

## Research Article

# The Effect of Oxetane as Active Diluent on Cationic UV Curing System of Fluorine-Containing Epoxy Prepolymer

Baihong Chi,<sup>1</sup> Mengying Wei,<sup>2</sup> and Yong He<sup>2,3</sup>

<sup>1</sup>Beijing Institute of Satellite Information Engineering, Beijing 100086, China

<sup>2</sup>College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

<sup>3</sup>Changzhou Institute of Advanced Materials, Beijing University of Chemical Technology, Changzhou, Jiangsu 213164, China

Correspondence should be addressed to Yong He; heyong@mail.buct.edu.cn

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A series of fluorine-containing polyacrylic epoxy (FPAE) prepolymers with different fluorine content and molecular weight are synthesized by solution free radical polymerization of hexafluorobutyl methacrylate (HFBMA), butyl acrylate (BA), and glycidyl methacrylate (GMA). The synthesized prepolymers show high conversion and low volume shrinkage. The effect of different types of active diluent for the cationic UV curing of FPAE was investigated, among which oxetane exhibits better comprehensive property than epoxy and vinyl ether. The formulations with the optimal ratio of different functionality oxetane combination show good flexibility, adhesion, hydrophobicity, and antistain property.

## 1. Introduction

Because of the advantages of a fast curing rate, high efficiency, solvent free, and ambient temperature requirement, UV curing has been fast-growing and widely used in versatile industrial applications for decades [1–5]. Fluorinated prepolymers have also absorbed many attentions due to their excellent properties, such as chemical and thermal stability, low refractive index and surface energy, and high hydrophobicity and oleophobicity [6–9]. Thus, combining the fluorinated compounds with a UV curing technique has been believed as very significant and prospective in design and application of new materials [10].

Although there are many reports about fluorinated UV curable prepolymers for both radical and cationic mechanisms [11–13], their poor compatibility with most of organic hydrocarbon compounds and high cost are still problems to hinder its further development.

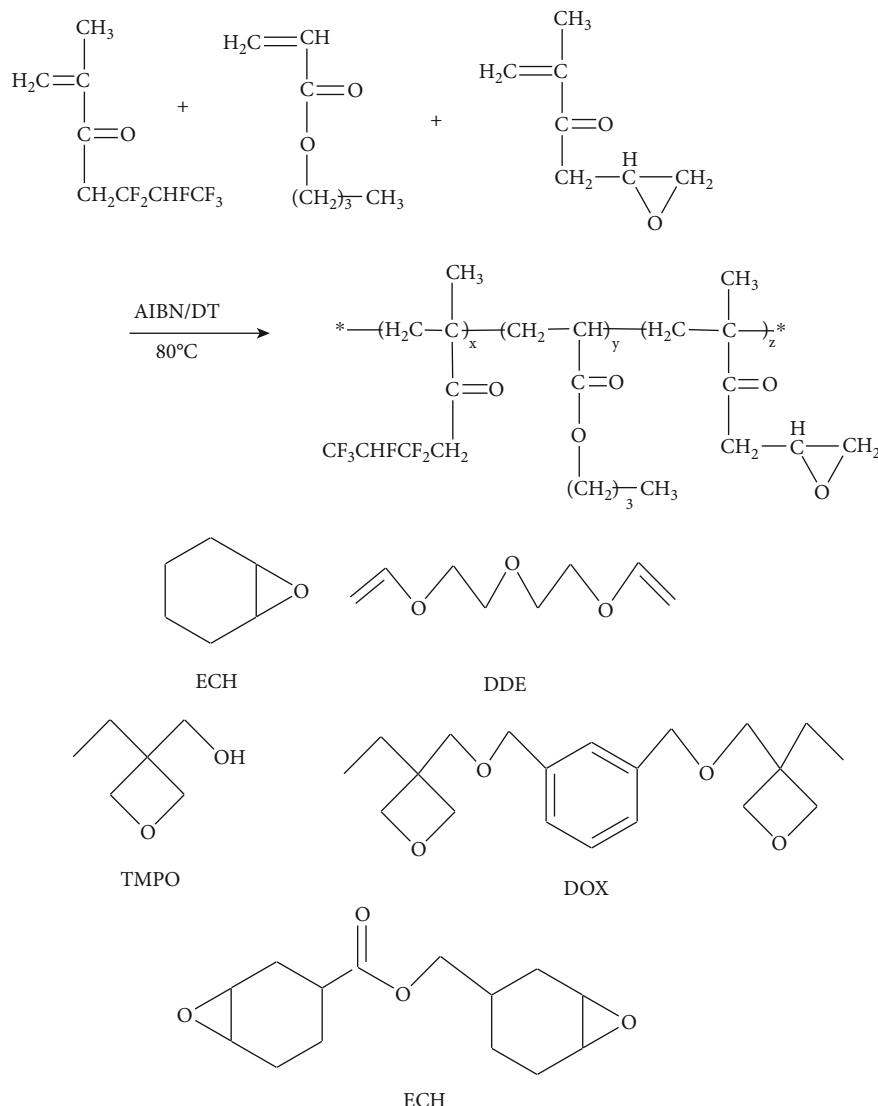
We [14] previously developed a kind of fluorinated polyacrylic acrylate prepolymers through free radical copolymerization of commercial fluorinated alkyl acrylate and hydrocarbon acrylate monomers to achieve excellent compatibility and good UV radical curing kinetics by introduction of

