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## Mechanical properties of polymer layers fabricated via hybrid free radical-cationic polymerization of acrylate, epoxide, and oxetane binders

Ondřej Škola<sup>1</sup>, Bohumil Jašůrek<sup>1</sup>, David Veselý<sup>2</sup>, and Petr Němec<sup>1\*</sup>

<sup>1</sup> Department of Graphic Arts and Photophysics, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

<sup>2</sup> Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

\* corresponding author

E-mail: [petr.nemec@upce.cz](mailto:petr.nemec@upce.cz); Tel.: +420466038502; Fax: +420466037068

### Abstract

This work is aimed at the hybrid free radical-cationic polymerization of acrylate, epoxide, and oxetane monomers. Studied hybrid systems were prepared as mixtures of binders polymerizing via free radical mechanism (pentaerythritol triacrylate, thioacrylate dendritic oligomer) and binders polymerizing through cationic mechanism (3, 4-epoxycyclohexylmethyl-3, 4-epoxycyclohexanecarboxylate epoxy monomer, bis[1-ethyl(3-oxetanyl)]methyl ether oxetane monomer) in various ratios. As radical and cationic photoinitiators, 2-hydroxy-2-methyl-1-phenylpropan-1-one and (4-methylphenyl) [4-(2-methylpropyl) phenyl] iodonium hexafluorophosphate, respectively, were used. The process of polymerization was monitored using Fourier-transformed infrared spectroscopy giving degree of conversion data for each reaction. Cured polymer layers were evaluated in terms of their mechanical properties. Based on experimental data, best mechanical properties (adhesion and flexibility) and the highest degree of conversion were achieved in hybrid samples containing thioacrylate dendritic oligomer radical binder in combination with (3, 4-epoxycyclohexylmethyl-3, 4-epoxycyclohexanecarboxylate and bis[1-ethyl(3-oxetanyl)]methyl ether (ratio 1:1) cationic monomers.

### Keywords:

free radical, cationic, hybrid, polymerization, mechanical properties

### Highlights:

Positive effect of hybrid polymerization on conversion degree of monomers  
Ratio of monomers in hybrid systems significantly influence the conversion degree  
Dendritic oligomer DTEA increases the elasticity/adhesion of hybrid samples  
PETA monomer increases the hardness/brittleness of hybrid samples

## 1 Introduction

To date, systems cured by UV/visible radiation are used in many industrial applications. For example, UV curable compositions are exploited for coatings of various materials such as fibres, wood, metals, plastics or paper [1]. Other applications cover production of adhesives, solder mask [2], inks [3], microelectronic photoresists, and stereolithography [4]. Systems cured by visible light are used in the printing industry, imaging, medical applications, holographic recording, and nanoscale micromechanics. Dental filling materials, photoresists, printing plates, highly pigmented inks/coatings are only some of the applications where these systems are utilized [5, 6]. The big advantage of UV curable compositions lies in the instant curing and high efficiency. This technology is environmentally friendly with adjustable performances (from brittle to very flexible films) [1]. In comparison with conventional coatings (e.g. solvent-based coatings), UV cured layers offer energy saving and low content of volatile organic compounds [7].

Systems cured by UV radiation generally employ free radical or cationic mechanism; both mechanisms have their distinct advantages and disadvantages. Acrylates, polyurethane acrylates, polyester acrylates, and acrylic acrylates are commonly used binders cured by free radical mechanism [1]. Their main advantages are fast curing (fraction of a second) and great offer of existing monomers, oligomers, photoinitiators, and additives to set the final properties [8]. On the other hand, main drawbacks of free radical polymerization are the inhibition of curing by atmospheric oxygen, irritant effect of some acrylate monomers [2], and contraction of the coating's volume during curing (shrinkage between 10–15 % can occur) [1]. On the other hand, through cationic mechanism, epoxides, oxetanes, vinyl, propenyl and butenyl ethers [2, 9, 10] can be cured. Main advantages of cationic polymerizations are as follows: 1) there is no inhibition of the polymerization by atmospheric oxygen [6], 2) polymerization leads to small shrinkage only (for epoxides approximately 5 %), and 3) formation of a large amount of hydrogen bonds, which leads to increased adhesion between the coating and the substrate [1]. Cured coatings have also high heat resistance and good chemical resistance [10]. In contrast with free radical polymerization, cationic polymerization is much slower (final properties of the cured film can be obtained after approximately 24 hours) [9] and this type of polymerization can be inhibited by humidity and bases [2, 9].

