ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 17, No. 4. 2011

Properties of UV-Curable Hyperbranched Urethane-Acrylate Modified Acrylic Monomer Coatings

Asta MILINAVIČIŪTĖ [1 *], **Virginija JANKAUSKAITĖ** [1], **Pranas NARMONTAS** [2]

[1] *Faculty of Design and Technologies, Kaunas University of Technology, Studentu str. 56, LT-51424 Kaunas, Lithuania*
[2] *Institute of Materials Science, Kaunas University of Technology, Savanoriu av. 271, LT-50131 Kaunas, Lithuania*

crossref http://dx.doi.org/10.5755/j01.ms.17.4.772

Received 30 July 2011; accepted 10 October 2011

In this work it is suggested to modify trimethylolpropane ethoxylate triacrylate (TMPETA) with solvent born difunctional urethane acrylate oligomer (UA) of hyperbranched structure and high molecular weight. In this case the photopolymer composition initial UV-precuring was replaced by thermal action. Under heating at 70 °C temperature solvent (butyl acetate) evaporates and layer with proper deformation properties for microrelief embossing was obtained. After microrelief embossing UV-curing of photopolymer follows and photoinitiator initiated radical photopolymerization of TMPETA monomer and UA oligomer proceeds. The goal of this work – to investigate the influence of the acrylic composition on the UV-cured coating mechanical properties and on the geometrical parameters and optical properties of replicated microrelief. It was defined that coatings with UA oligomer possess higher deformation and mechanical properties due to the increase in layer flexibility. The replicated microrelief of geometrical parameters and diffraction efficiency close to those of master matrix to be used was obtained using compositions containing 30 wt.% – 40 wt.% of UA.

Keywords: UV-curing, polyfunctional acrylic monomer, urethane acrylate oligomer, mechanical properties, scratch test, optical properties.

1. INTRODUCTION

Simple preparation, self developing capability, response for visible light, high diffraction efficiency, energetic sensitivity and dry processing are significant advantages of photochemical curable photopolymers making them suitable for scientific, research and industrial purposes. Formed in photopolymer diffraction gratings with controllable geometry attract great interest and are used for manufacture of optical data storage, humidity and temperature sensors, fine measurement systems, transparent screens, solar cells, holograms, 3D display systems, flexographic plates, high sensitivity humidity and temperature sensors, microoptical structures, optical document security devices, new generation functional organic elements, high density data storage, information processing devices [1].

The main components of UV curable photopolymer compositions are monomers and (or) oligomers, and initiator. Majority of commercially used UV curable compositions are based on acrylic functional monomers and oligomers [2]. Such compositions perhaps are the most popular radically polymerizing systems with good response for optical applications and allow replicating a microrelief with controllable geometry.

Polyfunctional acrylics are relevant monomeric compounds for the polymer network, since it has polyvinyl bonds at the end to be formed a dense network structures [3]. However, such UV curable coatings have high hardness, shrinkage and often poor adhesion due to the low surface free energy of polymer substrates as compared to solvent based compositions. Such properties can be improved using oligomeric compounds such as hyperbranched urethane acrylates (UA). UA exhibit very high cure rates and lower shrinkage upon curing than conventional acrylates. These polymers are characterized by highly branched, tree-like structure and large number of end-groups which can be chemically modified. Their physical and chemical properties are to a large extent dependent on number and nature of the end-groups. Those materials are available with molecular weights ranging from 600 g/mol to 6000 g/mol and with functionalities ranging from 2 to 6. They provide good combination of toughness and elasticity and depending on molecular weight, functionality and chemical structure other valuable properties (high mechanical properties, chemical resistance, scratch resistance, small amounts of residual unsaturation, low amounts of extractables and low shrinkage) characteristic to polyurethane cured films [4]. On the other hand, they have rather high viscosities, especially those to the requirements for UV curing applications where highly reactive compositions allowing a high speed of processing are desirable. Their physical and chemical properties are to a large extent dependent on number and nature of their end-groups, which can be chemically modified [2]. UV-cured acrylates are known for their high reactivity and not high amount of photoinitiator, which generates reactive species upon UV exposure and initiates radical-type polymerization [5] (Fig. 1).