long alkyl chain and controlling the molecular weight of prepolymers.

Then, we [15] extended this strategy to prepare epoxy-containing fluorinated polyacrylic prepolymers successfully, which exhibited good compatibility and UV cationic curing rate. Continually, in this work, we focused on the effect of different active diluent combination on the UV curing kinetics and mechanical properties of this kind of epoxy-containing fluorinated polyacrylic prepolymers, because active diluents are also a very important key component to decide the final mechanical properties of cured materials besides prepolymers. Three kinds of active diluents are adopted, including vinyl ether, epoxy, and oxetane [16–18]. Among them, oxetane is rarely investigated in this kind of system but was reported to possess higher activity than epoxy with same functionality [19–21] and lower shrinkage than epoxy and vinyl ether [22–24]. This work could deepen the understanding of fluorinated UV cationic curing materials.

## 2. Experimental

**2.1. Materials.** Hexafluorobutyl methacrylate (HFBMA) was purchased from Harbin Xuejia Fluorosilicone Chemical



SCHEME 1: Synthesis route of FPAE and structure of used active diluents.

Company (Heilongjiang, China). Butyl acrylate (BA) was purchased from Fuchen Chemical Reagents Factory (Tianjin, China). Glycidyl methacrylate (GMA), 1,2-epoxycyclohexane (ECH), and *n*-dodecanethiol (DT) were purchased from Aladdin Agents Company (Beijing, China). 2,2-Azobis(2-methylpropionitrile) (AIBN) was purchased from Energy Chemical (Beijing, China) and recrystallized by ethanol at 60°C. Diethyleneglycol divinyl ethers (DDE) were purchased from Jiaozuo Xinjing Chemical Company (Henan, China). 3,4-Epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate (EEC) was purchased from Xiaogan Shenyuan Chemical Company (Hubei, China). 3-Ethyl-3-oxetanemethanol (TMPO), bis((1-ethyl(3-oxetanyl))methyl)ether (DOX), and triarylsulfonium hexafluoroantimonate (6976) were purchased from Tronly Company (Jiangsu, China).

**2.2. Synthesis of Fluorine-Containing Polyacrylic Epoxy (FPAE).** The synthesis of FPAEs was performed according to our previous work [15] with 2 wt% AIBN as the initiator

TABLE 1: Monomer compositions and molecular weight of synthesized FPAE.

	HFBMA/mol%	GMA/mol%	BA/mol%	$M_w$	PDI
C0	0	30	70	18533	4.01
C1	10	30	60	34059	3.05
C2	20	30	50	28623	2.92
C3	30	30	40	23825	2.64

and 2 wt% DT as the chain transfer agent. The synthesis route and comonomer compositions are listed in Scheme 1 and Table 1.