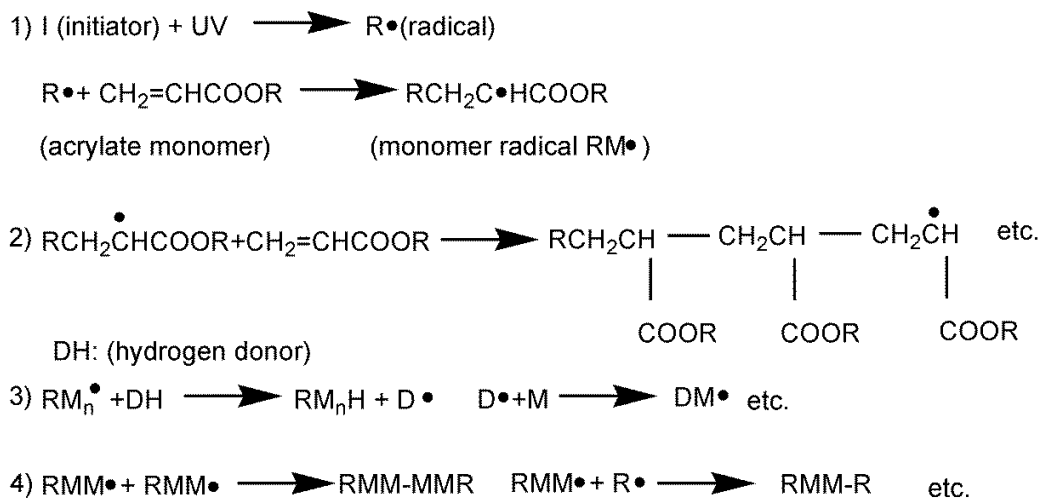
The disadvantages of free radical and cationic mechanisms can be significantly suppressed by the use of hybrid polymerization, which can be performed sequentially or simultaneously via free radical and cationic mechanism [11]. Materials prepared in this way show many desirable chemical and mechanical properties that are difficult to achieve through separate free radical/cationic polymerization. Hybrid systems combine or modify the properties of both polymers (produced simultaneously by free radical or cationic polymerization) such as glass transition temperature, melting temperature, strength, toughness etc. [3, 9]. These hybrid polymerizations may lead to the preparation of unusual hybrid polymer structures such as the multiblock, graft, random copolymers [1, 12], and interpenetrating polymeric networks, which are considered to be very promising materials in the field of coatings [1]. They may be used in various applications, such as hard plastics, ion exchange resins, and materials damping sound and vibrations [3]. Other advantages of hybrid compositions include increased cure speed, faster development of final properties of the cured films, lower sensitivity to inhibition of curing by atmospheric oxygen, moisture and other inhibitors, and creation of films of improved properties [9].

The objective of this work is to determine the optimal composition of hybrid polymerizing samples in scope of the final degree of conversion (hereinafter DC) and mechanical properties of cured films. Samples evaluated in this work differ in the type of used monomers (acrylates, epoxides, oxetanes) and in the used ratios of these monomers. DC was determined based on results obtained with Fourier-transformed infrared (FTIR) spectroscopy. Mechanical properties of

the prepared films were evaluated with cylindrical mandrel bend test, falling weight test, cupping test and pendulum hardness.

## 2 Theory

Photopolymerization by radical mechanism takes place in four steps: initiation, propagation, chain transfer, and termination (Fig. 1). In the first step (initiation), absorption of radiation by photoinitiator takes place which causes the decay of photoinitiator and formation of radicals. Radicals react with present molecules of monomers and oligomers (e.g. with acrylates) and a reactive alkyl monomer is formed. The radical monomer is highly reactive and reacts in chain reaction with other monomers or oligomers present in the formulation (propagation). Chain transfer is a reaction during which transfer of the reactive centre takes place from one molecule to another one. By proton transfer from the donor of hydrogen, the growth of the polymer radical is terminated and a new reactive centre is created on the molecule of donor (it can react with present molecules of monomers and oligomers which leads to formation of a new polymer chain). Termination is the last phase of the chain reaction during which an interaction or recombination of two radicals and termination of reactive centres on both molecules is taking place. Polymerization is terminated at using up all monomers or at increase of viscosity to the limit of molecule movement and interaction inhibition, even if the system still contains unreacted monomers [13].



**Figure 1: Mechanism of free radical polymerization: 1) initiation, 2) propagation, 3) chain transfer, 4) termination. [11]**

Cationic polymerization proceeds also in four phases as stated above. In contrast to the radical polymerization, the reactive centre does not have a form of radical but cation. During initiation, as in previous case, the absorption of radiation by a photoinitiator (e.g. iodonium or sulfonium salt) and its decay takes place. For example, when using iodonium aromatic salt, the carbon-iodine bond splits which leads to the formation of aryl cation. In the presence of a hydrogen donor (from polyethers commonly used in the formulation), the aryl cation produces a proton which, coupled with the anion, provides the Brønsted acid which initiates the polymerization reaction. Depicted mechanism is illustrated in Fig. 2.

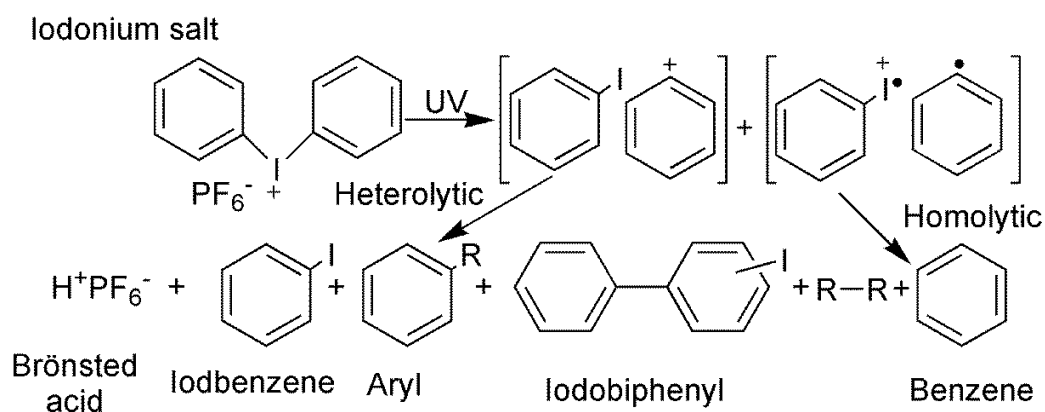


Figure 2: Photo decomposition of iodonium salt. [11]

For cationic polymerization, epoxides, oxetanes, and vinyl ethers are frequently used monomers and oligomers. Figure 3 depicts the scheme of epoxide polymerization during which, by reaction with Bronsted acid, the epoxide ring opens up and forms a carbonium cation. This cation is then attacking other epoxide groups leading to polyether formation. Alcohols are mostly used as compounds causing the transfer of the chain and modification of properties. Termination reaction in cationic polymerization does not proceed as in the case of radical polymerization by reaction of two growing reactive centers (both have the form of cation) but mostly by reaction with proton [13].

