Modification of photosensitive resin with fumed silica

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Abstract: The effect of fumed silica (3 and 5 wt%) on the structure, viscosity, tensile and flexural properties, and hardness of photosensitive acrylic resins used for 3D printing was investigated. The optimal set of functional properties was obtained with a silica content of 3 wt%. In this case, the resin had the appropriate viscosity, degree of cross-linking, hardness (90 ShD), tensile strength (47 MPa) and flexural strength (96 MPa). The obtained results indicate that the addition of silica effectively reinforce the resin.

Keywords: photocuring, 3D printing, photosensitive resin, fumed silica.

Modyfikacja żywicy światłoczułej krzemionką płomieniową

Streszczenie: Zbadano wpływ krzemionki płomieniowej (3 i 5 % mas.) na strukturę, lepkość właściwości mechaniczne przy rozciąganiu i zginaniu oraz twardość światłoczułych żywic akrylowych stosowanych do druku 3D. Optymalny zespół właściwości użytkowych uzyskano przy zawartości krzemionki 3% mas. W tym przypadku żywica miała odpowiednią lepkość, stopień usieciowania, twardość (90 ShD), wytrzymałość na rozciąganie (47 MPa) i wytrzymałość na zginanie (96 MPa). Uzyskane wyniki wskazują, że dodatek krzemionki skutecznie wzmacnia żywicę.

Słowa kluczowe: fotoutwardzanie, druk 3D, żywica światłoczuła, krzemionka płomieniowa.

3D printing, also known as additive manufacturing, constructs complex object shapes by designing 3D digital models and accumulating materials layer by layer on the printer [1-6], and finally obtains physical samples. 3D printing technology has the characteristics of low cost, high precision, complexity and refinement [7], and is highly personalized. It plays an important and irreplaceable role in many fields such as electronics, printing, medical treatment, construction, communication, aviation, and automobile [1, 8]. Among them, light-curing 3D printing technology is a new manufacturing technology with high efficiency, environmental protection and energy saving [9], it is mainly through the irradiation of a specific light source to trigger the rapid cross-linking and polymerization of photosensitive resins into solid materials [10,11], and finally complete the printing of physical objects through layer-by-layer stacking [12].

As the most basic curing molding material in photocurable 3D printing [13], photosensitive resin is one of the main consumables for photocurable 3D printing. Photosensitive resin is a kind of polymer colloidal substance that changes its chemical structure when exposed to light [14]. The photochemical reaction of photosensitive resin in the curing process mainly includes two processes [15]: The first is the excitation process. Under the irradiation of ultraviolet light, the photoinitiator molecules absorb light energy and undergo photolysis reactions to generate active factors. Then the second process is carried out, that is, the active factor and the prepolymer undergo a cross-linking polymerization reaction to generate a solid substance, while the part not irradiated by ultraviolet light is still a soft segment.

However, there are few studies on photosensitive resins at present. Photosensitive resins have disadvantages such as low crosslink strength [16, 17] and large shrinkage, which seriously restricts the application of photocuring 3D printing technology in more fields. With the advancement of equipment and the maturity of technology, higher and more specific requirements are put forward for photosensitive resins. Not only photosensitive resins with high curing speed and low shrinkage rate are required, but also excellent mechanical properties and more functions.

Therefore, the aim of the work was to study the effect of fumed silica on the structure, rheological, tensile and flexural properties, impact strength and hardness of hybrid photosensitive acrylate resin system for 3D printing. SEM and FTIR were used to evaluate the structure of the composites.

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EXPERIMENTAL PART

Materials

The following raw materials were used in this work: fumed silica (CAS: 7631-86-9), which the D50 is 20 nm, were purchased from Tansail New Materials. Bisphenol A epoxy acrylate (CAS: 71281-65-7), urethane acrylate (CAS: 68987-79-1), acryloylmorpholine (ACMO, CAS: 5117-12-4), photoinitiator 1173 (2-hydroxy-2-methyl-phenyl-propane-1-one, CAS: 7473-98-5), photoinitiator 819 (phenyl bis(2,4,6-trimethylbenzoyl)phosphine oxide, CAS: 162881-26-7), ultraviolet absorber UV-531 (2-hydroxy-4-(octyloxy)benzophenone, CAS: 1843-05-6) were purchased from RYOJI.

Preparation of hybrid resin system and composites with fumed silica

Urethane acrylate, ACMO and photoinitiators (1173, 819) were successively added to the bisphenol A epoxy acrylate, and then the mixture was heated and stirred using HWCL-3 magnetic stirrer (GreatWall, China) until the initiator was completely dissolved (about 30 min). In the next step, fumed silica (3 or 5 wt.%) was added to the hybrid resin system and ball milled for 6 hours to obtain a homogeneous composite.