**2.3. Instruments.** Real-time infrared spectroscopy (RTIR) is recorded by coating the UV curable formulations on a KBr plate to form about 2  $\mu\text{m}$  thick liquid film and degree of conversion of the epoxy group could be calculated by the

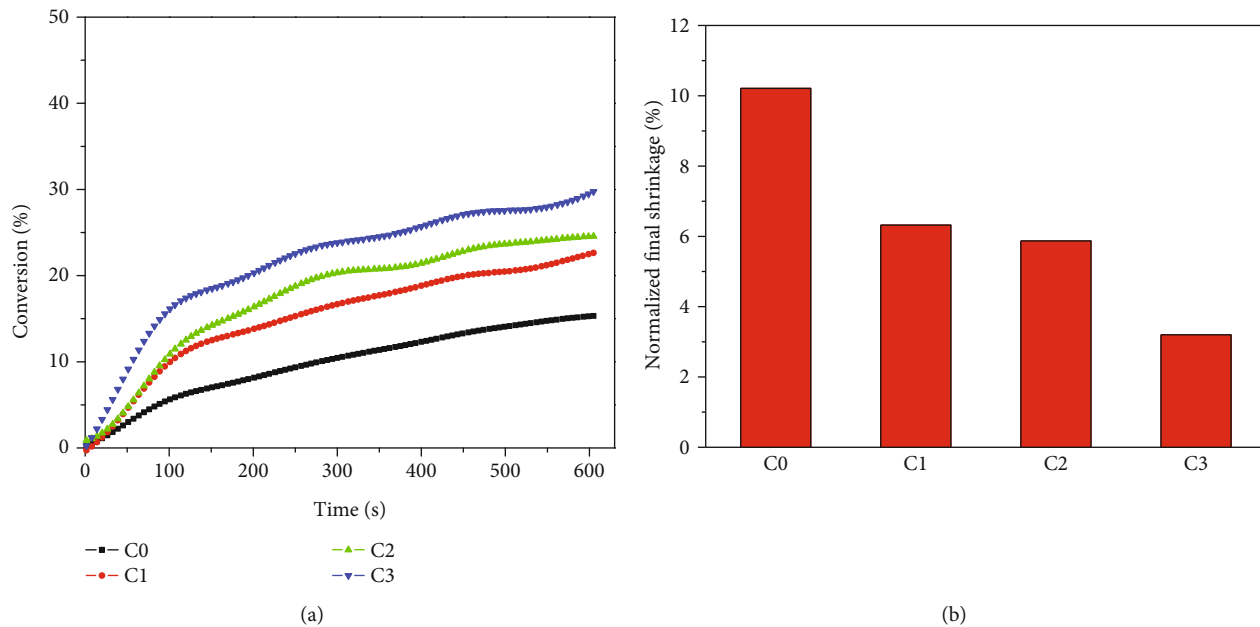


FIGURE 1: Epoxy conversion (a) and normalized final shrinkage (b) of different FPAE.

decrease of the peak area at  $910\text{ cm}^{-1}$  through the following equation:

$$\text{Conversion (\%)} = \left(1 - \frac{A_t}{A_0}\right) \times 100\%, \quad (1)$$

where  $A_0$  and  $A_t$  represent the epoxy group absorption peak area before and at time  $t$  UV irradiation.

The tensile modulus ( $E'$ ) and tensile loss factor ( $\tan \delta$ ) are obtained through dynamic mechanical analyzer (DMA, NETZSCH 242C, Germany) at a frequency of 5 Hz and a heating rate of  $10^\circ\text{C}/\text{min}$  in the temperature range of  $-80$  to  $100^\circ\text{C}$  with  $14 \times 10 \times 1$  mm sample.

Adhesion is tested using a cross-cut test, and the peel status was graded from 0 to 5, where 0 represents the best adhesion on the substrate. Pencil hardness is rated according to GB/T 6739-2006 to 6B-6H; 6B represents the softest, and 6H represents the hardest. Flexibility is rated according to GB/T 1731-1993 to 1-7; 7 means the best.

Shrinkage is directly measured by the laser reflection method base on the laser displacement sensor (LK-G10, Keyence, Japan), in which the thickness change of the sample is recorded by recording the motion of a mirror reflecting laser as the function of time [25, 26]. Shrinkage ( $S_t$ ) is defined as the equation (2), and normalized shrinkage is obtained through divided  $S_t$  by conversion at the same time.

$$S_t = \left(1 - \frac{H_t}{H_0}\right) \times 100\%, \quad (2)$$

where  $H_0$  is the initial thickness and  $H_t$  is the thickness at time  $t$ .

Contact angles are measured on the air-side surface of the coating films with a JC2000A instrument at room tempera-

ture by means of the sessile drop technique (each droplet volume was  $2\ \mu\text{L}$ ). More than five measurements are performed on each sample, and then, the values are averaged to get a reliable value for each sample.