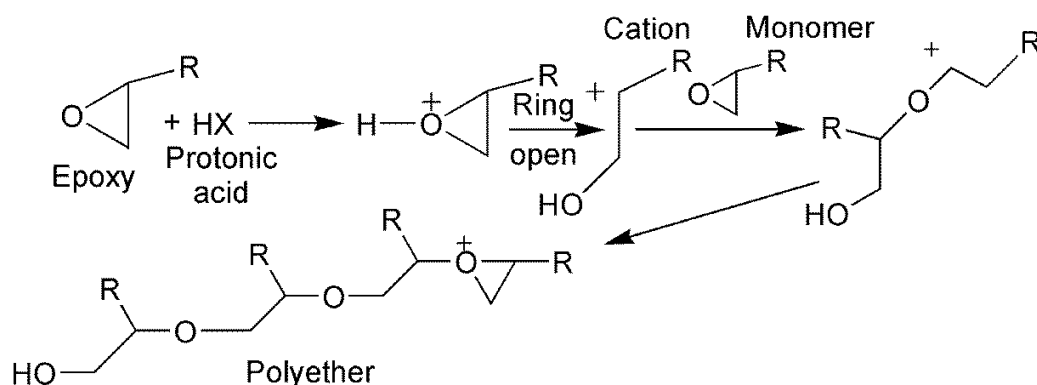


Figure 3: The ring-opening epoxy polymerization. [11]

### 3 Materials and methods

#### 3.1 Materials

2-hydroxy-2-methyl-1-phenyl-propan-1-one photoinitiator (Darocure 1173, BASF), pentaerythritol triacrylate acrylic monomer (hereinafter PETA, Sigma-Aldrich), and thioether acrylate dendritic oligomer with functionality 18 (Bomar XDT-1018, hereinafter DTEA, DYMAX) were used as raw materials for free radical polymerization. For cationic polymerization, (4-methylphenyl) [4-(2-methylpropyl) phenyl] iodonium hexafluorophosphate photoinitiator (Irgacure 250, BASF), 3, 4-epoxycyclohexylmethyl-3, 4-epoxycyclohexanecarboxylate epoxy monomer (Uvacure 1500, hereinafter EPOX, SpecialChem), and bis[1-ethyl(3-oxetanyl)]methyl ether oxetane monomer

(OXT-221, hereinafter DOX, Synasia) were employed. Irgacure 250 was supplied in a mixture containing 25 wt% of propylene carbonate. Chemical structures of used substances are shown in Fig. 4.

The monomers selected for this study are compounds, which are typically used in UV curable inks/varnishes. Acrylates are known for their high reactivity; they polymerize rapidly in the presence of free radicals. Epoxides and oxetanes are less reactive, but they are not sensitive to oxygen due to cationic mechanism of their polymerization. A hydroxyl phenyl ketone (Darocure 1173) and an arylidonium salt (Irgacure 250) were used as photoinitiators because they produce free radicals and protonic species upon UV exposure with high quantum yields. The next advantage of this initiating system is that Darocure 1173 promote decomposition of iodonium salts [11, 14].

