. A variety of resin can be used to increase dimensional stability, thermal, mechanical, and chemical resistance. The systems used for coating include epoxy resin, phenolic resin, polyurethanes, melamine resin, and unsaturated polyesters, etc. ¹⁻⁷. Epoxy and polyurethane resins have been widely used because of their outstanding performance towards adhesive, dielectric properties, microelectronic encapsulated materials, and other coating properties ^{8,9}. To obtain desired properties the specific curing agents are impregnated in the coating systems. The specific curing agents are responsible for increase cross-link network which has a major influence on the chemical and physical performance of the coating materials ^{10,11}. In attention of wood materials are being widely used in furniture, decorative, architectural use, and other devices. There is no uncertainty about the degradation of wood and decomposition due to fire. Thus on the impregnation of flame retardants with a polyurethane coating to the surface is an effective way to increase global flame retardancy. Halogenated flame retardants have been restricted in commercial use because they emitted toxic gases during the curing process which affects the environment. As result, the flame retardant compounds having high flame retardant properties but barely contaminates the environment are predominantly needed ^{12,13}. The phosphorous-nitrogen-containing flame retardants are frequently being replaced by halogenated flame retardant because these types of compounds performs condensed and vapor phase mechanism. In general phosphorous-based flame retardant ($-\text{PO}_2$, $-\text{PO}_2$, HPO_2 , etc.) radicals act as gas-phase mechanism via inhibition of chain reaction. While phosphonates and phosphates by promoting char residue exhibit as condensed phase mechanism. The phosphorous-nitrogen chemistry has been studied

in the last decades owing to its capability to reduce flammability ^{14–16}. It is well known that in fire, the destruction of products occurs with the evolution of smoke and many toxic gases. Fire retardant polyurethane is preferred due to minimum or not producing smoke while they burn. Hence, polyurethane coating is used in a variety of products like rubbery, plastics, adhesive, insulation, and packaging industries ¹⁷.

Literature studies have found that, melamine polyphosphate and melamine cyanurate act as an effective flame retardants in various polymeric coatings. The coating materials like ethyl-vinyl acetate copolymer, polypropylene, epoxy compounds, polyamides, and melamine polyphosphate in polyureas ^{18–23}. There is narrow research on the application of melamine derivatives as flame retardant materials in polyurethane foam. The effects of ammonium polyphosphate mixed with the melamine cyanurate on physical-mechanical properties and flame retardant performance of polyisocyanurate–polyurethane foams blown with n-pentane ²⁴. The hyperbranched polymers are having a faster curing rate and lower viscosity as compared with linear co-polymer and having great applications in UV-curable coating systems ^{24–28}.

In this work, the design of a novel tri-functional melamine-phosphate oligomer was synthesized via melamine diol as a monomer followed by the reaction of (hydroxyethyl)-methacrylate (HEMA). Here we describe synthesis of the trifunctional polymer (MPTO) via polymerization of AA'A" monomer with B3 monomer, due to commercial accessibility of monomers, superficial preparation, and easy-to-tailor structures with higher conversion of required products ²⁹. Then it was impregnated into polyurethane acrylate to prepare various coating formulations and executed in a UV-curing system. The flame retardant properties were studied by vertical burning test and limiting oxygen index (LOI). Thermal degradation was analyzed by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC).

2. Experimental

2.1 Materials

Melamine was purchased from Gujarat chemicals, Gujarat, India. Formaldehyde solution (37%) and phosphorous oxychloride were purchase from sigma Aldrich, Mumbai, Maharashtra, India. Hydroxyethyl methacrylate, triethylamine, and methylene dichloride were purchased from Merck India Pvt. Ltd. All the chemicals were used without further purification in the synthesis of MTPO, and distilled water was used received from Pratap College Amalner, Maharashtra, India, in all the experiments. Commercial polyurethane resin and galvanized steel panels used as a substrate for the coatings were provided by Champion Advance materials Pvt. Ltd. Jhagadia, Gujarat.