Stain resistance were investigated using tea, coffee, cola, and ink as contaminants to the cured films. Four kinds of liquids are dropped on cured films and gently wiped off with cotton after 1, 5, and 12 hours, respectively, and pollution trails on the cured films are observed.

**2.4. Sample Preparation.** The pure FPAE formulations are prepared by mixing 60 wt% FPAE and 37 wt% ethyl acetate as solvent and 3 wt% 6976 as photoinitiator, and the curable samples were obtained after complete evaporating of solvent. The mixture formulations composed of different ratios of FPAE and active diluents (80:20, 60:40, 40:60, and 20:80 ( $w/w$ ), labeled as 1, 2, 3, and 4, respectively) and 3 wt% 6976 as the photoinitiator is coated on a glass slide by means of a spreader applicator to obtain about  $30\ \mu\text{m}$  film thickness. The shortest exposure time is decided by a finger pressure method upon exposure to UV light resource. The properties of cured films are tested after overnight standing. The UV light resource is a mercury arc lamp (RW-UVA C301-40bh, Runwing, China) with irradiation intensity of  $25\ \text{mW}/\text{cm}^2$  for all measurements.

### 3. Results and Discussion

**3.1. Conversion and Shrinkages of FPAE.** The epoxy group conversion curves in Figure 1 demonstrate the poor curing reactivity of non-fluorinated prepolymer (C0), just very low final conversion (14.7%) obtained, while the fluorinated prepolymer C3 shows much higher value (31.7%). While the fluorine content goes up, not only the final conversion but also the curing rate increases, even though their epoxy

TABLE 2: Effect of different monomers on the mechanical properties of different fluorinated prepolymers formulations.

	Curing time(s)			Pencil hardness			Adhesion			Flexibility		
	C0	C1	C3	C0	C1	C3	C0	C1	C3	C0	C1	C3
ECH												
FE1	15	15	30	5B	H	3B	4	3	2	7	2	7
FE2	45	45	30	6B	H	B	4	3	1	7	4	7
FE3	90	60	30	5B	3H	B	4	3	0	7	6	7
FE4	120	60	30	5B	3H	HB	4	1	0	7	7	7
TMPO												
FT1	15	30	45	H	H	5B	1	1	1	7	4	7
FT2	15	60	45	2H	3H	B	1	1	0	7	6	7
FT3	30	60	45	2H	2H	HB	1	0	0	7	7	7
FT4	30	60	45	HB	3H	H	2	0	0	7	7	7
DOX												
FO1	15	15	30	2H	3H	H	4	5	6	3	6	3
FO2	15	15	30	3H	3H	H	4	5	6	5	6	4
FO3	15	30	30	2H	H	H	4	1	6	7	7	6
FO4	15	30	45	HB	H	H	4	1	5	7	7	7
DDE												
FD1	15	15	15	5B	2H	5B	4	4	6	6	6	6
FD2	15	15	15	6B	B	5B	4	2	4	6	6	7
FD3	30	30	\	6B	B	\	4	2	\	7	6	\
FD4	60	60	\	6B	B	\	2	1	\	7	7	\

\: phase separation.

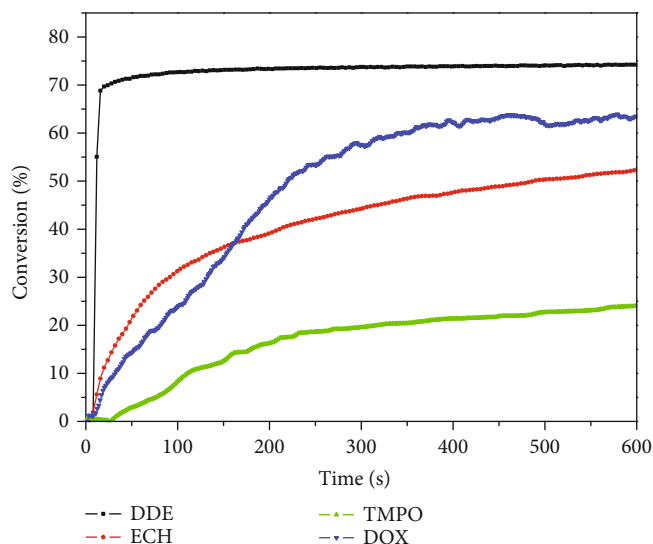


FIGURE 2: Epoxy conversion curves of different monomers.

contents are same. This can be explained that the introduction of fluorine atoms could improve the polarity of the molecular segments and reduce the degree of winding between the segments by the mutual repulsion, which can enable the epoxy group move more easily. What is more, the volume shrinkage increases when the UV irradiation start and the normalized final shrinkage of C3 is only 3.20% as shown in Figure 1, while nonfluorinated prepolymer C0 gives a 10.21% value. Because the free volume of the fluorinated

TABLE 3: Effect of the oxetane ratio on the mechanical properties of 60 wt% prepolymer C1 formulations.