In previous works [6] the possibility of the periodical structures replication by direct contact embossing in large area of photopolymer layer was investigated. For this purpose method that composes of several steps was proposed. At first, coating of thin photopolymer layer was UV-precured and after microrelief was transferred using

---

[*] Corresponding author. Tel.: +370-37-300207; fax.: +370-37-353989.
E-mail address: *asta.milinaviciute@ktu.lt* (A. Milinavičiūtė)

nickel master matrix. Then geometry of the embossed structures was fixed during final UV curing of the photopolymer. The trifunctional acrylic monomer – trimethylolpropane ethoxylate triacrylate was used for the microrelief formation. This acrylate has three vinyl bonds at the end that induces a high degree of cross-linking and results low flexibility and brittleness in films due to dense network structure creation [7].

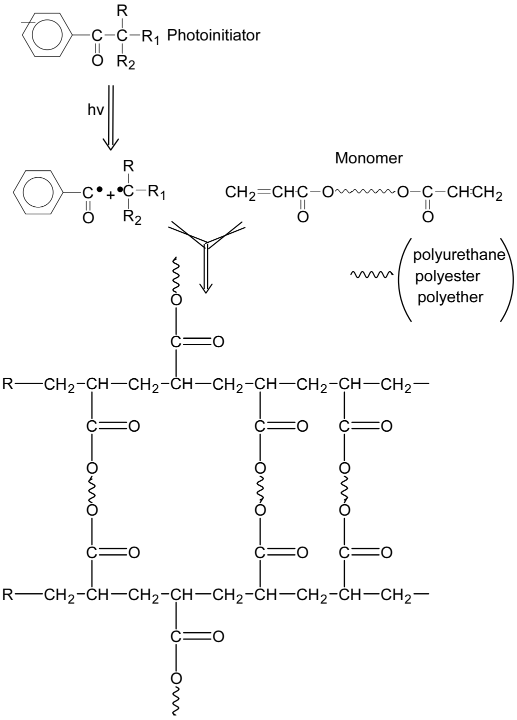


Fig. 1. UV-induced radical polymerization of a diacrylate monomer leading to a photo crosslinked polyacrylate network

In this study the possibility obtaining mechanical properties and flexibility of photopolymer coating preferable for microrelief replication has been investigated. For this purpose trifunctional acrylic monomer was composed with hyperbranched urethane acrylate and mechanical, optical properties and geometry of hardened layer and embossed microstructure were studied.

2. EXPERIMENTAL

2.1. Materials and their mixture

Different formulations of the UV-curable coating consisting from urethane acrylic oligomer, monomer and photoinitiator were prepared. As monomer trimethylolpropane ethoxylate (14/3 EO/OH) triacrylate (TMPETA) polyfunctional monomer (Aldrich, Germany) was used, while for the initiation of radical photopolymerization reactions 2.2-dimethoxy-2-phenylacethophenone (DMPA) (Ciba, Switzerland) photoinitiator was applied. Their chemical structures and main properties are presented in [6]. For modification of monomeric composition commercially available solvent borne urethane acrylate (UA) "Ebecryl 8200" (Cytec, Germany), which is tack free after evaporation of the solvent, was applied. Its chemical structure is shown in Fig. 2 and properties of 50 % solution in butyl acetate are listed in Table 1. Cured Ebecryl 8200 is characterized by high flexibility.

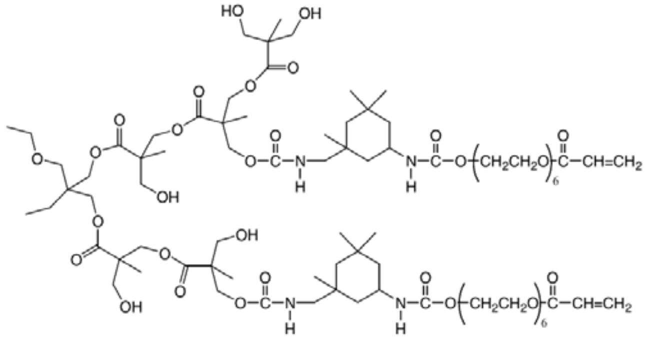


Fig. 2. Chemical structure of the difuntional urethane acrylate oligomer

Table 1. The main properties of EBECRYL 8200 solution in butyl acetate (concentration of 50 %)

Property	Value
Molecular weight M_n , g/mol	8000
Dynamic viscosity η, mPa·s (at 25 °C)	1200 ±200
Density ρ, g/ml (at 25 °C)	1.11
Refraction index, n	1.585
Flash point T, °C	> 93

In each chemicals formulation were mixed in round-bottom flask by mechanical stirring (100 min^{-1}) in the dark. At first, the photoinitiator (5 wt. %) was mixed with TMPETA monomer until the homogenous solution was obtained at 1 hour mixing duration. After that the definite content of UA was added (10 wt. % – 70 wt. %) and blend was further stirred at the same rate at ambient temperature for 1 hour.

