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# Fabrication and characterization of novel polyacrylate films with hindered phenol structures and fluorine groups

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**Abstract.** A series of novel fluorinated-damping polyacrylate (OFDA) emulsions based on a series of novel hindered phenol fluorinated acrylates (OFIP-AO 1010-HEA) were prepared successfully. The structure of OFIP-AO 1010-HEA was characterized by fourier transform infrared spectroscopy (FTIR). The influence of OFIP-AO 1010-HEA on different properties of the OFDA films was investigated by using dynamic mechanical analysis (DMA) and the measurement of contact angle. The results showed that the OFDA6 film owns 0.75 in  $\tan \delta_{\text{peak}}$  and its loss factors  $\geq 0.3$  was spanning widely from -80 °C to 200 °C. So the OFDA6 film had the best damping properties. While OFDA4 had the best in the contact angle of water and the lowest surface free energy.

## 1. Introduction

Recent years, the study on the development of polymer/small molecule hybrid damping materials has attracted people's attention [1-3]. Novel damping materials consist of polar polymers, such as chlorinated polyethylene, chlorinated polypropylene, and acrylate rubber, as well as some functional organic small molecules [4,5]. This method can not only improve the intensity of the damping peak, but also regulate the position of the damping peak. It is a damping modification method with good development prospects. Wu [6] proposed hybridization of organic small molecules with polar polymers, which can significantly improve the damping properties of polymers, and obtain hindered phenol/polymer hybrid damping materials. Liu [7,8] synthesized a series of polyurethane prepolymers terminated with hindered phenol AO-80 and AO-2246 and polyurethane damping materials were prepared by curing reaction. Then, the damping material of hindered phenol terminated polyurethane / epoxy resin blend with excellent mechanical properties and wide damping temperature range was prepared by blending hindered phenol terminated polyurethane prepolymer with epoxy resin. Wide range of hindered phenol terminated polyurethane/epoxy blend damping materials. Therefore, determination of the properties of small molecules as well as effects of small molecules on the polymer, which exert significant influences on the damping performance of the materials, is worthy of discussion.

Polyacrylate materials have been proven to be interested in materials because of their good processing and optical properties and thermal stability. These characteristics allow polyacrylate to be used as binders, textiles, or damping materials. However, the polyacrylate material has a low hydrophobicity, which leads to a significant reduction in its material life. Therefore, fluorine groups or silicon groups are introduced into the polymer to lower the surface tension and improve the material surface properties.



In this study, a series of novel hindered phenol fluorinated acrylates (OFIP-AO 1010-HEA) were designed and prepared to significantly improve the damping performance and obtain low surface free energy of polyacrylate films. The structures of the F-A-Hs were characterized by FTIR. The fluorinated-damping polyacrylate emulsions (OFDA) were synthesized with F-A-Hs and acrylic monomers by core-shell emulsion polymerization. And the damping properties and surface properties of the OFDA films were investigated.

## 2. Experimental

### 2.1. Materials

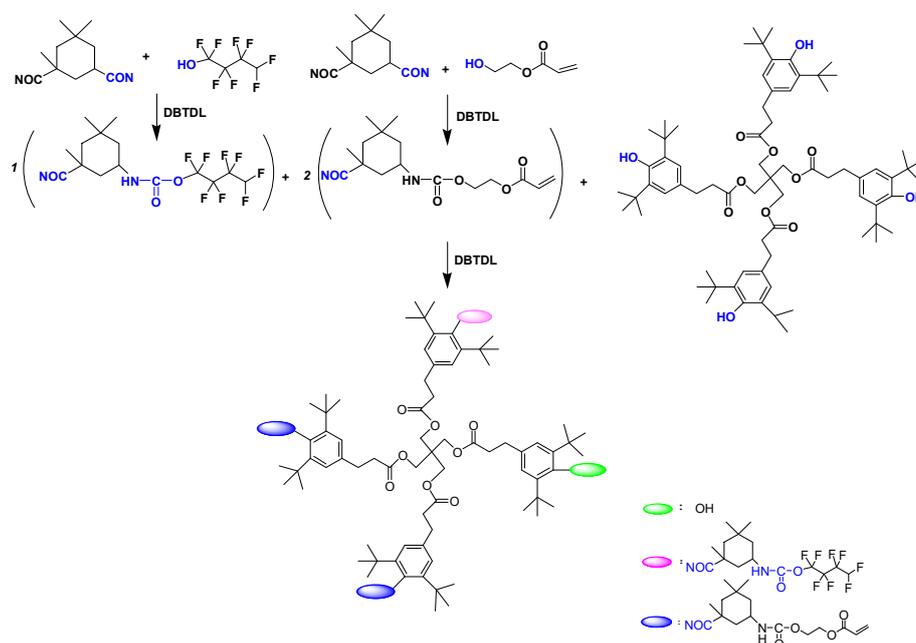
Pentaerythritol tetrakis 3-(3,5-ditert-butyl-4-hydroxyphenyl) propionate (AO 1010) was supplied by Shandong Uoslf Chemical Technology, Co., Ltd., China. Isophorone diisocyanate (IPDI) was supplied by Wanhua polyurethane Co., Ltd, Yantai, China. 2,2,3,3,4,4,5,5-Octafluoro-1-Pentanol (OFIP) was supplied by Weng Jiang Reagent, China. Dibutyltin dilaurate (DBTDL) was supplied by Shanghai Titan Technology, Co., Ltd., China. Hydroxyethyl acrylate (HEA) and Butyl acrylate (BA) used after dehydration from molecular sieve 4 Å were supplied by Shanghai Aladdin Bio-Chem Technology, Co., Ltd., China. Methyl methacrylate (MMA) and Sodium Dodecyl Sulfate (SDS) were supplied by Shanghai Titan Technology, Co., Ltd., China. Vinyl Versatate 10 (VV10) was supplied by Foshan Jinjia New Material Technology, Co., Ltd., China. Diacetone Acrylamide (DAAM) and Adipic Acid Hydrazide (ADH) were supplied by Chong Jun Chemical Technology, Co., Ltd., China. Potassium persulfate (KPS) was supplied by Shanghai Aijian Reagent Factory, Co., Ltd., China.

