

Effects of Multifunctional Monomers on the Properties of UV Cured Films

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Nantong Fengtian Agent Factory Co. has entered in radiation curing field since 2002 and engaged in the production of multifunctional monomers. Few years ago the company mainly produced around 10 monomers, such as TMPTA, TPGDA, HDDA, DPGDA, EO3-TMPTA, MPTMA, PO2-NPGDA, NPGDA. However, more multifunctional monomers, such as PETA, PDDA, EO4-BPDA, Di-TMP4A, DPHA, DPPA, THFFA, PEHA, LA, EOEOEA, as well HEA, HPA and 2-EHA are mass-produced in recent years. The company has become one of several leading companies in radiation curing field in China. And the company also starts to produce UV/EB curable monomers and oligomers containing phosphorus used for flame retardant coatings and adhesives. The increasing environmental concerns and ongoing legislation to cut the emissions of volatile organic compounds (VOCs) have been the major driving force in China in recent years. The selection of monomers for used in UV/EB curing field is very critical, such as that low odor and toxicity, low viscosity, less shrinkage and color, higher reactivity, solubility and purity, as well appropriate transition temperature and low cost need to be considered. Actually, VOC emission during producing process, residual solvents in the products, un-reacted raw materials, and byproducts are mostly controlled by production procedure.

1. Effect of monomers on the properties of UV cured films

Gas chromatography is usually used to determine the VOC content in a monomer. Trifunctional monomer TMPTA is mostly used in UV/EB curing formulations. The VOC content in TMPTA is very important for further applications. We used gas chromatography to measure the VOC content in TMPTA. The gas chromatography trace and the identification of peaks are given in Figure 1 and Table 1.

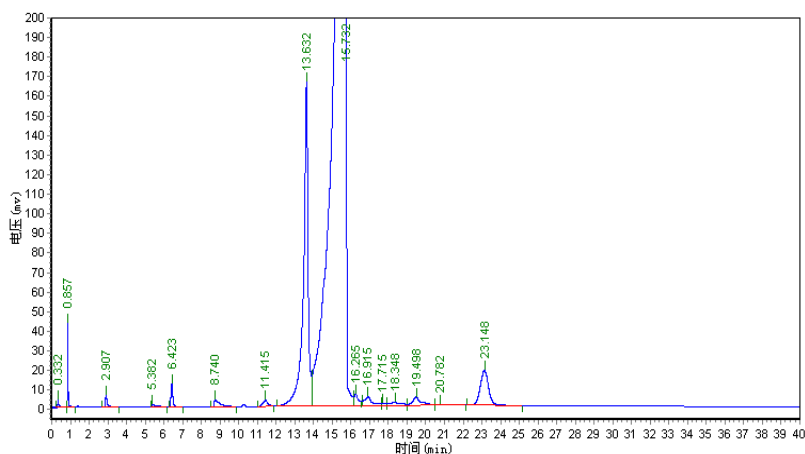
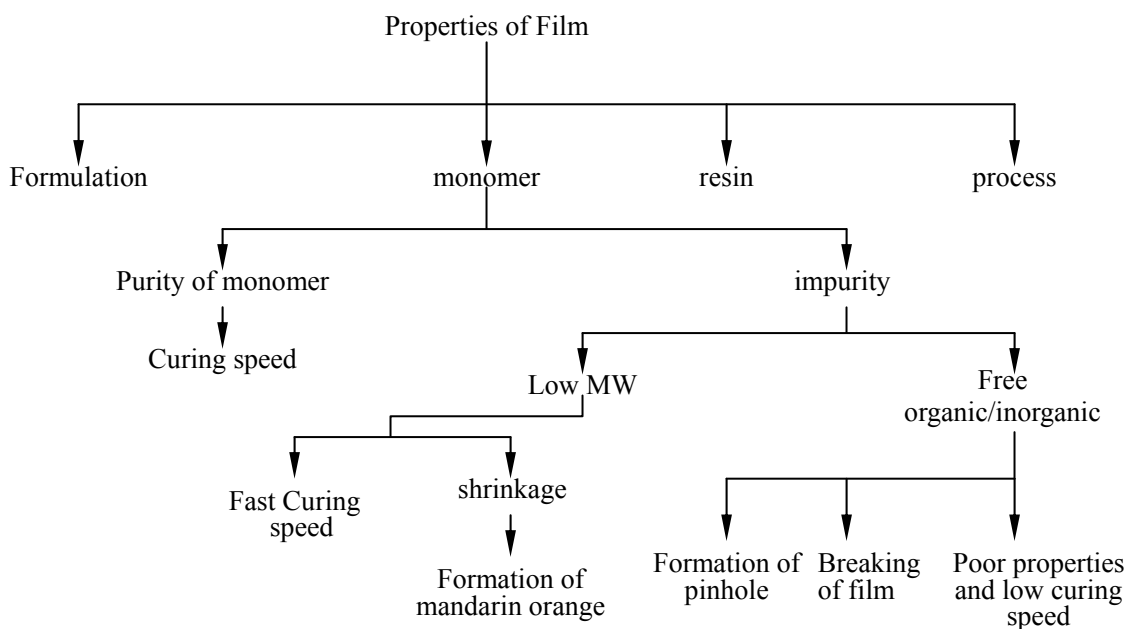