2.2. Coating and microrelief formation

The photopolymer layer was formed on the surface of oxygen plasma treated polyethylene terephthalate (PET) film. The treatment parameters are presented in [6]. The deposition of photopolymer layer of 5 μm in thickness was performed by anilox rolls [6]. After layer coating it was heated for 50 s at 70 °C temperature in order to evaporate butyl acetate. After evaporation of low molecular weight solvent, the distance between molecules of acrylic components become close significantly restricting molecules mobility [8]. Therefore, the layer with proper deformation properties for microrelief embossing is obtained. Thereafter, the relief features of microstructured nickel master matrix (period 4 μm, depth 1.0 μm) were transferred to the surface of the photopolymer coating by direct contact embossing at ambient temperature, embossing pressure of $p = (0.5 \pm 0.02)$ MPa and embossing duration of $\tau = 3$ s. After the embossing of microrelief UV-curing of photopolymer was applied. The UV curing was performed for duration of 20 s with irradiation intensity of $I = (35 \pm 5)$ W/m^2 and temperature of 20 °C at the surface of the specimen. The distance of 10 cm from UV source ($\lambda = 436$ nm) was used.

Schematic diagram of UV-curing process of reactive acrylic monomer and solvent based UA oligomer composition used for investigations is presented in Fig. 3.

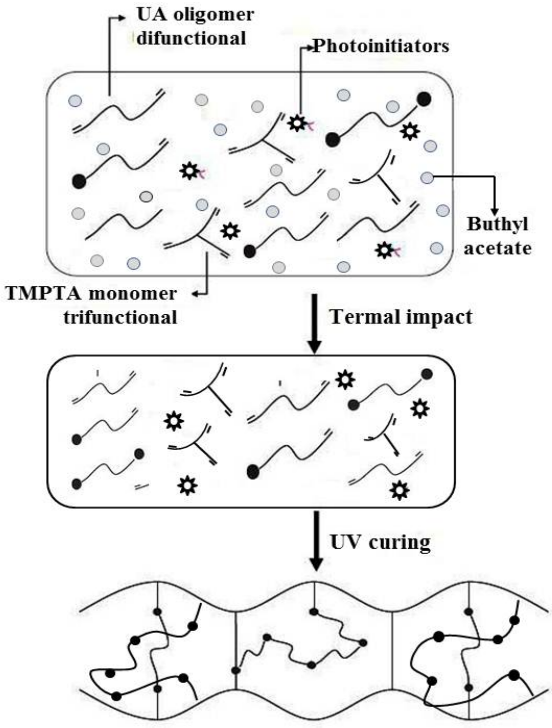


Fig. 3. Mechanism of UV induced radical polymerization of photopolymer composition coating

After UV exposure photoinitiator generates reactive species which initiate radical polymerization of TMPETA monomer and UA oligomer. The chemical interaction between TMPETA and UA is possible, also.

2.3. Testing methods

In order to evaluate mechanical properties of UV-cured coating constant load scratch tests was performed using an original KTU MMI (Lithuania) Micro-Scratch Tester with diamond indenter moving linearly along the sample (normal force $P_n = 100$ mN, constant speed 10 mm/min, lateral sample movement, scratch length 10 mm). After the performance of scratch test geometrical parameters of obtained groove were measured. Thereafter, the scratch resistance was evaluated using equation [9]:

$$R_s = x \cdot \frac{4L}{\pi b^2}, \tag{1}$$

where R_s is the scratch resistance; L is the normal force; b is the scratch width; x is the coefficient dependent upon material deformation properties ($1 < x < 2$).

The surface topography of formed coating was studied from images obtained by emission scanning electron microscope (SEM) JEOL JSM-IC25S (resolution 15 nm, acceleration voltage 25 KV, operating voltage 115 V).

The changes in surface topography of photopolymer coatings were investigated by surface roughness tester TR200 with a diamond tip of 5 μm radius. Surface roughness was evaluated by commonly used surface roughness statistical parameters: arithmetic mean roughness R_a (nm), root-mean-square roughness R_q (nm) and mean profile height H_{mean} (nm).