2.2 Synthesis of HMM

In four neck round bottom flask equipped with a magnetic stirrer, charge melamine (10.0 g, 0.079 mmol) and formaldehyde solution (37%) (142.72 g, 1.42 mmol). Stir reaction mass for 10 min. and adjusted pH to 8.5 to 9.5 using 10% sodium hydroxide (1.2 ml) solution. Stir and maintain the reaction temperature at

60-65°C. Clear reaction mass get solidify represents the HMM formation monitor by thin-layer chromatography. Cool the reaction mass to 25-30°C. The product was filtered and washed by distilled water several times, and then dried in oven at 70°C for 8h to obtained white product (yield: 93.54%)^{30,31}. The reaction scheme for the synthesis of HMM is shown in Scheme 1.

2.3 Synthesis of HMC

In 50 ml three-necked flask equipped with stirring rod, thermometer sensor, and reflux condenser charge HMM (5.0 g, 0.016 mol), added phosphorous oxychloride (45.06 g, 0.293 mmol). Stir and heat the reaction mass to 75-80°C for 4h. Distilled out excess phosphorous oxychloride under vacuum at 50-55°C gives pale yellow color oil as product HMC (yield: 98.87%). The literature found that HMC is chloro-compound which is highly reactive, moisture sensitive. Hence it is used in the next stage immediately³². The reaction scheme for the synthesis of HMC is shown in Scheme 2.

2.4 Synthesis of MTPO

In 100 ml three-necked flask equipped with stirring rod, thermometer sensor, and nitrogen inlet charge hydroxyethyl methacrylate (5.09 g, 0.039 mmol), charge methylene dichloride (50 ml) and triethylamine (7.89 g, 0.087 mmol). Stir and cool the reaction mass to 5-10°C, added HMC (5.0 g, 0.006 mmol) drop wise over 10-15 min. Monitor the progress of the reaction by thin-layer chromatography (Mobile phase - methylene dichloride: ethanol 8.5:1.5) and charged distilled water (100 ml) on completion of the reaction. Separate the lower organic layer and wash with distilled water. Finally, the clear pale yellow oil as a product (MTPO) was obtained on evaporation of the solvent (yield 91.35%). The reaction scheme for the synthesis of tri-functional melamine-phosphate oligomer (MPTO) is shown in Scheme 3.

2.5 Synthesis of cured polyurethane resins

Formulation of polyurethane resin-modified via blending tri-functional melamine-phosphate oligomer (MPTO) and photo initiator as shown in Table 1. The uniform mixture was applied over steel (3' × 6' inch), wood panels (2' × 6' inch), and glass strips (1' × 3' inch) using a brush rod. The coated panels were cured over ultraviolet-light 400 Watts/inch with a focal point of 10 cm. The coated panels were irradiated for 15-20 sec. to form a rigid film over the surface. The panels were used to study the impact on adhesion, pencil hardness, solvent resistance, flexibility, corrosion test, and gloss. Whereas, the cured MPTO films obtained from glass strips were used for thermal stability, mechanical and surface morphology.

Table 1
Formulations of polyurethane acrylate with MPTO

Sr. No	Ingredients	MPTO oligomer weight %			
		0	10	20	30
1	Polyurethane acrylate	97	87	77	67
2	MPTO oligomer	0	10	20	30
3	Photo-initiator	3	3	3	3
4	Total	100	100	100	100

2.6 Characterization

The chemical structure of HMM and MPTO was identified by Fourier transform infrared (FTIR) on Shimadzo 8400s. The spectra were scan from 4000 to 400 cm⁻¹ wavelength range. The structural conformation of HMM and MPTO was done by gas-chromatography mass spectral analysis (GC-MS) on Shimadzu (QP 2010. The proton nuclear magnetic resonance (1H-NMR, 13C-NMR) spectra were conducted on Advance AV500WB Bruker at 400 MHz spectrophotometers in solvent CDCl₃.