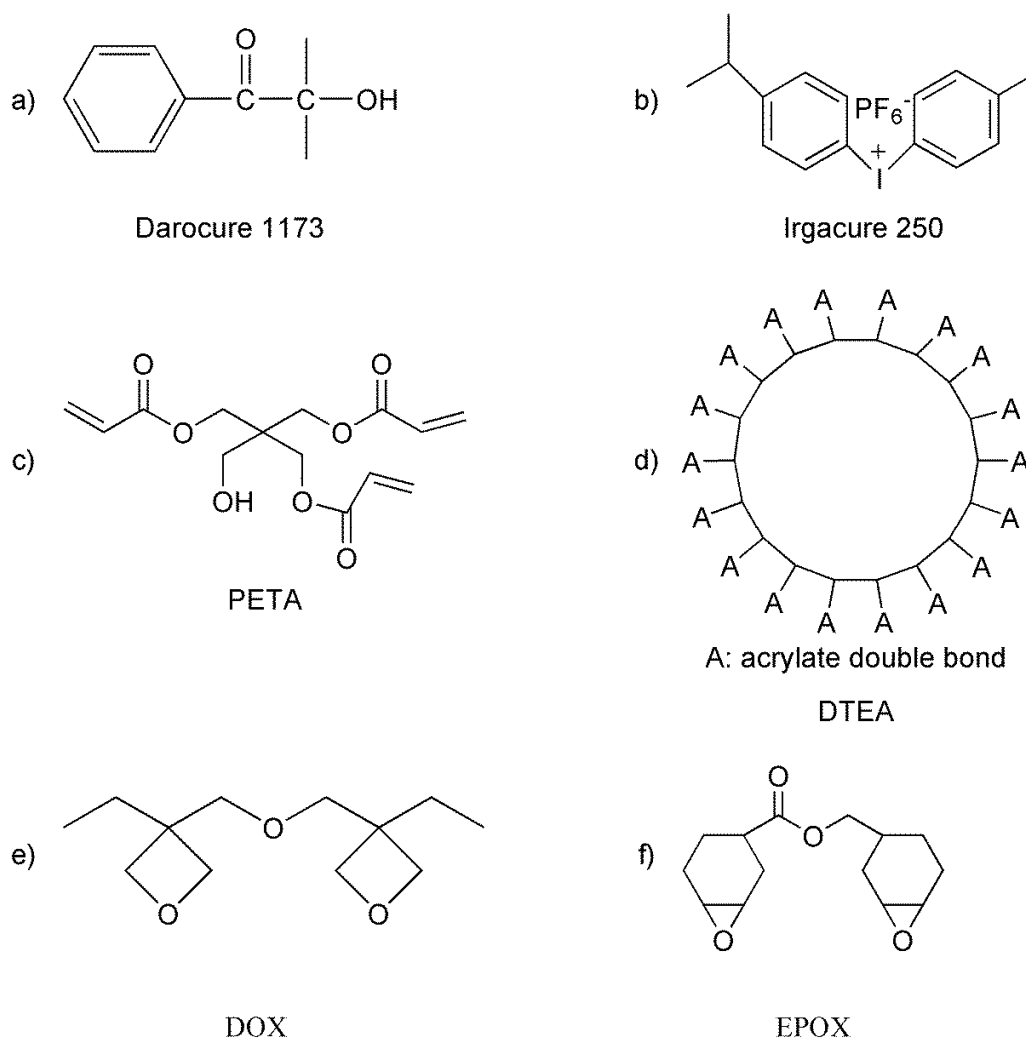


Figure 4: Chemical structure of a) 2-hydroxy-2-methyl-1-phenyl-propan-1-one photoinitiator, b) (4-methylphenyl) [4-(2-methylpropyl) phenyl] iodonium hexafluorophosphate, c) pentaerythritol triacrylate, d) thioether acrylate dendritic oligomer, e) bis[1-ethyl(3-oxetanyl)]methyl ether, f) 3, 4-epoxycyclohexylmethyl-3, 4-epoxycyclohexanecarboxylate.

### 3.2 Preparation of the samples

All studied compositions and their labelling are shown in Table 1. The concentration of photoinitiators in all samples was kept at 3 mol%. R-labelled samples polymerize by only free radical mechanism, C-labelled samples polymerize by only cationic mechanism, and H-labelled samples polymerize by free radical and cationic mechanism proceeding simultaneously.

**Table 1: Compositions of samples and their labels.**

	Photoinitiators	Free-radically polymerizing monomers and oligomers	Molar concentrations of monomers and oligomers [%]	Cationically polymerizing monomers and oligomers	Molar concentrations of monomers and oligomers [%]
PETA (R)	Darocure 1173	PETA	97	–	–
DTEA (R)	Darocure 1173	DTEA	97	–	–
EPOX (C)	Irgacure 250	–	–	EPOX	97
DOX (C)	Irgacure 250	–	–	DOX	97
H1(1:1)	Darocure 1173, Irgacure 250	PETA	47	EPOX	47
H1(1:3)	Darocure 1173, Irgacure 250	PETA	22	EPOX	72
H1(3:1)	Darocure 1173, Irgacure 250	PETA	72	EPOX	22
H2(1:1)	Darocure 1173, Irgacure 250	PETA	47	DOX	47
H2(1:3)	Darocure 1173, Irgacure 250	PETA	22	DOX	72
H2(3:1)	Darocure 1173, Irgacure 250	PETA	72	DOX	22
H3(1:1)	Darocure 1173, Irgacure 250	DTEA	47	EPOX	47
H3(1:3)	Darocure 1173, Irgacure 250	DTEA	22	EPOX	72
H3(3:1)	Darocure 1173, Irgacure 250	DTEA	72	EPOX	22
H4(1:1)	Darocure 1173, Irgacure 250	DTEA	47	DOX	47
H4(1:3)	Darocure 1173, Irgacure 250	DTEA	22	DOX	72
H4(3:1)	Darocure 1173, Irgacure 250	DTEA	72	DOX	22

All the samples were coated on an aluminium foil using Sheen coating spiral; the thickness of all layers was  $12 \pm 3 \mu\text{m}$ . For the evaluation of mechanical properties, the samples with the same thicknesses were coated on Q-Panels (Q-LAB, thickness  $55 \mu\text{m}$ ) and glass plates.

### 3.3 Measurement of degree of conversion

The prepared layers were measured using FTIR spectrometer (Avatar 320, Thermo Scientific, USA) before curing with UV exposure and after a dose of irradiation (UV tunnel Miniterm UV220 Q with medium-pressure mercury lamp, Aeroterm, CZ).

In the case of pure free radical polymerization (R), layers were irradiated ten times (one UV dose of  $150 \text{ mJ/cm}^2$ ). The DC after each exposure was evaluated from the decrease of the absorption double-band (maxima at  $1617$  and  $1634 \text{ cm}^{-1}$ ) area belonging to the acrylate double bond [15, 16].

Samples that polymerize via cationic polymerization (C) were irradiated one time with UV dose of  $450 \text{ mJ/cm}^2$ . Infrared spectra were collected every two minutes after the irradiation in the period of 2 hours and once more after 24 hours. DC of the oxetane group was evaluated from the reduction of absorption band corresponding with oxetane group (maximum at  $980 \text{ cm}^{-1}$ ) during polymerization [15, 17, 18]. DC of the epoxy group was evaluated in two ways. The first way ( $\text{EPOX}_{w1}$ ) tracks the reduction of the absorption triple band of epoxy group (maxima at  $788$ ,  $798$ ,  $808 \text{ cm}^{-1}$ ) [19] and the second way ( $\text{EPOX}_{w2}$ ) tracks only a fragment of this triple band

(maximum at 788 cm<sup>-1</sup>). This is due to a partial overlap of the absorption band of epoxide group (bands with maxima at 798 and 808 cm<sup>-1</sup>) with the band belonging to deformation vibrations of acrylate double bond in hybrid PETA/EPOX composition. Both ways of evaluation give very similar results (differences within the frame of the standard deviation), depicted in Figure 5.