### 2.2. Synthesis of a hindered phenol fluorinated acrylate (OFIP-AO 1010-HEA)

The example synthetic route of F-A-H is shown in Scheme 1. A four-mouth flask was equipped with a mechanical stirrer, a reflux condensing tube, a thermometer and a nitrogen catheter. It contained IPDI and heated to 38 °C. With stirring, the mixture of appropriate amount of DBTDL, OFIP and HEA (the molar ratio of OFIP/IPDI and IPDI/HEA is 1:1) was added into the flask in drops through constant pressure drip funnel during 1 hour under N<sub>2</sub> atmosphere and reacted for 4 h at 38 °C. Another four-mouth flask, which contained the mixture of MMA (40 g) and AO 1010 (39.3 g), was stirred at room temperature for 30 min under N<sub>2</sub> atmosphere, then heated to 80 °C. Then the prepolymer of OFIP-IPDI and HEA-IPDI were added into AO 1010/MMA in drops during 2 hours under N<sub>2</sub> atmosphere and reacted for 23 h at 98 °C. The basic recipes are shown in Table 1. ('F' represents 'OFIP-IPDI', 'A' represents 'AO 1010' and 'H' represents 'IPDI-HEA'. '3F-A-H' represents three OFIP-IPDI, one HEA-IPDI and one AO 1010 had reacted.)

Table 1. The basic recipes of OFIP-AO 1010-HEA

Sample	OFIP (mol)	IPDI (mol)	HEA (mol)	AO 1010 (mol)
3F-A-H	3.00	4.00	1.00	1.00
2F-A-2H	2.00	4.00	2.00	1.00
F-A-3H	1.00	4.00	3.00	1.00
2F-A-H	2.00	3.00	1.00	1.00
F-A-2H	1.00	3.00	2.00	1.00
F-A-H	1.00	2.00	1.00	1.00



Scheme 1. Synthesis of F-A-2H

### 2.3. Preparation of fluorinated-damping polyacrylate emulsions (OFDA)

A four-mouth flask contained 0.9 g SDS, 40 g H<sub>2</sub>O, and 1/3 of the mixture (7.5 g BA, 4 g MMA, 1 g DAAM) equipped with a mechanical stirrer, a reflux condensing tube and a thermometer. It was stirred with a high-speed dispersion at 60 °C for 30 min under N<sub>2</sub> atmosphere. Next, 1/3 of initiator aqueous solution (0.21g KPS and 6g H<sub>2</sub>O) was added into this flask in drops through constant pressure drip funnel during 20 min at 70 °C with a reducing stirring rate and heated to 80 °C for 40 min. Then, the rest mixture of the acrylic monomer was added into the pre-emulsion in drops and reacted for 1 h. The other mixture (6.25 g VV-10, 1.5 g BA, 3 g MMA and 4.5 g OFIP-AO 1010-HEA) was added into the core-emulsion in drops and reacted for 1 h. After, the polymerization was continued for another 1 h at 90 °C. Finally, the emulsion was obtained after cooling to room temperature. The basic recipes of OFDA emulsions are shown in Table 2.