Figure 1 Gas chromatography trace of TMPTA produced by Nantong Fengtian.

Table 1 Identification of peaks in gas chromatography trace of TMPTA.

No.	Retaining time	Height of peak	Area of peak	Content
1	0.332	3691.656	15954.400	0.0447
2	0.857	41701.141	97512.750	0.2734
3	2.907	5950.385	46695.602	0.1309
4	5.382	1321.420	32386.768	0.0908
5	6.423	11943.005	84223.227	0.2362
6	8.740	3746.757	78362.547	0.2197
7	11.415	3014.864	51455.648	0.1443
8	13.632	166088.641	2830026.500	4.4010
9	15.732	1481340.000	31436532.000	88.1546
10	16.265	5826.405	92152.641	0.2584
11	16.915	4470.572	126235.945	0.3540
12	17.715	882.625	14950.959	0.0419
13	18.348	1597.250	63008.223	0.1767
14	19.498	4102.701	131437.547	0.3686
15	20.782	513.493	20121.236	0.0564
16	23.148	17747.111	539637.625	1.5133
Total		1753938.026	35660693.617	100.0000

The quality of domestic produced monomers is greatly improved in recent years, and some parameters are equal with foreign products. Here give an illustration to explain the crucial factors which affect the properties of UV/EB cured films.



The Company has broken through the producing process of monomers in 2007. The solid catalyzing approach was applied, which has several advantages such as higher catalyzing reactivity, unrequired reaction of bellow 5%, long life of catalyst, simple regeneration process, higher purity of monomers, and without generation of wastes.

2. UV curable phosphorus-containing monomers

Since last seventies, the radiation curing technology has enjoyed an uninterrupted growth in the field of coatings, printing inks and adhesives and this trend is expected to continue into the first twenty of this century. The major factors fuelling the growth of radiation-cured formulations include the outstanding performance of the coatings, such as very fast curing, low process costs per square meter of surface, environmental protection, and saving of energy^{1,2}. The main types of oligomers used in the field are acrylated epoxies, acrylated polyurethanes, unsaturated polyesters, and acrylated polyesters. However, these oligomers generally give final cured films, which are flammable. To increase their flame retardancy, the incorporation of flame-retardants is necessary when they are used in some special applications such as matrix for optical fibres³ and wood coatings⁴.

Phosphorus-containing flame-retardants used as monomers for UV curable systems have drawn much attention recently, since they generally give off nontoxic and non-corrosive volatile products during combustion⁵. Among most of the flame-retardant compounds, those containing phosphorus are known to produce incombustible char during combustion mainly through a condensed-phase mechanism, which leads to less toxic gas evolution into atmosphere⁶.

2.1 Methacrylated phosphate (MAP) and methacrylated diphosphate (MADP)

Methacrylated phosphate (MAP) with low viscosity and methacrylated diphosphate (MADP) with relatively high viscosity are synthesized (Figure 2). The ratios of these two compounds render the blends with tunable viscosity and physical properties.

Table 2 Viscosity (cPs) of MAP, MADP and their blends at different temperatures.