In case of hybrid polymerization (H), the infrared spectra were collected following the procedure used for the cationic polymerization. Each sample polymerizing by hybrid mechanism was irradiated once with a UV dose of 450 mJ/cm<sup>2</sup>. The DC of acrylate double bond and oxetane group was extracted in the same way as for R and C samples mentioned above. The DC of epoxy group was evaluated based on a fragment of epoxy triple band (maximum at 788 cm<sup>-1</sup>, EPOX<sub>w2</sub>) due to reason mentioned above. The DC of the reactive functional groups was calculated from the following equation [20]:

$$DC [\%] = \frac{A_0 - A_t}{A_0} \cdot 100 \quad (1),$$

where  $A_0$  is the peak area of the reactive functional group before irradiation and  $A_t$  is the peak area after UV irradiation.

### 3.4 Measurements of mechanical properties

#### 3.4.1 Cylindrical mandrel bend test

Bend test is used to determine the resistance of the coating to cracking or peeling from the substrate after bending around a cylindrical mandrel. When a coated panel is bent tightly around a cylinder of a known diameter, the damage caused by distending of coating may result in cracking of the coating. Flexibility and the adhesion of the coating are given by the extent of resistance to cracking and flaking. These damages are caused by bending of the coated panels on cylinders of various radii. The smaller the radius of the cylinder, which causes no damage to the coating, the more flexible the coating [21].

The testing was performed using a set of mandrels with diameters 4–30 mm. The sample was loaded into the bending apparatus with the coated side facing out. The result of the test is the smallest diameter of mandrel that caused no violation to the coating.

#### 3.4.2 Falling weight test

This method evaluates the resistance of coatings to cracking or peeling from the substrate due to deformation caused by the fall of balls (20 mm in diameter). In this method, the maximum free fall height is determined that caused no violation to the coating. The higher the height of fall, the greater the resistance of the coating [22].

#### 3.4.3 Cupping test

The cupping test is used to assess the resistance of coatings to cracking and peeling from the substrate under different conditions of controlled deformation using Erichsen testing machine [23].

During testing, the resistance was evaluated as the maximal depth of penetration of a hard steel ball (20 mm in diameter) which causes no damage to the coating. The steel ball was pressed into the sample at rate of 0.2±0.1 mm/s. Higher depth of penetration means higher flexibility/adhesion of the coating.

#### 3.4.4 Pendulum hardness

The hardness of the samples was determined by pendulum hardness (Persoz). The measurement result is expressed as the number of cycles or the time at which the displacement is reduced within a defined range. The harder the coating, the longer the period of downturn of



the pendulum. First, standard hardness was determined which is the time of attenuation of a glass standard oscillation amplitude from 12° to 4°; in our experiments, the value of attenuation time for a glass standard was found to be 430±10 s. In the same manner, time of oscillation attenuation of the studied samples was measured [24]. The relative hardness of the polymer film is determined by equation:

$$T = \frac{t_1}{t_2} \cdot 100 [\%] \quad (2),$$

where T is the relative hardness of the coating [%],  $t_1$  is attenuation time of the pendulum on the coating [s] and  $t_2$  is attenuation time on the glass standard [s].

### 3.4.5 Determination of the overall mechanical resistance score

Scores on the 100–0 scale were derived from the mechanical tests to assess the physicochemical properties of the coated layers. The overall mechanical resistance (*OMR*) of the coated layers was calculated as the arithmetic average of the individual scores [22]:

$$OMR = \frac{Y1+Y2+Y3+Y4}{4} \quad (3).$$

In Eq. 3, Y1 is the result obtained from the cupping test, Y2 is the result obtained from the falling weight test, Y3 is the result obtained from the bend test, and Y4 is the result obtained from the pendulum hardness.

## 4 Results and discussion

### 4.1 Degree of conversion of free radical and cationic samples

The DC of free radically polymerizing samples or cationically polymerizing samples is shown in Fig. 5. Cationic sample (EPOX) was evaluated in two ways as described above; however, the final DC (24h after the irradiation) is very similar (EPOX<sub>w1</sub> 90.2%, EPOX<sub>w2</sub> 90.8%). Contrary, other cationic sample (DOX) reached only 70.4% after identical time. Both cationically polymerizing binders (EPOX, DOX) contain two reactive functional groups. At the same functionality, similar molecular weight (EPOX 252 g/mol, DOX 214 g/mol), and identical curing conditions (UV dose and content of photoinitiator), a markedly higher DC (about 20 %) and therefore also higher degree of interlinkage is clearly reached for EPOX.

The DC for PETA and DTEA samples after the last irradiation (total UV dose of 1500 mJ/cm<sup>2</sup>) is 58.4 and 92.9%, respectively. The difference in the reached DC is distinctive. On the other hand, it is not possible to use DC values for evaluation of the degree of interlinkage of individual monomers as in case of the monomers mentioned above. This is due to extensive differences in functionality, structure, and molecular weight (DTEA 8000 g/mol, functionality 18, a large molecule with dendritic structure; PETA 298 g/mol, functionality 3).