	TMPO (wt%)	DOX (wt%)	Curing time (s)	Pencil hardness	Adhesion	Flexibility
F0	0	40	15	H	4	7
F1	8	32	15	H	5	7
F2	16	24	30	H	4	7
F3	24	16	30	2H	1	7
F4	32	8	45	2H	1	7
F5	40	0	60	H	0	7

prepolymer is very small due to smaller atomic radius of fluorine than hydrogen, the increasing of the fluorine content can remarkably decrease the volume shrinkage in UV curing [27].

**3.2. Properties of the Cured Films with Different Active Diluents.** The effect of different types of active diluent on the cured films was investigated in prepolymer C0, C1, and C3 systems with 20, 40, 60, and 80 wt% active diluents (Table 2), in which X represents different active diluents. The C1 exhibited obviously better pencil hardness than that of C3 series, which is due to its higher epoxy conversion, and similar with curing rate, flexibility and adhesion. However, C3 encounters some compatibility problem with monomer. Thus, C1 is selected in further work for its less fluorinated monomer content.

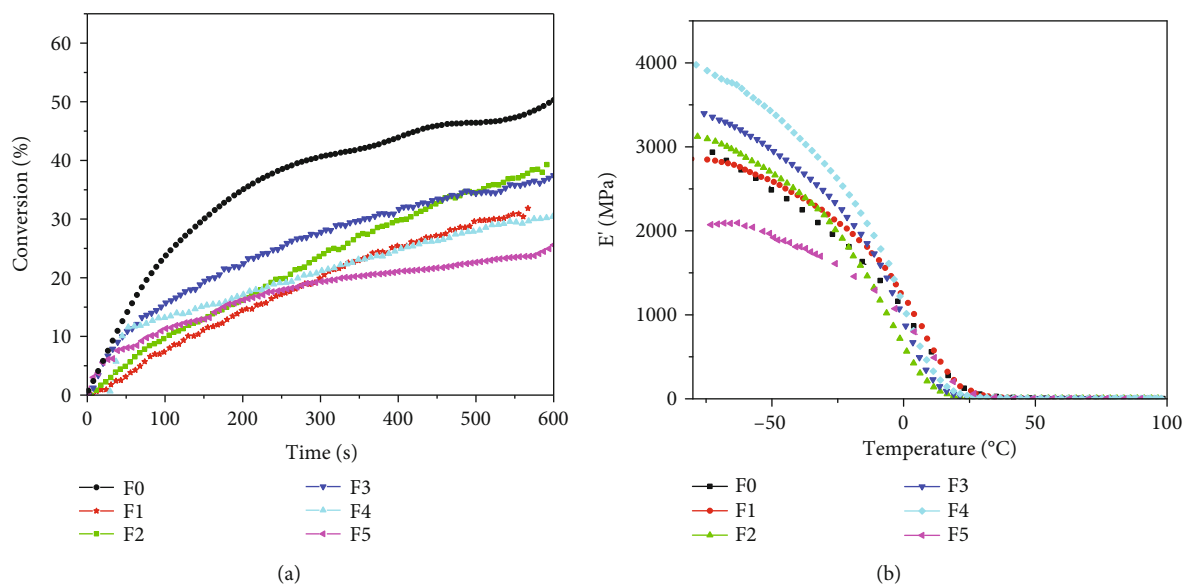


FIGURE 3: Conversion curves (a) and tensile module (b) of 60 wt% prepolymer C1 formulations with different TMPO/DOX combination.

In C1 series (Table 2), as the fluorinated prepolymer content is increasing, the flexibility improves and the adhesion increases. But the flexibility and adhesion of 80 wt% prepolymer formulation do not show obvious improvement comparing with 60 wt% one, which is due to that higher viscosity of the 80 wt% formulation decreases molecular diffusion ability and results in the lower curing rate. The optimal content of prepolymer in the formulation is determined to be 60 wt% for next step investigation.