	MAP	MA0.8P-0.2DP	MA0.6P-0.4DP	MA0.4P-0.6DP	MA0.2P-0.8DP	MADP
30°C	342	1300	7900	>10000	>10000	>10000
50°C	140	318	1250	1920	9400	>10000
70°C	95	128	295	420	1400	5000

The limited oxygen index (LOI) values of the UV-cured films are shown in Figure 3. It has been reported that the LOI value of a phosphorus-containing resin increases with the final char yield. However, the resins studied here follow the reverse order. The char yield decreases from MAP to MADP while the LOI value increases from MAP to MADP. This may be interpreted as follows: the MAP with the lower molecular weight is a monofunctional methacrylate and the addition of MAP to MADP results in a decrease of the gel content in the UV cured film. The sol part in the cured films can easily catch fire, making the MAP film having the lowest LOI value although it has the highest char yield. As well known, the LOI test is a useful tool to rank the flammability of polymers in a small-scale fire.

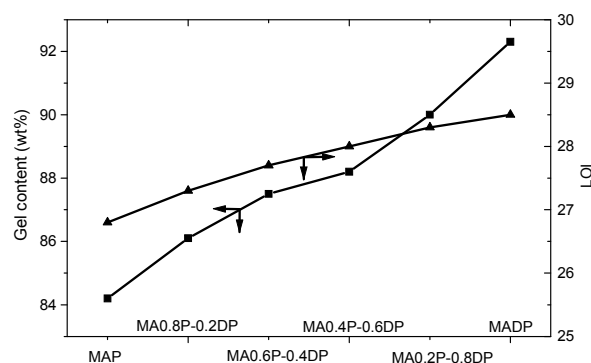


Figure 3 LOI values and gel contents of the UV cured films of MAP, MADP and their blends.

2.2 Tri(acryloyloxyethyl) phosphate (TAEP) and di(acryloyloxyethyl)ethyl phosphate (DAEEP)

The synthesis of TAEP and DAEEP was performed by the reaction of POCl_3 with HEA, and first with ethyl alcohol and then HEA, respectively, as illustrated in Figure 4. DCEP was prepared by the reaction of ethyl alcohol with POCl_3 .

The ^1H NMR spectra of TAEP and DAEEP are shown in Fig. 2, indicating the expected molecular structures, except for the very small peak at 3.6 ppm corresponding to the (eCH_2eOH) proton of HEA, which existed as a trace in the products.

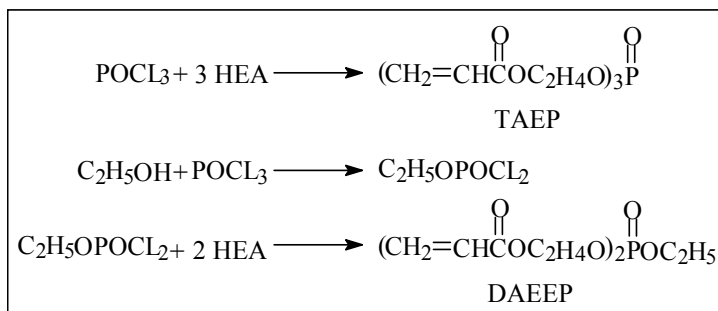


Figure 4 Synthesis route for tri(acryloyloxyethyl) phosphate and di(acryloyloxyethyl)ethyl phosphate.

Table 3 lists the TGA and DTG data of the UV cured films in air. It can be seen that two films have similar thermal behaviour, where three characteristic temperature regions are observed. The first region can be assigned to the decomposition of phosphate, whereas the second is due to the thermal pyrolysis of side chains Thermogravimetric and LOI data of UV cured DAEEP and TAEP.