The geometry of replicated periodical structure was investigated using an atomic force microscope (AFM) NANOTOP-206 with a silicon cantilever operating in contact mode (cantilever force constant 3 N/m). Surface roughness was evaluated by R_a, R_q and H_{mean} statistical parameters. For the investigation of replicated periodical structure geometry an image processing and analysis of AFM data were performed using standard software “Surface View” version 2.0.

Optical properties and geometry variation of replicated periodical structure from those of master matrix were evaluated by computer simulations. In order to calculate relative diffraction efficiency (DE) of sinetrapezoidal periodical structure embossed on the surfaces of composition coating the standard software (“PCGrate”) was employed. The simulations were performed following all the experimental details, including incidence angles and wavelength ($\lambda = 632.8$ nm) of laser beam.

3. RESULTS AND DISCUSSION

3.1. The properties of photopolymer thin layer

The roughness of composition coating before relief formation impacts its optical, frictional and mechanical properties. Therefore, it may be supposed that surface topography of thermally hardened composition layer influence the microrelief embossing process. The changes of surface roughness statistical parameters upon TMPETA/UA composition are shown in Fig. 4.

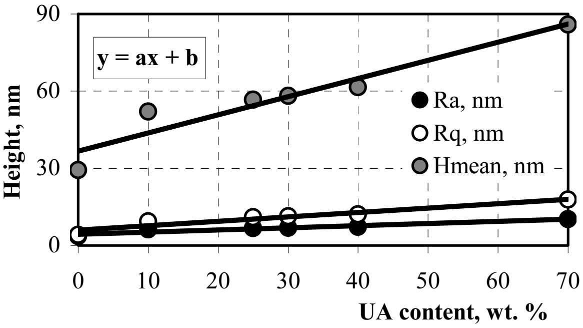
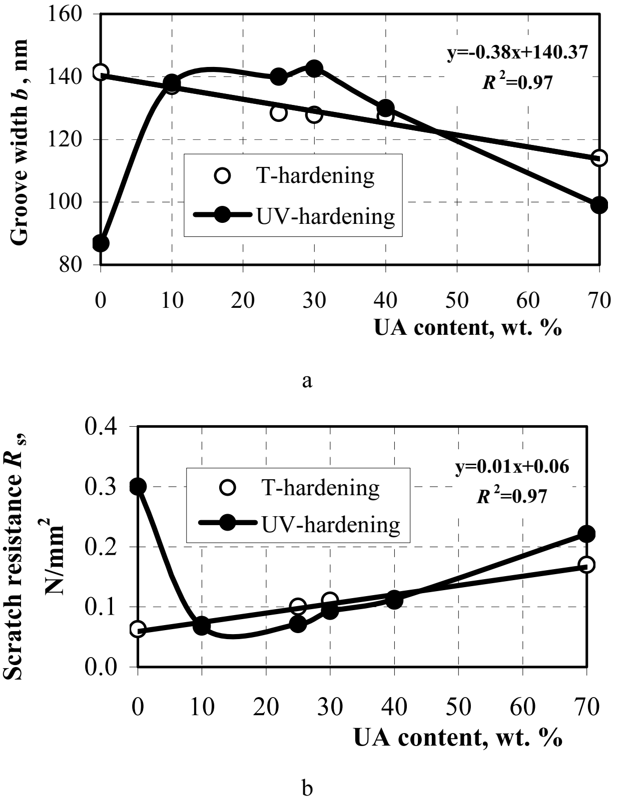


Fig. 4. The influence of UA content on the surface roughness statistical parameters of thermally hardened photopolymer coating

The increase in surface roughness with increasing amount of oligomeric compound was found. Almost 3 times higher mean height of profile H_{mean} was obtained in the case of 70 wt. % of UA in TMPETA/UA composition as compared to that of pure TMPETA coating. Generally, R_a and R_q will be similar, if there are no large deviations from the mean surface level. It can be seen that increasing UA content influences larger deviations from H_{mean}. The maximal irregularities comprise 9 % of overall master matrix depth and are characteristic to the surface with highest UA content. The relations between statistical parameters of surface roughness and UA content were obtained to be coincident and varied according to linear dependence.