It can be also seen clearly that the DDE systems show a higher curing rate and final conversion than others (Figure 2), but relatively poor adhesion and pencil hardness (Table 2). The high polymerization rate and conversion comes from the chain reaction process, while the poor adhesion is due to the biggest volume shrinkage resulted from highest conversion and nonring open mechanism and the low pencil hardness is obviously attributed to its soft ether structure. It means that DDE should just be used as additive in the formulation to improve the curing rate. For the rest of active diluents, the curing rate of ECH and DOX systems are higher than TMPO and the shortest curing time are also lower, which is the results of higher ring tension for ECH and higher active group content for DOX. The monofunctional oxetane (TMPO) system possesses better adhesion and flexibility than monofunctional epoxy (ECH), which is decided by the better softness of the branched alkane structure for TMPO-cured product than that of the cycloalkane for ECH. What is more, the difunctional oxetane (DOX) can even lead to higher curing conversion and almost same adhesion and flexibility comparing with ECH. Thus, active diluent combination of TMPO and DOX may supply better comprehensive mechanical properties.

The best ratio of TMPO and DOX should be the next issue that needs exploration. In 60 wt% C1 series, although formula F3 has only the second highest conversion and tensile modulus ( $E'$ ), it shows the best combination of curing speed and mechanical properties (Table 3 and Figure 3). It

possesses best pencil hardness and second best adhesion. Its third highest curing rate is lower than F0 and F1, which adhesion cannot reach the industrial standard.

**3.3. Comparison between Oxetane and Epoxy Systems.** To verify the practicality of the mixture oxetane active diluent system, the commercial epoxy mixture active diluent composed of ECH and EEC was tested based on formulation F3. At the same time, DDE was added at different ratios due to its good solubility and fast curing rate. As shown in Table 4, comparing with FE series, the FO series exhibit better adhesion and flexibility, which can be explained that the volume shrinkage of oxetane is substantially lower than comparable epoxy [28]. What is more, the pencil hardness of the cured films of FO series is higher than FE, which can be related with higher conversion of FO than FE (Figure 4). These advantages can be attributed to similar ring strain and higher nucleophilicity of the oxetane comparing with epoxy, so it is generally more active and less volume shrinkage than epoxy [29, 30]. The pencil hardness, adhesion, and flexibility of cured films are similar when the content of the DDE varied from 0 (F3) to 16 wt% (FO2), but the curing rate and final conversion of FO2 is higher than F3, which means fast processing and less residue.

The surface energy of fluorinated prepolymer is very low, which enables them usually be adopted as antistain materials. Thus, the stain resistance properties of FOx and FEp series are examined. As shown in Table 5, the cured films of whole FEp series and FOx3 and FOx4 have good resistance to tea, coffee, and cola, and almost no mark is left on the film after 1 h, 5 h, and 12 h. But their antistain property to ink-water is not satisfied, the stain trails were observed for FE series after 1 h and for FOx3 and FOx4 after 5 h, while the degree of contamination increases over time. Antistain properties of the cured films have an important relationship with chemical composition, cross-linking density, and conversion. Because of higher conversion, the formulations of FOx1 and

TABLE 4: Properties of 60 wt% prepolymer C1 formulations with different monomer combinations.

	DDE/wt%	M1/wt%	M2/wt%	Curing time/s	Pencil hardness	Adhesion	Flexibility	CA/°
FOx1	8	32		45	2H	0	7	85.88
FOx2	16	24	0	45	H	1	7	86.44
FOx3	24	16		45	H	5	7	87.92
FOx4	32	8		30	5B	6	7	89.69
FEp1	8		32	45	5B	6	6	83.20
FEp2	16	0	24	45	5B	6	6	85.77
FEp3	24		16	45	5B	6	6	87.32
FEp4	32		8	45	5B	6	6	87.03

M1: TMPO/DOX = 60/40, *w/w*; M2: ECH/EEC = 60/40, *w/w*.