Table 2. The basic recipes of OFDA emulsions

Emulsion	OFIP-AO 1010-HEA	BA (wt%)	MMA (wt %)	VV10 (wt %)	DAAM (wt %)
OFDA0		36	35	25	2
OFDA1	3F-A-H	36	35	25	2
OFDA2	2F-A-2H	36	35	25	2
OFDA3	F-A-3H	36	35	25	2
OFDA4	2F-A-H	36	35	25	2
OFDA5	F-A-2H	36	35	25	2
OFDA6	F-A-H	36	35	25	2

### 2.4. Preparation of the OFDA films

The OFDA emulsion was neutralized with ammonia to pH = 8 to 9, then added with 0.5 g ADH and reacted for 30 min. The OFDA films were prepared by casting the emulsions onto a cleaned Teflon disc and then dried at room temperature for four days in a fume cupboard.

## 2.5. Characterization

**2.5.1. Fourier Transform Infrared Spectroscopy (FTIR).** The spectra of FTIR were recorded in the range of 4000-500  $\text{cm}^{-1}$  on a Nicolet 560 infrared spectrometer using KBr pellet technique. 32 scans were averaged for each sample at a resolution of 4  $\text{cm}^{-1}$ .

**2.5.2. Dynamic Mechanical Analysis (DMA).** The DMA of the OFDA films was carried out from  $-80\text{ }^{\circ}\text{C}$  up to  $200\text{ }^{\circ}\text{C}$  at 1 Hz, heating at  $5\text{ }^{\circ}\text{C}/\text{min}$  on a DMA 242 C analyzer (NETZSCH Instruments, Germany). All the samples were measured under tension mode.

**2.5.3. Contact angle test.** The contact angles of water on the OFDA films were measured on a contact angle goniometer (DSA30, Kruss Company) at room temperature by averaging three fresh points.

## 3. Results and discussion

### 3.1. FTIR

Figure 1 presents the FTIR spectra of F-A-Hs. There was a broad band O-H at  $3400\text{ cm}^{-1}$  in all spectra. The peaks near  $2900\text{ cm}^{-1}$  and  $2800\text{ cm}^{-1}$  were assigned to the  $-\text{CH}_2$  ( $-\text{CH}_3$ ) stretching vibrations. It was also noted the presence of the C=O at  $1741\text{ cm}^{-1}$ , which was associated to ester groups. The band near  $1550\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$  corresponded to benzene ring group. The absorption peak at  $517\text{ cm}^{-1}$ ,  $767\text{ cm}^{-1}$ ,  $894\text{ cm}^{-1}$  and  $1263\text{ cm}^{-1}$  should be attributed to the stretching vibration of C-F. Moreover, the absorption of the  $-\text{NCO}$  group ( $2250\text{ cm}^{-1}$ ) was not observed, while the stretching vibration of C-F still remained. Furthermore, the band at  $1643\text{ cm}^{-1}$  corresponded to C=C which enabled the free radical polymerization. These results indicated the successfully synthesis of F-A-H.

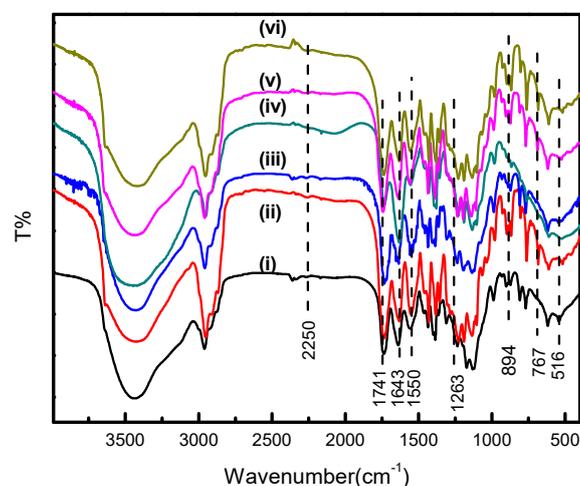


Figure 1. FTIR of (i) 3F-A-H, (ii) 2F-A-2H, (iii) F-A-3H, (iv) 2F-A-H, (v) F-A-2H and (vi) F-A-H

### 3.2. DMA

The damping property of materials could be evaluated by the peak height ( $\tan \delta_{\text{peak}}$ ) and peak range (TR,  $\tan \delta \geq 0.3$ ) of temperature dependence of loss factor ( $\tan \delta$ ) curve [9]. Six OFDA films were prepared and their characteristics of damping properties are showed in Table 3.