3D printing

Samples for mechanical tests were printed on an LCD printer (MASTER Pro 7K 3D, Shandong Industrial Ceramics Research and Design Institute, China). The printer light source used was 405 nm, and the single-layer printing time was 3.5 s. The printing layer thickness was 50 μm.

Methods of testing

Digital rotary viscometer (NDJ-5S/8S from Shenzhen Sanuo, China) was used to characterize the resin viscosity, and the S61 spindle was used at 20 rpm. The structure of the sample was analyzed using a field emission scanning electron microscope (Apreo form FEI) at 10 kV. Double bond conversion rate [18] was determined by Fourier Transform Infrared Spectrometer (FT-IR Thermo Nicolet Corporation, USA). Infrared spectrum of the resin was measured before and after the cured reaction. C=C group at a wavenumber 1638 cm^{-1} and C=O at 1730 cm^{-1} were analyzed. Tensile properties were determined according to GB/T 1040.2-2006. The test was carried out at room temperature and at a speed of 50 mm/min on a universal testing machine (C43.104 by New think, China). Type I specimens were used. Flexural properties were evaluated according to GB/T 9341-2008 by universal testing machine (C43.104 from New think, China). Hardness was measured according to GB/T 2411-2008 using a Shore hardness tester (LX-D of Weidu, China). An ultraviolet lamp with a wavelength of 405 nm (UVHX RUNLED, China) was used to irradiate the photosensitive resin.

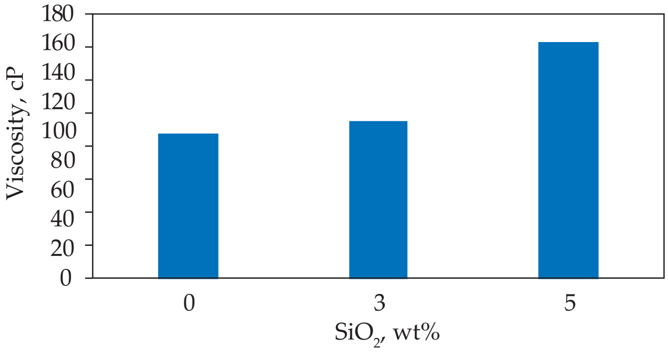

Fig. 1. Effect of SiO_2 content on the resin viscosity

RESULTS AND DISCUSSION

Viscosity

As can be seen in Figure 1, the viscosity of the tested samples increases from 98 to 161 cP as a function of fumed silica (SiO_2) content. It is known that the lower the viscosity of the resin, the shorter its flow time [19, 20], which results in fewer defects of the 3D printing [21]. From this point of view, the optimal silica content is 3 wt%.

SEM

The morphology of composites was observed by SEM, as illustrated in Figure 2. The silica is homogeneously dispersed in the resin matrix. However, there are agglomerates and clusters. The addition of silica can effectively increase interfacial interactions, resulting in higher fracture toughness and better mechanical properties [22].

Double bond conversion rate

Figure 3 compares the infrared spectra of the resin before and after curing and calculates the double bond conversion factor (DC%) of the resin by calculating the peak area of the C=C aliphatic group at 1638 cm^{-1} and the C=O group at 1730 cm^{-1}. The effect of silica on the conversion rate of double bonds during resin curing was also compared and the data are presented in Table 1. After curing, the double bond conversion rate for the resin without filler was 41.5% and gradually decreased as a function of the filler content, reaching 38.6% with a filler content of 5 wt%. The addition of silica limits the cross-linking process of the resin. The higher the silica content, the bigger the effect.

Mechanical properties

It is well known that silica nanoparticles considerably enhance mechanical properties of polymers. Tensile