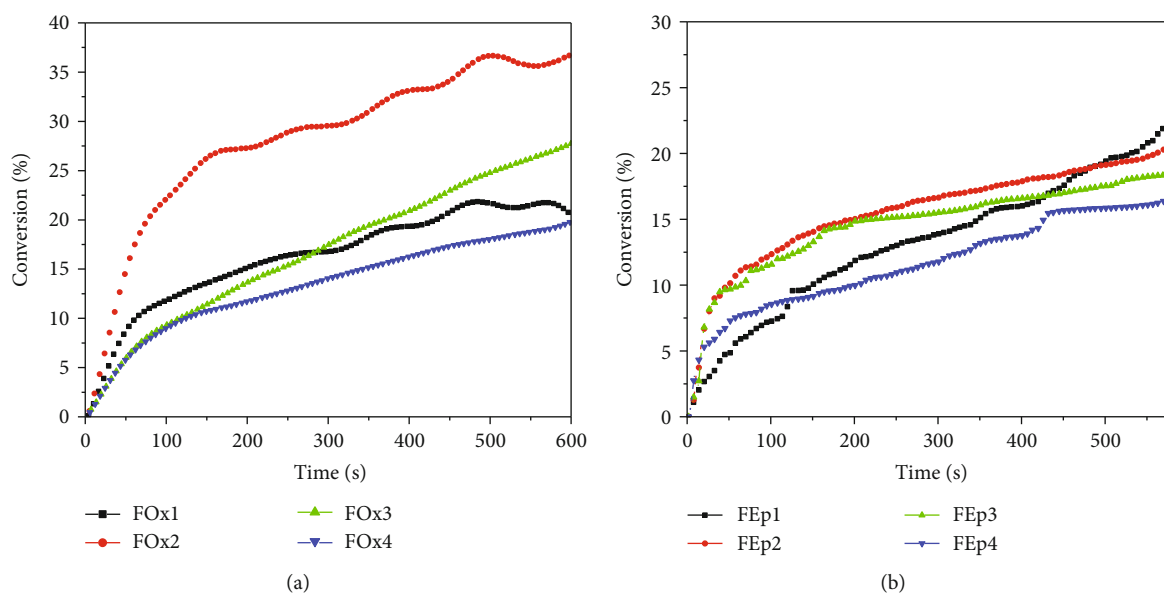


FIGURE 4: Conversion curves of 60 wt% prepolymer C1 formulations with DDE and M1 (a) and M2 (b) monomer system, M1: TMPO/DOX = 60/40 (*w/w*); M2: ECH/EEC = 60/40 (*w/w*).

TABLE 5: Antistain performance of cured films for different formulation.

	C1 60%	DDE/M1				DDE/M2			
		FOx1	FOx2	FOx3	FOx4	FEp1	FEp2	FEp3	FEp4
1 h	Tea	√	√	√	√	√	√	√	√
	Coffee	√	√	√	√	√	√	√	√
	Cola	√	√	√	√	√	√	√	√
	Ink-water	√	√	√	√	☒	×	×	×
5 h	Tea	√	√	√	√	√	√	√	√
	Coffee	√	√	√	√	√	√	√	√
	Cola	√	√	√	√	√	√	√	√
	Ink-water	√	√	☒	☒	×	×	×	×
12 h	Tea	√	√	√	√	√	√	√	√
	Coffee	√	√	√	√	√	√	√	√
	Cola	√	√	√	√	√	√	√	√
	Ink-water	√	√	☒	☒	×	×	×	×

√: no stain; ☒: little stain; ×: stain.

FOx2 show excellent antistain property even to ink-water; no trail left on the cured films after 12 h, although the contact angle (CA) does not show obvious difference. These two formulations could find potential application in antistain materials.

#### 4. Conclusion

The effect of different types of active diluents on the cationic UV curable fluorinated-containing system was investigated. A series of prepolymers with different fluorine content were synthesized. When the fluorine content goes up, the curing rate and conversion increased, and the curing volume shrinkage decreased at the same time. In the investigated active diluent types, oxetane exhibited the best comprehensive properties, including the curing rate, pencil hardness, adhesion, and flexibility. Furthermore, the combination of difunctional oxetane (DOX) and monofunctional oxetane (TMPO) showed the best effect. Comparing with commercial epoxy active diluent system, the oxetane system composed of 60 wt% C1 prepolymer, 16 wt% of TMPO, and 24 wt% DOX exhibited much better pencil hardness, adhesion, flexibility, and similar contact angle. What is more, the antistain effect of oxetane-containing system is obviously better than corresponding epoxy-containing systems.

#### Data Availability

All the data used to support the findings of this study are included within the article.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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