The variation of coating topography can be referred to the differences of material chemical structure and molecular weight that has significant influence on the viscosity of acrylates [4]. Significantly higher molecular weight and viscosity (see Table 1) are characteristic to UA as compared to that of TMPETA (912 g/mol and 60 mPa·s, respectively). Therefore, the increase of UA content enhances molecular weight and viscosity of TMPETA/UA composition. Consequently, those have influence on the changes in surface tension of the interfaces and impair compositions ability to wet PET substrate, which affects surface roughness of the coating [10].

It is known, that surface roughness have influence on mechanical properties of polymeric coatings [11]. Those properties are dependent upon material structure and have significant influence on microrelief embossing process. Thus, they had been investigated in dependence on UA content and hardening stage using scratch test (Fig. 5).



a

b

Fig. 5. The influence of UA content in TMPETA/UA composition and hardening stage on the width of scratched groove (a) and scratch resistance (b)

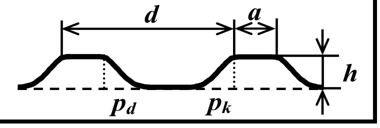
The evaluation of scratched groove width after thermal hardening reveals linear dependence of parameter value on UA content (Fig. 5, a). Small amount (10 wt. %) of UA decreases width by 3 % and 20 % lower parameter value was obtained in the case of TMPETA/UA modification of 70 wt. % of oligomeric compound as compared to pure TMPETA. While the performance of UV hardening reveals quite different character of UA content influence on the groove width. Significant increase in the parameter value (59 % – 60 %) is characteristic to the grooves scratched on the surface of UA (10 wt. % – 30 wt. %) modified TMPETA/UA coating than that of pure TMPETA. Though, the increase of 14 % is found in the case of 70 wt. % of UA content. According to scratched groove width the influence of UA content on the scratch resistance of thermally hardened TMPETA/UA coating was calculated using Eq. (1). The results are presented in Fig. 5, b. It is evident that linear dependence upon UA content is characteristic to the scratch resistance of the coating. It is obtained that the addition of 10 wt. % of oligomeric UA compound improves scratch resistance of pure TMPETA coating by 8 %. Further addition of UA (up to 70 wt. %) steadily increases the parameter values up to 54 %. Though, negligible plateau in the cases of 30 wt. % and 40 wt. % can be observed and scratch resistances are obtained to be 31 % higher than that of unmodified TMPETA layer. It is known that the presence of solvent in TMPETA/UA decreases coating glass transition temperature, thereby, influencing scratch resistance and other mechanical properties [12]. Therefore, the improvement of thermally hardened TMPETA/UA layer resistance to induced scratching is defined due to solvent evaporation and increasing amount of solid UA content in composition.

Mechanical properties and flexibility of the coating plays a key role in microrelief replication process. Those can be achieved and adjusted by thermal hardening of TMPETA/UA composition coating with the effective content of UA oligomer. And application areas of replicated microrelief are dependent upon the properties of UV cured photopolymer layer which are dependent upon UA content, also. Significantly (more than 4 times) lower scratch resistance is characteristic to the coating of 10 wt. % of UA oligomer as compared to that of pure TMPETA coating. In general, the TMPETA/UA layer properties may be attributed to the differences in cross-linking density of composition due to oligomeric compound addition of high molecular mass [13]. Though, further increase in scratch resistance of TMPETA/UA composition coating is observed with the increasing UA content (up to 70 wt. %) due to improvement in flexibility of UV cured coating.

3.2. The properties of replicated microrelief

The influence of UA content on the quality of periodical structure embossed on thermally hardened TMPETA/UA coating can be determined according to the coincidence of its geometry and optical properties to those of master matrix. Geometrical parameters and profiles of embossed microrelief in dependence on UA amount obtained by AFM investigations are presented in Table 2 and Fig. 6, respectively.

Table 2. The influence of UA content on the geometrical parameters of replicated microrelief

UA content in composition, wt. %	Period d, μm	Depth h, μm	Ridge width a, μm	Side width p, μm	
				p_k	p_d
10	4.0	0.9	1.5	1.1	1.0
25	4.0	0.9	1.5	1.0	0.9
30	4.0	0.9	1.6	1.0	0.9
40	4.0	0.9	1.6	1.0	0.8
70	4.1	1.0	1.7	0.8	0.7
Ni matrix	4.0	1.0	1.6	1.0	0.8
Sinetrapezoidal geometry of microrelief profile					