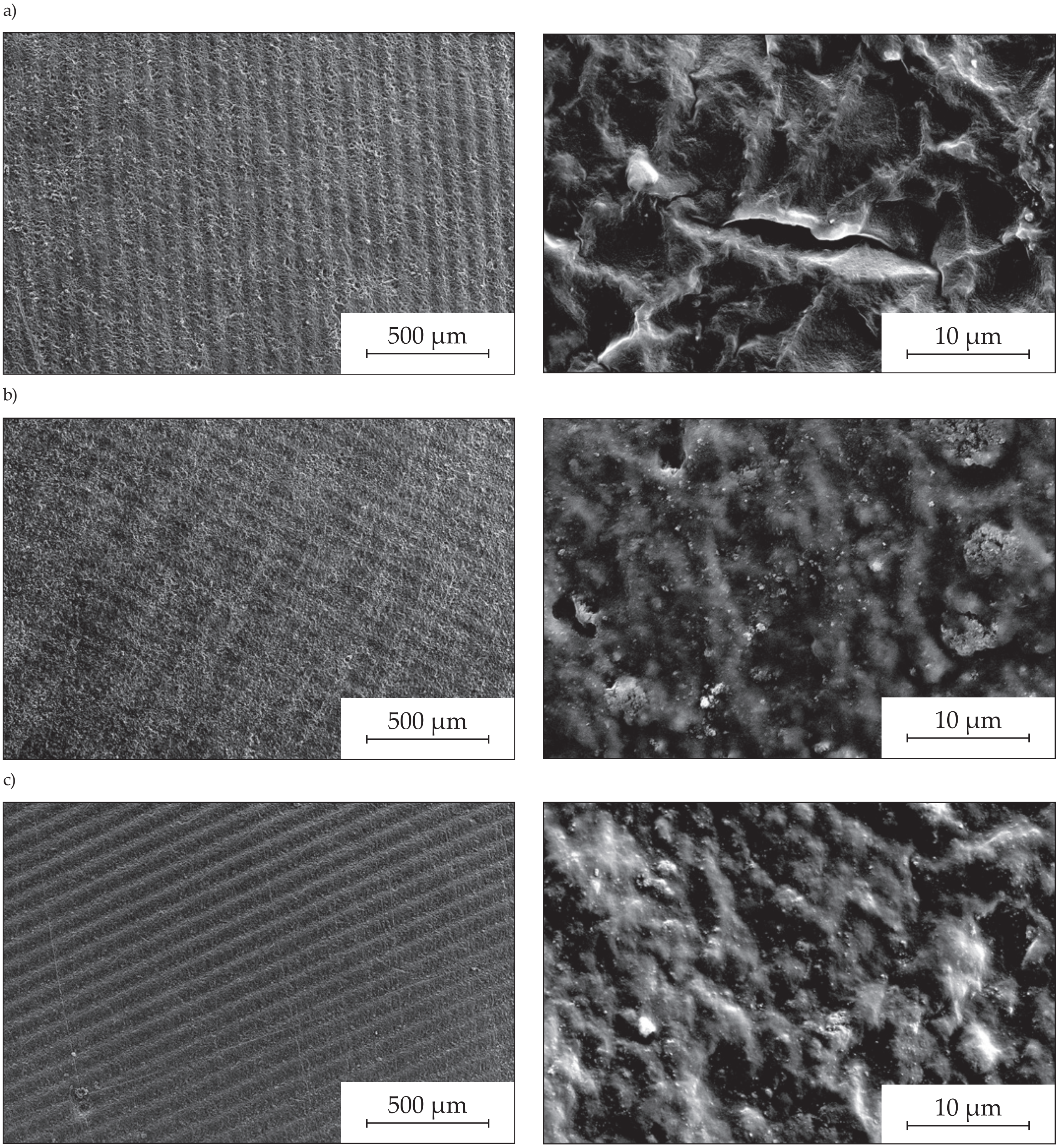

Fig. 2. SEM images of the composites differing in silica content: a) 0 wt% SiO_2, b) 3 wt% SiO_2, c) 5 wt% SiO_2

T a b l e 1. Double bond conversion rate of uncured resin and the composites

Samples	Peak area of C=C	Peak area of C=O	Double bond conversion rate DC%
Uncured resin	27.3	28.9	–
0 wt% SiO_2	10.6	19.2	41.5
3 wt% SiO_2	11.0	19.9	41.1
5 wt% SiO_2	10.0	17.3	38.6