Thermogravimetric analysis (TGA) of UV-cured films was performed on TGA Q500 V20.13 build 39, Universal V4.5A TA instrument under the nitrogen atmosphere. Thermal analysis monitored in the temperature range 0–800°C with 10°C/min heating rate. The glass transition temperature (*T_g*) of UV-cured films was performed via Differential scanning calorimetry (DSC) (TA Q100 analyzer, USA). The film sample was weighed accurately in an aluminum pan and heated in a 0 – 100°C temperature range with a heating rate of 5°C/min. The flame retardancy of coated films were analyzed by the underwriter's laboratories (UL-94) vertical burning test and limiting oxygen index (LOI) measurements as per ASTM D3801, ASTM D 2863-97 respectively. The qualitative methods for flammability and thermal behavior of the materials were achieved by LOI analysis. The coated films were ignited on the LPG Bunsen burner vertically and ignited for 10 s. The coating's performance was evaluated by various mechanical properties as per ASTM standards. The adhesion of coating panels was examined according to the cross-cut test ASTM D-3359. On the surface of coated panels 1 cm² lattice marking was made until the surface was exposed over the adhesion tape. The adhesion tape was then dragged over the surface and failure in adhesion was observed on the lattice marking. The pencil hardness test was performed according to ASTM D-3363. Scratch was made over the panels using pencil 6B-6H range with an angle of 45°. The performance on the coatings was carried by the weighted ball of 1.46 kg ranging from extreme height 60 cm over the surface. Rhopoint gloss meter was used to the performed gloss of coated panels at 60° angle according to ASTM D523-99. The gel content of UV-cured films were determined as per ASTM D2765-16. The gel content of the cured film was weighed carefully deep in xylene at room temperature for 24 h then the films were removed and dried at 75°C until constant weight achieved.

3. Results And Discussion

3.1 Structural Characterization

3.1.0 Functional group analysis by FTIR

The FTIR spectra of HMM are shown in Figure 1. The spectra of (1,3,5-triazine-2,4,6-triyltrinitrilo) hexamethanol (HMM) shows a characteristic absorption band at 3199.91 cm^{-1} corresponds to stretching vibrations of alcohol -O-H. The peak at 2962.67 cm^{-1} is due to the C-H stretching vibration of N-CH₂ group. The sharp peak at 1554.63 cm^{-1} is due to -C=N ring vibration. The peak at 1492.91 cm^{-1} and 1390.68 cm^{-1} corresponds to the methylene -C-H bending vibrations. The absorbance peak at 1193.94 cm^{-1} corresponds to aliphatic -C-N stretching vibration. The peak observed at 975.98 cm^{-1} and 869.9 cm^{-1} corresponds to the out-of-plane bending vibrations of the triazine ring of melamine derivative³³. From this spectrum of HMM, it is understood that the melamine has completely reacted with formaldehyde and there is no residual melamine and formaldehyde remains.

The FTIR spectra of MPTO is shown in Figure 2. The weak absorption peak at 3427.51 cm^{-1} corresponds to =C-H stretching of terminal methylene group of MPTO. Furthermore, methylene bending vibration of -C-H appeared at 1454.33 cm^{-1} . The strong absorbance at 1714.72 cm^{-1} corresponds to stretching vibrations of -C=O ester group. The characteristic peaks obtained at 1296.17 cm^{-1} and 1319.31 cm^{-1} are of -P=O, while the peak at 1161.15 cm^{-1} associated with -P-N stretch.

Since there is a decrease in the intensity of the peaks at 3427.51 cm^{-1} and 1161.15 cm^{-1} that corresponds to the terminal methylene stretching vibrations. This decrease in intensity may due to the extent of crosslinking. From these FTIR spectra, it was confirmed that the MTPO has reacted with polyurethane and formed strong crosslinking during the UV-curing process. The FTIR spectra HMM, MPTO, and UV-cured film is shown in Figure 3.

3.1.1 Structure confirmation of MPTO using ¹H-NMR and ¹³C-NMR

The structural conformation of MPTO was given by ¹H-NMR spectroscopy, and the spectra obtained are shown in Figure 4. The singlet around 1.96-2.0 ppm (a, 9H) is associated with the terminal methyl groups of olefinic carbon. The characteristic peaks of protons to attached O-CH₂-CH₂-O linkage observed triplet in the region at 3.72-3.88 ppm (d, 6H), similarly another triplet at 4.28-4.20 ppm (e, 6H). The methylene protons of the cyclic ring show peaks at 5.80-6.15 ppm (c, 12H) doublet due to germinal coupling. The peak at 7.27 ppm attributed to the olefinic protons of MPTO terminals. However, from the data of ¹H-NMR spectra, it is concluded that MPTO was successfully synthesized.