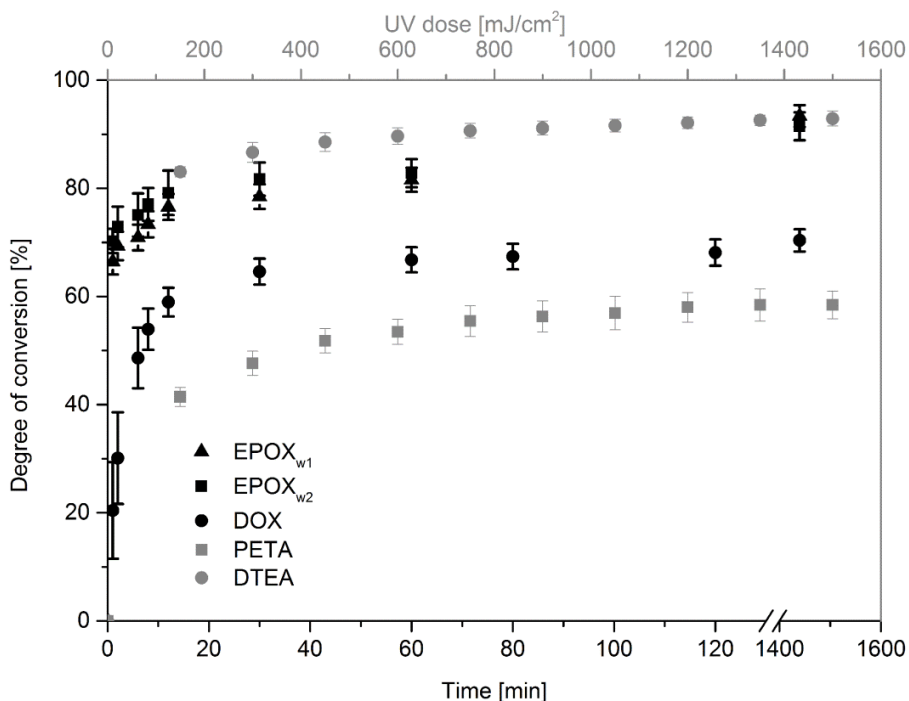


Figure 5: Degrees of conversions of samples polymerized by only free radical or cationic mechanism.

#### 4.2 Degree of conversion of hybrid compositions

In Fig. 6, the DC of PETA monomer in free radical and hybrid polymerizing systems (H1 and H2) are shown. In both hybrid systems (mixture of PETA with epoxide or oxetane monomer), PETA reached similar DC, therefore the chosen types of cationically polymerizing monomers did not influence the conversion. On the other hand, the ratio of free radically to cationically polymerizing monomers has an important influence on the reached DC of PETA monomer. The DC is increasing with higher amount of cationically polymerizing monomer in the hybrid compositions. In hybrid composition, PETA reached a higher DC where the ratio of radical:cationic monomers is 1:1 and 1:3 (Fig. 6) in contrast to the composition polymerizing only by free radical mechanism (51.8 %). Hybrid composition with higher amount of PETA (3:1 ratio) reached only a DC slightly lower than in the case of PETA. The higher DC of the radically polymerizing monomers (PETA) in hybrid samples could be explained by the presence of cationic monomers. Cationic polymerization is slower than the radical one and at simultaneous initiation of both types of polymerization the radical polymerization is finished earlier than the cationic. The presence of cationically polymerizing monomers decreases the viscosity of the sample during the radical polymerization thus letting the system reach a higher DC [8].

Figure 7 summarizes the DC values of DTEA oligomer in free radical and hybrid systems (H3 and H4). Here, no increasing nor decreasing trend of the DC influenced by the type or concentration of radically or cationically polymerizing binders (as it was in previous hybrid systems (H1 and H2)) was observed. The best results were achieved for hybrid polymerization of samples with 1:1 ratio of binders, where DC was higher than 98 %. For these types of samples, a higher DC was reached than in case of pure radical polymerization (DTEA, 88.6 %). The two remaining ratios of monomers show comparable or lower DC depending on the type of cationic monomer. From the point of view of the reached DC of the DTEA dendritic oligomer, a better solution is to use a cationic monomer EPOX than DOX.

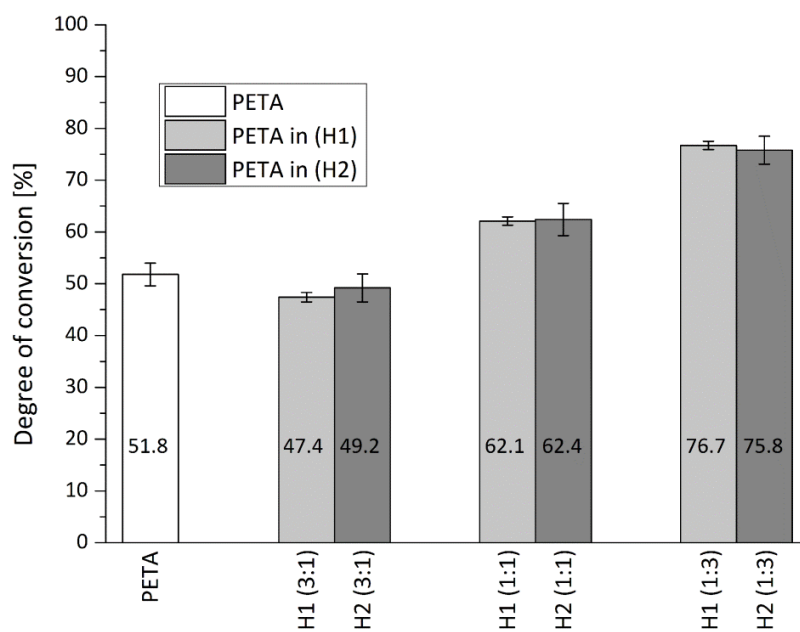


Figure 6: Degree of conversion of PETA in free radical and hybrid polymerizing systems (H1 and H2) evaluated 24 hours after irradiation.