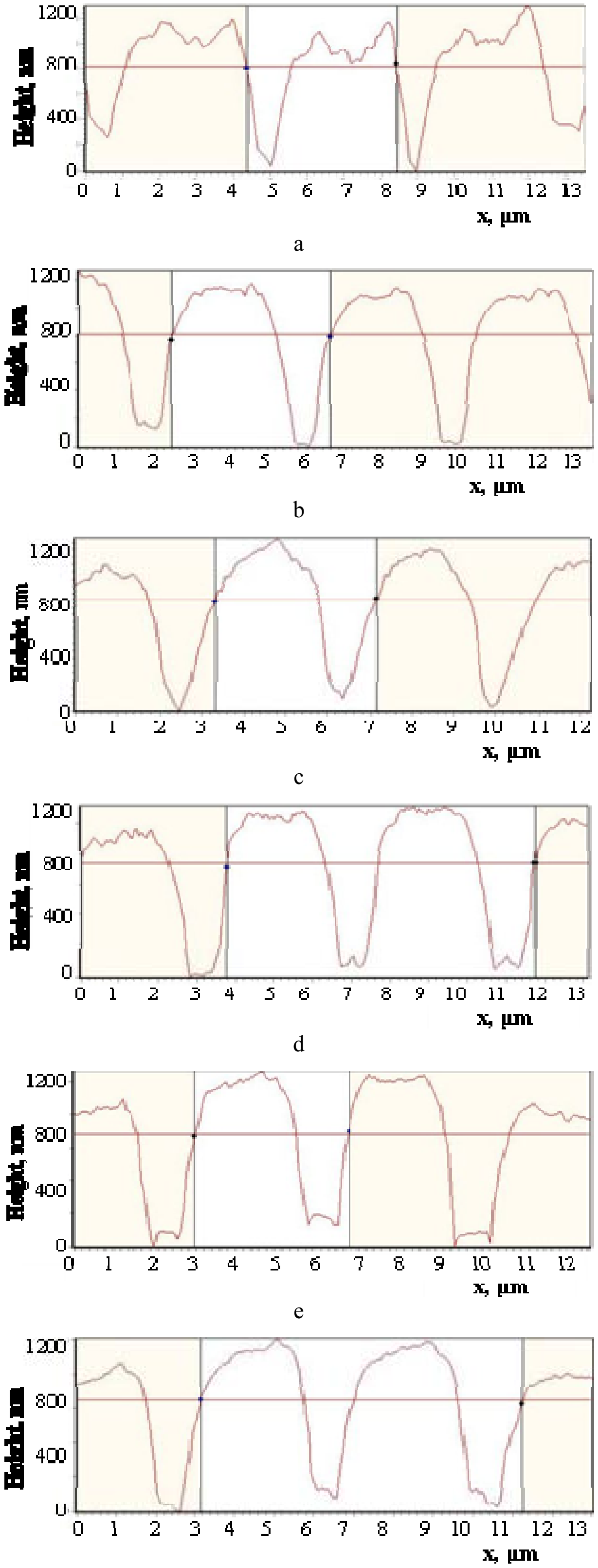


Fig. 6 AFM profiles of replicated periodical structures *vs* UA content in TMPETA composition, wt. %: a – 10; b – 25; c – 30; d – 40; e – 70; f – master matrix

The ripples on elevated regions of the photopolymer and bowings at the bottom have influence on the increase in replication height. The reason for those may be contamination during the separation of the matrix [14]. While geometrical shapes of periodical structures embossed on the coatings of 10 wt. % and 70 wt. % of UA, were particularly varied from that of master matrix. In the cases the highest ripples or bowings were attained and the variations of microrelief depths up to 20 % were obtained. In the cases of 30 wt. % and 40 wt. % of UA negligible ripples and small bowings may be caused by the contact of flowing photopolymer with irregularities on the edges of master matrix pattern during embossing process [14]. However, overall geometrical shapes of those periodical structures are rather good due to relative coincidence to that of master matrix. Therefore, the highest match of replication geometry and profile is characteristic to periodical structure embossed on the surface of TMPETA/UA coatings of 30 wt. % – 40 wt. % UA content. It can be referred to the effective monomeric and oligomeric compound ratio that has influence on deformation behavior of photopolymer, surface roughness and mechanical properties of obtained coating.