Figure 5 shows ¹³C-NMR spectra of MPTO. The chemical shift value of terminal carbon of methyl group 18.42 ppm (C₁). The intense peaks observed at 61.30 ppm (C₄) is due to -CH₂ bonded to oxygen atoms, while 66.51 ppm (C₅) is due to a carbon atom of a cyclic ring. The chemical shift values assign for olefinic carbon atoms at 126.18 ppm (C₂). The tertiary carbon attached to methyl shows the peak at deshielded region around 136.19 ppm (C₃) and carbon atoms of the heterocyclic aromatic ring show peak at 167.93 ppm (C₆). Hence, from the spectra of ¹³C-NMR spectra, it is concluded that MPTO was successfully synthesized..

3.1.2 Structural confirmation by Gas Chromatography-Mass spectroscopy (GC-MS)

Figure 6. Reveals the GC-MS spectrum of HMM. The molecular ion peak observed at *m/z* = 306.89 indicates the formation of melamine-hexanediol having a molecular weight 306.27. Hence it confirms that all primary amines of melamine get react with formaldehyde converted to HMM. Figure 7. shows the GC-MS spectra of MPTO. The peak at maximum intensity *m/z* = 827.53 confirms the formation of trifunctional MPTO having molecular formulae weight 828.54. Thus, from mass spectral data, the structure of oligomer MPTO was confirmed.

4.1 Thermal Analysis Of The Cured Films

The thermal decomposition of the cured PU-MPTO systems was studied via thermogravimetric analysis (TGA) as shown in Figure 8. The specific degradation temperatures and the final char yield at 800°C are summarized in Table 2.

Table 2
Thermal degradation of cured PU-MPTO Coatings

Sr. No.	Thermal Parameters	0% PU-MPTO	10% PU-MPTO	20% PU-MPTO	30% PU-MPTO
1	First Step (T ₁ °C)	278	285	289	290
2	Second Step (T ₂ °C)	335	339	345	352
3	Third Step (T ₃ °C)	500	506	511	518
4	T ₃₀ %	322	328	339	344
5	T ₅₀ %	402	407	413	429

As seen, the onset decomposition temperature of MPTO was 276.7°C and presented mainly three-stage decompositions with 15 wt% residual mass at 428.3°C. The temperature at the maximum mass loss rate (T_{max}) of MPTO was 279.6°C, 398°C, and 502°C, respectively. The thermal behavior of the cure PU-MPTO coatings was studied by the TGA. All the cured PU-MPTO coatings showed three steps of degradation pattern. The first, second, and third steps of decompositions are shown in Table 2. All cured PU-MPTO

shows the first, second, and third step decomposition at temperature ranged from 250°C to 304°C, 371°C to 426°C, and 453 to 539°C, respectively. The degradation in the first initial step was obtained due to the decomposition of polyurethane. The second step was shown due to the decomposition of an ester of MPTO. While the third step was obtained due to the degradation of aliphatic, and dehydrogenation of melamine moieties present in all coatings^{34–36}. All cured PU-MPTO coatings show a high degree of cross-linking and greater thermal stability than polyurethane acrylate.

4.2. Differential Scanning colorimeter (DSC)

DSC thermograms of cured polyurethane-MPTO oligomer for different formulations are shown in Figure 9. The glass transition temperature (Tg) performance of cured PU-MPTO coatings with growing MPTO was investigated by DSC. The Tg of cured PU-MPTO coating films shows an increasing trend with increasing MPTO content. From Figure 9, it is clear that the glass transition thermograms of PU-MPTO show single glass transition regions, which proves that MPTO is molecularly miscible with polyurethane oligomer. The increase in Tg values belongs to higher conversion of unsaturated, brittleness, and presence of rigid melamine-based structure, which leads to an increase in cross-link polymer network of cured PU-MPTO coatings. Therefore, more heat energy is required to break the molecular segments of PU-MPTO materials to move from hard glassy to soft rubbery region^{37–39}.