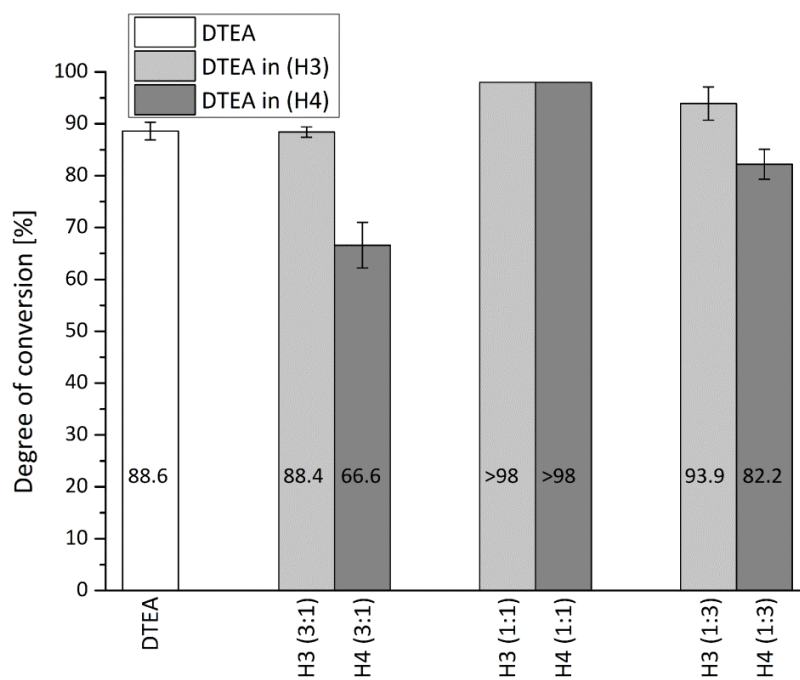
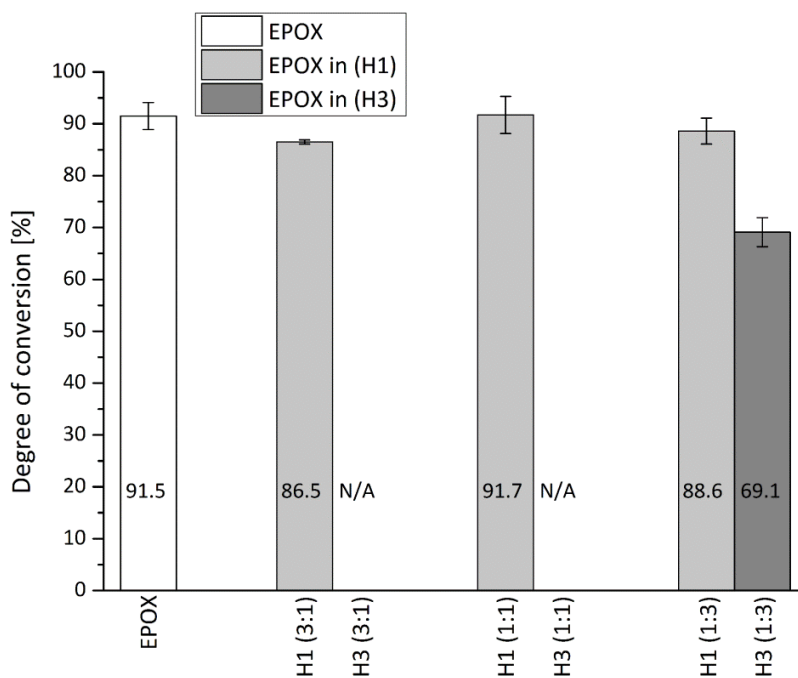


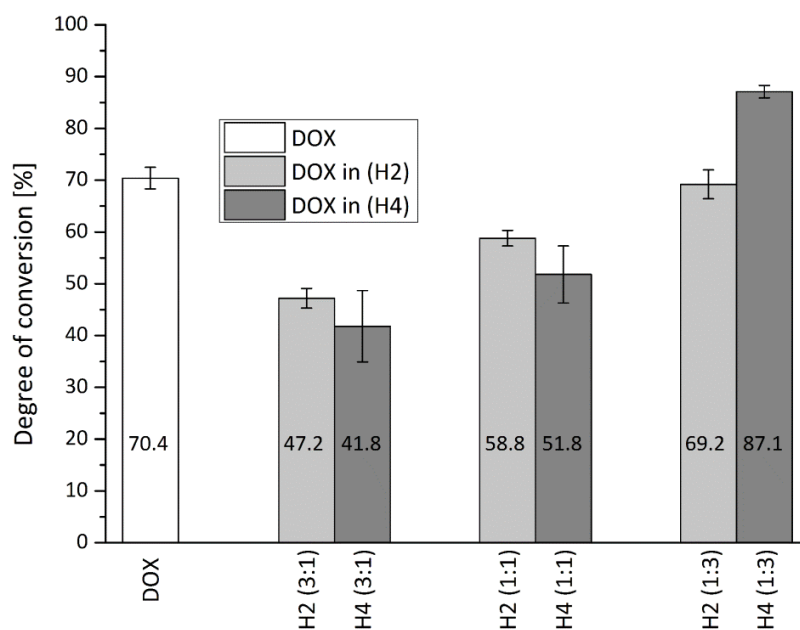
Figure 7: Degree of conversion of DTEA in free radical and hybrid systems (H3 and H4) evaluated 24 hours after irradiation.

Figure 8 depicts the DC of EPOX monomer in cationic and hybrid compositions (H1 and H3). In H1 hybrid composition (mixture of PETA with EPOX), EPOX reached in all samples (1:1, 1:3 and 3:1) very similar or slightly lower DC than in cationic EPOX composition. In H3 hybrid composition (mixture of DTEA with EPOX) with higher amount of epoxide (sample 3:1), EPOX reached a lower DC (about 22 % decrease) when compared with pure cationic polymerization. When H3 composition contains higher amount of DTEA (DTEA:EPOX 1:1 or 3:1), the DC could not be estimated due to very strong overlap of IR active absorption bands of acrylate double bonds with epoxy group.