It is know that geometry of embossed microstructure, refraction index of material and wavelength of laser have influence on the light intensity distribution and determine optical properties of periodical structure [15, 16]. Therefore, DE distribution of replication was measured versus UA content. The results are presented in Fig. 7, a. The highest coincidence of DE distributions was obtained in the cases of periodical structures embossed on 30 wt. % – 40 wt. % of UA content compositions coatings. It can be referred to the effective combination of mechanical properties and flexibility. It is obvious that correspondence of DE distribution of replication to that of master matrix determine the effectiveness of microrelief geometry transference to photopolymer coating. The changes in DE distribution obtained for other amounts of UA can be referred to variation of geometrical parameters which produce diffraction maximas at different angular distributions [16, 17].

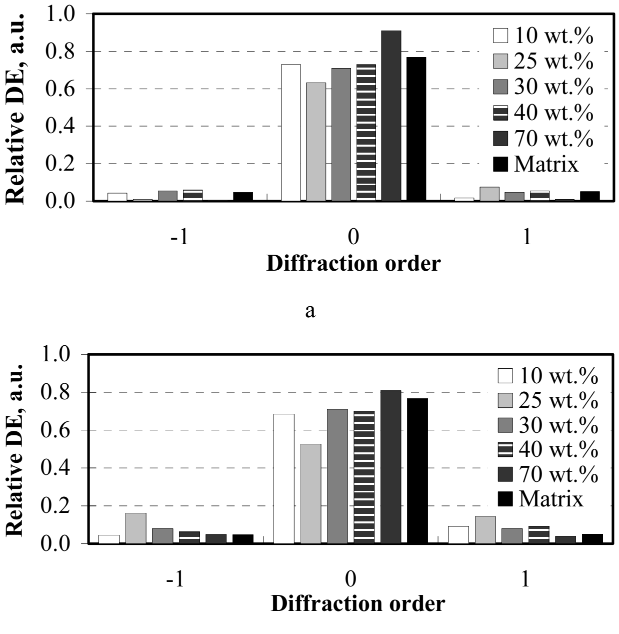


Fig. 7. Measured (a) and theoretical (b) DE distributions of replicated periodical structure vs. UA content in TMPTA/UA composition

The main experimental results were compared with computer simulations where the standard software ("PCGrate") was employed to calculate DE distribution of periodical structure. For the calculations geometrical parameters presented in Table 2 were used (Fig. 7, b). The results obtained using different computer simulated and experimental methods show relative correspondence for obtained DE values [16]. Though, in the cases of 25 wt. % and 70 wt. % of UA contents the experimental DE values are 16 % and 11 % higher than simulated ones, respectively. It is attributed to highest distortion in geometries of replicated periodical structures.

It is obvious that DE distributions show highest correspondence of replication geometry to that of master matrix in the cases of 30 wt. % and 40 wt. % of UA amounts in TMPETA/UA. Therefore, the results confirm the influence of UA content on variation in geometrical parameters resulting change in optical properties of replicated periodical structures.

4. CONCLUSIONS

Bi-component photopolymer layer was proposed for microrelief replication. Trimethylolpropane ethoxylate triacrylate polyfunctional monomer (TMPETA) and solvent borne urethane acrylate difunctional oligomer (UA) in butylacetate (50 %) were selected for the composition with increasing UA content. UA amount in TMPETA/UA composition determines topography, deformation and mechanical properties of the coating which ratio has significant influence on the quality of replicated periodical structure. Increasing content of oligomeric compound 10 wt. % – 70 wt. % has influence on the increase in surface roughness, improvement of flexibility and scratch resistance of TMPETA/UA composition coating. Both, thermal hardening and UV curing have influence on mechanical properties of obtained coating, also. Increasing amount of UA increases flexibility and improves scratch resistance of hardened TMPETA/UA composition coating.

Thermally hardened TMPETA/UA coating of effective composition (30 wt. % – 40 wt. % of UA content) reflects the favorable setting of mechanical properties and flexibility. Periodical structures embossed on the surface of those coatings reveal the highest coincidence of geometry and optical properties to those of master matrix indicating on the highest quality of replication. Therefore, the compositions of TMPETA/UA 70/30 wt. % – 60/40 wt. % were found to be efficient for microrelief transference by contact embossing of microstructured nickel master matrix.