4.3 Flame retardancy and combustion behavior of cured PU coating

Flame retardant behavior of MPTO was investigated by LOI and UL-94 tests. As seen in **Table 3**, cured-PU is flammable with an LOI value of 24.6% and almost failed to UL-94 test. However, on the impregnation of 10%, MPTO oligomer in PU, it passes UL-94 V-1 rating and LOI value of achieved 26.3%. On further increase in the MPTO to 20% LOI values reaches to 28.5% and passing UL-94 V-1 rating as self-extinguishing the fire. Finally, MPTO (30%) had the highest LOI values 31.8% and successfully reached a V-0 rating. It proves that novel tri-functional melamine-phosphate oligomer (MPTO) was mainly worked as a condensed-phase mechanism, and the phosphorous synergists melamine as fuel dilution effects was inefficient at high oxygen concentration atmosphere^{40,41}.

Table 3 UL-94 and L.O.I. results of cured PU-MPTO

Sr. No.	Samples	L.O.I. (%)	UL-94 ratings	Time of Burning (Sec.)
1	Cured PU	24.6 ± 0.5	V-2	40
2	10% MPTO-PU	26.3 ± 0.5	V-1	Self-extinguished
3	20% MPTO-PU	28.5 ± 0.5	V-1	Self-extinguished
4	30% MPTO-PU	34.8 ± 0.5	V-0	Self-extinguished

4.4 Study of the crystallinity of the coatings by XRD

The microstructure of the cured PU-MPTO composites was studied by X-ray diffraction (XRD) measurement. As shown in Figure 10, the XRD profile of the PU-MPTO oligomer confirms the presence of amorphous nature with a diffractogram. The diffused diffraction peak appearing around $2\theta = 16-22^\circ$ corresponds to an amorphous structure. The hybrid materials cured PU-MPTO forming a strong interpenetrating polymer network ranging from 10% PU-MPTO, 20% PU-MPTO, and 30% PU-MPTO respectively. The literature found that systematic arrangement of any polymeric compounds enhances the crystallinity and irregular arrangements shows amorphous nature of coating films. The amorphous nature in cured PU-MPTO was due to a hyperbranched and cross-linking polymer network^{42,43}. This indicates that PU-MPTO has chemically incorporated into the hybrid materials and formed a cross-linked network between PU and MPTO consistent with the results of FTIR analysis.

4.5. Gel content

The gel content in the cured films was determined by the weighting method as per ASTM D2765-16. We know that cross-linked gel can only be swelled, while those uncross-linked moieties like diluents, photo-initiators, etc. can be dissolved in acetone. The UV-cured films were immersed into a 30 ml glass vial containing xylene for 48 h at room temperature. Then, xylene was decanted and the left swelling gel of films was dried in an oven at 70°C till constant weight achieved. Finally, the gel content in each cured film can be calculated by the equation³⁶.

$$\text{Gel Content} = W / W_i \times 100$$

Where W_i is the initial weight and W is the weight after extraction in xylene, respectively.

Literature studies found that the properties of UV-cured coating films are directly related to gel content⁴⁴.

The gel contents of UV-cured PU-MPTO films are illustrated in Figure 11. The result reveals that PU without MPTO films had lower gel content than the films impregnated with tri-functional melamine-phosphate, indicating the introduction of tri-functional melamine-phosphate facilitated crosslinking and thus boosted crosslinking density.

4.6. Application performances for UV-coated galvanized steel

Coating properties studied for hybrid PU-MPTO are crosshatch adhesion, pencil hardness, solvent resistance, and flexibility test. The crosshatch adhesion, pencil hardness, methyl ethyl ketone (MEK) double rubs, and flexibility were measured as per ASTM D3359, ASTM D3363, ASTM D4752, and ASTM D4145, respectively.

Table 4
Coating properties of cured PU-MPTO

Cured PU-MPTO	Adhesion	Pencil hardness ^a	Solvent resistance	Flexibility test	Salt spray ^b
PU	5B	2H	>450	Pass	2
10% PU-MPTO	5B	2H	> 450	Pass	2
20% PU-MPTO	4B	3H	> 450	Pass	1
30% PU-MPTO	4B	4H	> 450	Pass	1
a HB - H Poor Soft film. Prone to rapid wear and ease of scuffing, 2H - 3H Fair Moderate performer, 4H - 6H Good Durable film with projected good wear.					
b Salt spray results are expressed using a comparative scale: 1 is the best corrosion protection, 3 is the worst one.					