**Figure 8: Degree of conversion of EPOX in cationic and hybrid compositions (H1 and H3) evaluated 24 hours after irradiation.**

Finally, Fig. 9 shows the DC of DOX monomer in cationic and hybrid samples (H2 and H4). The DC of DOX in both hybrid samples is increasing with higher amount of DOX (3:1 < 1:1 < 1:3) but in comparison with pure cationic polymerization of sample DOX, DOX in hybrid samples (except H2 and H4, 1:3 ratio) reached clearly lower DC.



**Figure 9: Degree of conversion of DOX in cationic and hybrid samples (H2 and H4) evaluated 24 hours after irradiation.**

### 4.3 Mechanical properties

The results of all performed mechanical tests (bend test, falling weight test, cupping test and pendulum hardness, and overall mechanical resistance) are summarized in Table 2.

The best flexibility and resistance to cracking/peeling reached coating containing DTEA oligomer prepared via hybrid polymerization. The bend test showed that coatings containing DTEA are resistant to cracking/peeling even if the smallest mandrel (4 mm) was used (Table 2). Contrary, bend test of samples containing PETA monomer resulted in a peeling of the coating already when the largest mandrel (30 mm) was used.

The falling weight test showed that coatings containing DTEA, except for sample H3 (1:3), exhibit much greater flexibility and resistance to cracking/peeling (Table 2). Sample H3 (1:3) reached lower values, which could be caused by higher content of EPOX monomer. Samples H1 and H2 reached generally low values of resistance to cracking and elasticity. Hybrid samples containing PETA monomer achieved slightly better performance with the DOX monomer when compared with EPOX one.

Cupping test revealed that the best resistance to cracking and elasticity have samples with DTEA (Table 2). Combinations with EPOX achieved higher flexibility/adhesion in comparison with DOX. Finally, hybrid samples containing PETA exhibit very low adhesion/flexibility, which is higher only for coatings with higher content of cationically polymerizing monomer (1:3).

With the pendulum hardness tests, it was not possible to measure sample PETA and EPOX (both on glass substrate). This is due to a slightly tacky surface of PETA coating. EPOX layer became wrinkly during the polymerization process which is also limiting for the used hardness testing procedure.

**Table 2: Mechanical properties of fabricated polymer layers: bend test (minimal diameter of mandrel leaving the coating without damage), falling weight test (maximal height of fall causing no damage to the coating), cupping test (maximal depth of penetration in the cupping test), relative hardness evaluated by pendulum hardness (Persoz), and overall mechanical resistance (OMR) [%]. \* denotes that overall mechanical resistance was estimated based on 3 methods only (bend test, falling weight test, cupping test).**

Sample	Diameter of the mandrel [mm]	Height of falling balls [cm]	Penetration depth [mm]	Relative hardness [%]	OMR [%]	
PETA	30	10	1	–	7*	
DTEA	4	>100	7	100	93	
EPOX	30	55	5	–	35*	
DOX	30	80	3	82	48	
H1	(3:1)	30	15	1	89	29
	(1:1)	30	<5	1	90	26
	(1:3)	30	<5	3	78	28
H2	(3:1)	30	20	1	65	24
	(1:1)	30	15	1	64	22
	(1:3)	30	30	3	60	30
H3	(3:1)	4	>100	6	32	73
	(1:1)	4	>100	10	65	91
	(1:3)	4	35	10	78	78
H4	(3:1)	4	>100	9	33	81
	(1:1)	4	>100	9	37	82
	(1:3)	4	>100	7	33	76

Sole DTEA binder showed a very high hardness similar to the hardness of the glass standard. In contrast, the hybrid samples (H3 and H4) have a low hardness (about 33 %), except for H3 (1:3) and H3 (1:1) coatings which reached 78 and 65 % of relative hardness, respectively. Higher hardness can be thus achieved in hybrid samples where PETA and EPOX are combined; here, larger amount of EPOX leads to hardness decrease. When PETA is combined with DOX (H2 coating), similar relative hardness (60–65 %) was found. The coatings containing EPOX and PETA showed the highest hardness among samples polymerizing by hybrid mechanism. Lower hardness (greater elasticity) was obtained in sample containing higher ratio of cationically polymerizing binder (1:3). The highest hardness (90.4 %) was achieved with hybrid sample H1 (1:1). Hybrid samples containing monomer PETA are more brittle and have lower adhesion than samples based on DTEA.

Overall mechanical resistance revealed that the samples containing dendritic oligomer DTEA show markedly better mechanical properties than samples based on PETA binder. Sample H3 (1:1) appears to be the best of the prepared samples with score of 91 %.

## 5. Conclusions

To summarize, the hybrid mechanism of polymerization (free radical and cationic polymerization) and evaluation of mechanical properties of prepared layers was studied in this work. Measurements of degree of conversion of samples polymerizing via hybrid mechanism proved importance of optimization of sample composition. Various ratios of monomers in hybrid samples influence final degree of conversion and the differences between studied samples were found to

be significant. Consequently, other polymer layers' characteristics such as polymer density, mechanical properties, migration of unreacted substances, etc. are influenced. In the scope of the reached degree of conversion of individual components, best compositions seem to be H1 (1:1 and 1:3), H2 (1:3) and H4 (1:3) in which the degree of conversion of one component was markedly higher ~10–25 % (and the other one was comparable) than if using solely polymerizing monomers.

Measurements of mechanical properties showed that the samples containing the hybrid DTEA binder had a markedly better adhesion and flexibility of the cured film (independently on the used cationic monomer). Hybrid samples containing PETA showed higher hardness/brittleness and the adhesion was significantly lower than in case of hybrid samples with DTEA.

The best mechanical properties (adhesion/flexibility) were achieved in hybrid samples H3 (1:1) and H4 (3:1 and 1:1). These samples exhibit very good adhesion and flexibility of the cured film where sample H3 (DTEA with EPOX) has a higher relative hardness (65 %) than sample H4 (DTEA with DOX).

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