Table 3 TGA and DTG data of the UV cured films in air.

samples	Specific temperature of Weight loss from TGA (°C)			Char % at 800 °C	LOI	
	5% Loss	Step 1	Step 2			
DAEEP	226	240	300	686	8.90	29
TAEP	280	-	311	702	5.10	36

Tri(acryloyloxyethyl)phosphate (TAEP) and di(acryloyloxyethyl)ethyl phosphate (DAEEP) were used as reactive-type flame-retardant monomers along with commercial epoxy acrylate and polyurethane acrylate oligomers in ultraviolet (UV)-curable resins. The concentrations of the monomers were varied from 17 to 50 wt %. The addition of the monomers greatly reduced the viscosity of the oligomers and increased the photopolymerization rates of the resins. The flame retardancy and thermal degradation behavior of the UV-cured films were investigated with the limiting oxygen index (LOI) and thermogravimetric analysis. The results showed that the thermal stability at high temperatures greater than 400°C and the LOI values of the UV-cured resins, especially those containing epoxy acrylate, were largely improved by the addition of the monomers. The dynamic mechanical thermal properties of the UV-cured films were also measured. The results showed that the crosslink density increased along with the concentrations of the monomers. However, the glass-transition temperature decreased with an increasing concentration of DAEEP because of the reduction in the rigidity of the cured films, whereas the glass-transition temperature increased with the concentration of TAEP because of the higher crosslink density of the cured films.

Table 4 Flammability of the EB600 with DAEEP or TAEP addition

Resin	CY (%)	Flammability	
		LOI	UL-94
EB600	5	21	Fail
EB600-0.17DAEEP	13.0	26	Fail
EB600-0.25DAEEP	26.5	27	Fail
EB600-0.33DAEEP	35.6	27.7	V ₂
EB600-0.50DAEEP	46.0	28.3	V ₀
EB600-0.17TAEP	15.2	26	Fail
EB600-0.25TAEP	27.3	27.3	Fail
EB600-0.33TAEP	38.4	28.3	V ₁
EB600-0.50TAEP	45.5	31.5	V ₀

The properties of a UV-cured film, which are very important to its applications, depend not only on the resin's composition but also on its photopolymerization kinetics. The most important parameters characterizing the curing kinetics of a resin are the rate at the peak maximum (R_p^{\max}) and the final degree of doublebond conversion (P^f). Figures 5 shows the photopolymerization rates of resins obtained from photo-DSC measured at 50°C. The photopolymerization rate of each sample showed a steep increase at the start of reaction; it reached R_p^{\max} and then dropped rapidly. R_p^{\max} increased with increasing DAEEP and TAEP concentrations in the EB600 and EB270 resins. The higher R_p^{\max} values were attributed to the high concentration of double bonds and low viscosity. Moreover, narrower peaks for the polymerization rates were obtained as more DAEEP or TAEP was added. A shorter irradiation time to the leveling off of the unsaturation conversion curves was obtained with increasing concentrations of DAEEP and TAEP. The final unsaturation conversion of double bonds decreased as more monomers were added. The higher R_p^{\max} values could be due to the higher double-bond density of TAEP. The lower P^f values were attributed to the higher crosslinking density (Ve) values of TAEP, which were due to its trifunctionality (vs the difunctionality of DAEEP).

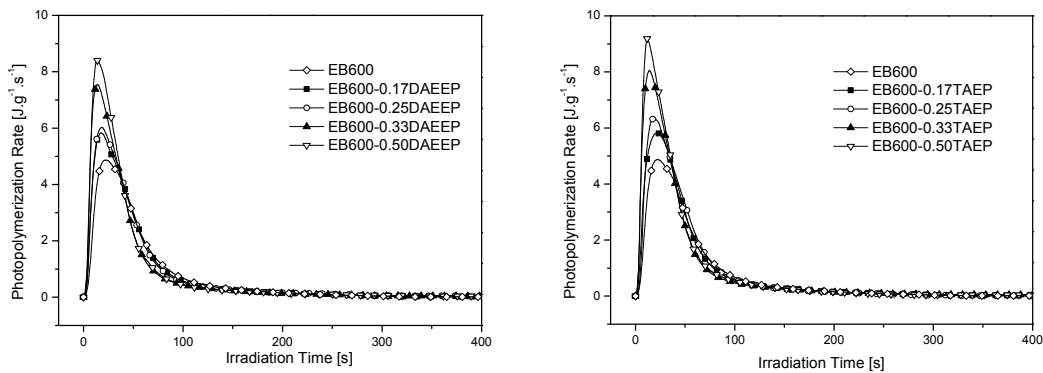


Figure 5 Photopolymerization rates of resins with monomers from photo-DSC at 50°C.

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