As summarized in Table 4, all polyurethane coating formulations performs better adhesion on a metal surface. Since the adhesion test concludes the proper balance of flexibility and hardness after the impregnation of MPTO oligomer in the PU system. The pencil hardness values of the cured PU-MPTO films was 2H, 2H, 3H, and 4H respectively. The results indicated that adding MPTO into PU resin could improve the pencil hardness of the cured films, and it was mainly due to the enhancement of the crosslinking network ⁴⁵. The solvent scrub resistance is dependent partially on the adhesion towards substrate while partially on the resistance to the solvent. The hybrid UV cured-PU demonstrated the highest solvent scrub resistance for all coating formulations. A flexibility test of all UV-cured coating panels was carried out on a conical mandrel bend tester. Films of all the coatings formulations were flexible enough to pass through the mandrel ⁴⁶.

The corrosion protective properties were characterized by the salt spray test and results were illustrated in **Table 3**. The mechanism of corrosion coatings can be explained as barrier creation between substrate materials, environments, inhibition of the corrosion processes, and coating acting as sacrificial materials. The coated PU-MPTO acting as barrier layers that will not allow the permeation of corrosive agents (salt solution) to the metal surface. It has been found that novel tri-functional melamine-phosphate can reduce the amount of corrosion and is strongly impacted by the MPTO.

4.7. Gloss of UV-cured coatings

The gloss of cured PU-MPTO coatings is depicted in Figure 12. The gloss is related to the surface smoothness of the materials. The effect of tri-functional melamine-phosphate oligomer on the surface smoothness behavior of the coating materials was determined by gloss measurement at 60° angle. Figure 12 shows that the gloss of the coating increases with MPTO content. This could be due to the higher extent of photo-polymerization and degree of crosslinking of the UV-cured PU-MPTO increasing with MPTO oligomer concentration, which improves the gloss of coatings. After examining the films at

60° angle, it is observed that all the coating panels were glossy. Coating films of 30% PU-MPTO shows the maximum gloss.

Conclusion

The current research demonstrated the synthesis of novel melamine-phosphate-based trifunctional acrylate oligomer (MPTO) and incorporated in PU acrylate for UV-curing technology. The UV cured PU-MPTO containing 30% of MPTO could reach a high LOI value of 34.8%, UL-94 V0, and performed as excellent flame retardant materials. From TGA and DSC results it can be concluded that MPTO had improved thermal stability at a high temperature which may due to dense cross-linking density, rigid melamine-phosphate moiety which reflected in thermal degradation, Tg values of PU-MPTO was better than normal polyurethane coatings. XRD spectrum of cured PU-MPTO had shown amorphous nature due to uniform a cross-linked network during UV-curing process. The insertion of MPTO into PU acrylate conclude that mechanical properties like gloss, adhesion, pencil hardness, chemical resistance, flexibility, and anti-corrosion behavior were superior as compared to pure PU. This may be attributed to a high degree of branching, higher extent of polymerization, and enhanced cross-linking density in PU-MPTO. Therefore tri-functional melamine-phosphate oligomer due to its structural features will be one of the promising material for coating industries.

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Scheme

Schemes 1-3 are available in the Supplementary Files section.

Figures

Figure 1

FTIR spectra of HMM

Figure 2

FTIR spectra of MPTO

Figure 3

FTIR spectra of HMM, MPTO and UV cured PU-MPTO

Figure 4

^1H -NMR of MPTO in DMSO

Figure 5

¹³C-NMR of MPTO

Figure 6

GC-MS spectrum of HMM

Figure 7

GC-MS spectra of MPTO

Figure 8

Thermogravimetric analysis of cured films.

Figure 9

DSC spectra of UV cured-films

Figure 10

The X-ray diffractogram of UV cured films.

Figure 11

Gel content of UV cured films

Figure 12

Gloss of cured coated steel panels

Supplementary Files

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- [GraphicalAbstract.png](#)
- [Scheme1.png](#)
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