REFERENCES

1. **Sanchez, C., *et al.*** Photoembossing of Periodic Relief Structures Using Polymerization-Induced Diffusion: a Combinatorial Study *Advanced Materials* 17 (21) 2006: pp. 2567 – 2571.
2. **Dzunuzovic, E., Tasic, S., Bozic, B., Dunjic, B., Jeremic, K.** Photoreactive Hyperbranched Urethane Acrylates Modified with a Branched Saturated Fatty Acid *Reactive & Functional Polymers* 66 2006: pp. 1097 – 1105. http://dx.doi.org/10.1016/j.reactfunctpolym.2006.01.016
3. **Jedrzejewska, B., Tur, M., Paczkowski, J.** Styrylbenzimidazolium Dye-Borate Complex as an Effective, Singlet State Photoinitiator in an Argon Laser-Induced TMPETA Photopolymerization *Journal of Photochemistry and Photobiology A: Chemistry* 209 2010: pp. 32 – 40. http://dx.doi.org/10.1016/j.jphotochem.2009.10.005
4. **Tasic, S., Bozic, B., Dunjic, B.** Synthesis of New Hyperbranched Urethane-Acrylates and Their Evaluation in UV-Curable Coatings *Progress in Organic Coatings* 51 2004: pp. 321 – 328. http://dx.doi.org/10.1016/j.porgcoat.2004.07.021
5. **Studer, K., Decker, C., Beck, B., Schwalm, R.** Thermal and Photochemical Curing of Isocyanate and Acrylate Functionalized Oligomers *European Polymer Journal* 41 2005: pp. 157 – 167.
6. **Milinavičiūtė, A., Jankauskaitė, V., Fataraitė, E., Narmontas, P.** Selection of Photopolymer for Microrelief Formation by Two-Stage Cold Stamping Method *Materials Science* (*Medžiagotyra*) 16 (3) 2010: pp. 210 – 216.
7. **Andrzejewska, E.** Photopolymerization Kinetics of Multifunctional Monomers *Progress in Polymer Science* 26 2001: pp. 605 – 665.
8. **Holmes, R. G., *et. al.*** Effect of Solvent Type and Content on Monomer Conversion of a Model Resin System as a Thin Film *Dental Materials* 23 2007: pp. 1506 – 1512.
9. **Hadal, R. S., Misra, R. D. K.** Scratch Deformation Behavior of Thermoplastic Materials with Significant Differences in Ductility *Materials Science and Engineering A* 398 2005: pp. 252 – 261.
10. **Bao, F., Shi, W.** Synthesis and Properties of Hyperbranched Polyurethane Acrylate Used for UV Curing Coatings *Progress in Organic Coatings* 68 2010: pp. 334 – 339. http://dx.doi.org/10.1016/j.porgcoat.2010.03.002
11. **Zhao, J., *et. al.*** Effects of Molecular Weight, Solvent and Substrate on the Dewetting Morphology of Polystyrene Films *Applied Surface Science* 236 2004: pp. 131 – 140.
12. **Kiil, S.** Mathematical Modeling of Simultaneous Solvent Evaporation and Chemical Curing in Thermoset Coatings: A Parameter Study *Progress in Organic Coatings* 70 2011: pp. 192 – 198. http://dx.doi.org/10.1016/j.porgcoat.2010.08.013
13. **Choi, J. S., *et. al.*** Effect of Acrylic Acid on the Physical Properties of UV-Cured Poly(Uretane Acrylate-Co-Acrylic Acid) Flms for Metal Coating *Progress in Organic Coatings* 71 2011: pp. 110 – 116. http://dx.doi.org/10.1016/j.porgcoat.2011.01.005
14. **Grigaliūnas, V., Jucius, D., Tamulevičius, S., Guobienė, A., Kopustinskas, V.** Optically Variable Imaging Using Nanoimprint Technique *Applied Surface Science* 245 2005: pp. 234 – 239. http://dx.doi.org/10.1016/j.apsusc.2004.10.015
15. **Kiryanov, V. P., Nikitin, V. G., Verkhogliad, A. G.** Development and Research of the Scanning Method for Testing of Diffraction Optical Elements *Measurement Science Review* 1 (1) 2001: pp. 159 – 162.
16. **Tamulevičius, T., *et. al.*** Formation of Periodical Microstructures Using Interference Lithography *Experimental Techniques* 32 (4) 2008: pp. 23 – 28.
17. **Tamulevičius, T., Šeperys, R., Andrulevičius, M., Tamulevičius, S.** Laser Beam Shape Effect in Optical Control of the μ-Fluidic Channel Depth Employing Scatterometry *Optics and Lasers in Engineering* 48 2010: pp. 664 – 670. http://dx.doi.org/10.1016/j.optlaseng.2010.01.012