The peak height variation is related to the hydrogen-bond density and interaction strength which can be reflected in  $T_g$  of the system. It can be seen that the peak height of three films in Table 3 decreased in the order of OFDA1, OFDA2 and OFDA3, contrary to the order with  $T_g$  of three films as seen in Table 2. But the peak heights of three films decreased in the order of OFDA6, OFDA5 and OFDA4, similar with  $T_g$  of three films. It may owe to the OFIP-AO 1010-HEAs had no phenolic

hydroxyl group in OFDA1, OFDA2 and OFDA3, so their damping capacity were just from interaction strength, lower than that from the hydrogen-bond density and interaction strength. While the OFIP-AO 1010-HEAs in OFDA6, OFDA5 and OFDA4 respectively held single, single and double phenolic hydroxyls, thus their damping capacity were from two effects. So their trend of peak height  $T_g$  were similar. Besides, the TR values of OFDA6 were the widest showed in Table 3, because the F-A-H in OFDA6 owned double phenolic hydroxyls, which can absorb of external mechanical vibration energy effectively. These results indicated the OFDA6 film owned the best damping capacity.

Table 3. Characteristic DMA of the OFDA films

Sample	$T_g$ (°C)	$\tan \delta_{\text{peak}}$	TR(°C)( $\tan \delta \geq 0.3$ )
OFDA1	57.06	1.16	(-8.94~200.00 °C)
OFDA2	72.78	0.76	(-80.00~130.78 °C)
OFDA3	74.16	0.66	(-2.84~200.00 °C)
OFDA4	58.03	0.61	(18.03~106.03 °C)
OFDA5	58.07	0.65	(-2.93~200.00 °C)
OFDA6	66.51	0.75	(-80.00~200.00 °C)

### 3.3. Surface Properties of OFDA

The effect of different kind of OFIP-AO 1010-HEA on the surface free energy of OFDA films was investigated by water as standard liquids through the equation [10]:

$$(1 + \cos \theta_1)\gamma_1 = 4\left(\frac{\gamma_1^d \gamma_s^d}{\gamma_1^d + \gamma_s^d} + \frac{\gamma_1^p \gamma_s^p}{\gamma_1^p + \gamma_s^p}\right) \quad (1.1)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (1.2)$$

where  $\theta_1$  is the contact angle of water on the surface of OFDA film.  $\gamma_s$ ,  $\gamma_s^d$ ,  $\gamma_s^p$  respectively represent the surface energy, dispersion component and polar component of OFDA films.  $\gamma_1$ ,  $\gamma_1^d$ ,  $\gamma_1^p$  represent the surface tension, dispersion component and polar component of water ( $\gamma_1^d = 21.8$  mN/m,  $\gamma_1^p = 51.0$  mN/m).

The calculated results are showed in Table 4. It can be found that the all OFDA films with OFIP-AO 1010-HEAs had higher contact angle of water and lower surface free energy than that of OFDA0. The reason was that the OFIP-AO 1010-HEAs contained hydrophobic C-F groups, which was introduced into the OFDA as the side chains, can prevent the entry of small molecules, so OFDA films with OFIP-AO 1010-HEAs had the better surface properties. However, the water contact angles of OFDA1 to OFDA6 were no higher than 90°. That may because the structure of AO 1010 had a huge spatial hindrance, which can hinder the movement of polymer segments. This reason led to the fluorine groups can't reach the air/polymer and formed thicker fluorinated shell to improve the properties of films' surfaces, though OFIP-AO 1010-HEAs were introduced into the OFDA as the side chains. Anyway, the OFDA4 film had the higher contact angle of water and lowest surface free energy in all OFDA films.

Table 4. The effect of OFIP-AO 1010-HEA on water contact angle and surface free energy values of OFDA films

Sample	Water contact angle (°)	$\gamma_s^d$ (mN m <sup>-1</sup> )	$\gamma_s^p$ (mN m <sup>-1</sup> )	$\gamma_s$ (mN m <sup>-1</sup> )
OFDA0	19.78	49.71	19.06	68.77
OFDA1	63.22	28.15	10.55	38.70
OFDA2	66.68	27.40	9.95	37.34
OFDA3	62.81	29.72	11.16	40.87
OFDA4	75.14	22.58	6.80	29.38
OFDA5	68.76	25.62	8.53	34.15
OFDA6	70.36	25.21	8.64	33.85

#### 4. Conclusion

A series of hindered phenol fluorinated acrylate were synthesized successfully. The chemical structures of OFIP-AO 1010-HEAs were characterized by FTIR. The OFDA latex was synthesized by core-shell emulsion polymerization. DMA indicated that all the films showed good damping properties. The OFDA6 owned the widest TR and modest  $T_g$ , which can absorb of external mechanical vibration energy effectively. The results of contact angle measurements indicated that all OFDA films with OFIP-AO 1010-HEAs had better performance in contact angles of water and surface free energy. Among all OFDA films, the OFDA4 owned the best surface properties. The convenient preparation method and outstanding performances of OFDA make it potential in the fields of functional coating.

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