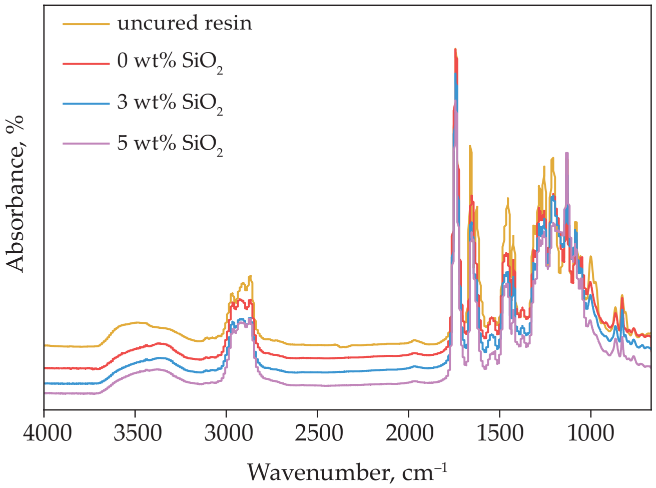

Fig. 3. FTIR spectra of the uncured and cured resins differing in SiO_2 content

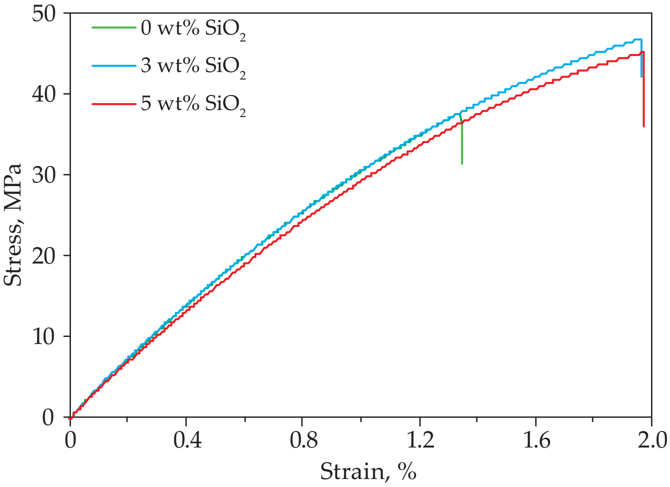

Fig. 4. Stress-strain curves of the composites with different SiO_2 content

Table 2. Tensile properties of the composites

SiO_2 %	Tensile strength MPa	Elongation at break, %
0	36.6	1.4
3	47.0	2.0
5	45.2	2.0

Table 3. Flexural properties of the composites

SiO_2 wt%	Flexural strength MPa	Flexural modulus MPa
0	76.4	2798
3	95.7	3013
5	89.4	3033

properties of the composites are shown in Table 2 and in Figure 4. The addition of fumed silica significantly improves tensile strength, which confirms the reinforcing effect of silica. Moreover, the elongation at break also increases, and is independent of the silica content. When 3 wt% fumed silica is added, the strength of the resin increases by about 28%, and the elongation at break by about 36%. The strength of the resin with 5 wt% silica is slightly lower than that with 3 wt%. This phenomenon can be explained by formation of agglomerates and clusters of silica particles. These results are consistent with morphology analysis (Figure 2) [23, 24].

Table 3 presents flexural properties of the composites. Silica improved flexural properties of the resin, which confirms the reinforcing effect of silica. Addition of 3 wt% filler increased flexural strength and flexural modulus about 25% and 8%, respectively. However, higher amount of silica slightly decreased flexural strength. The improvement of tensile and flexural properties results from the high aspect ratio and high mechanical properties of silica in combination with good interactions between resin and silica [25]. Indeed, good interfacial adhesion between the filler and the matrix with a homogeneous silica dispersion allows effective stress transfer from the matrix to the reinforcement, resulting in increased tensile and flexural strength. Similar results were reported in other studies [26–29].

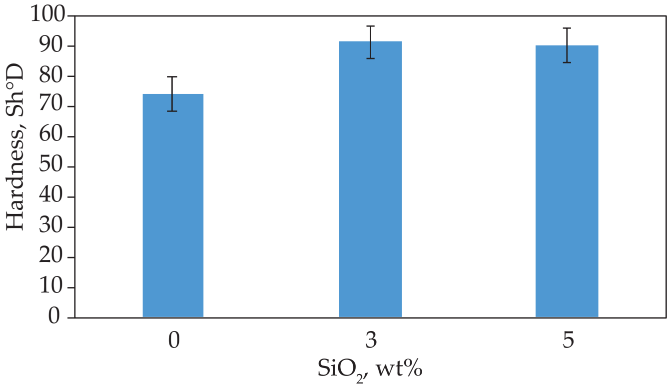

Fig. 5. Hardness of the composites with different SiO_2 content

As can be expected the addition of silica improved the resin hardness (Figure 5). However, there is only a slight difference in hardness between resin with 3 wt% and 5 wt% silica. This shows that silica has a reinforcing effect.

CONCLUSIONS

The addition of fumed silica significantly increases the viscosity as a function of the filler. SEM confirmed that silica effectively eliminated the problem of pure resin surface cracking. The mechanical properties of resins system with silica are significantly improved, especially in the case of hardness (from 74 to over 90 ShD). The tensile and flexural strengths also increase (from 36 MPa to over 47 MPa and from 76 MPa to over 95 MPa, respectively), due to the reinforcing effect. However, the strong interactions between the silica and the polymer matrix limit the cross-linking of the resin. The degree of conversion of double bonds is similar when the amount of SiO_2 is up to 3 wt% (above 41%). Above this value, the double bond conversion rate decreases slightly. Due to the viscosity, degree of cross-linking and mechanical properties, the optimal silica content is 3 wt%. The use of silica in such an amount can significantly extend the range of photosensitive resins application.

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REFERENCES

[1] Tan S., Wu Y., Hou Y. *et al.*: *Polymer* **2022**, *243*, 124609. https://doi.org/10.1016/j.polymer.2022.124609

[2] Rafiee M., Farahani R.D., Therriault D.: *Advanced science* **2020**, *7*, 1902307. https://doi.org/10.1002/advs.201902307

[3] Tan L. J., Zhu W., Zhou K.: *Advanced Functional Materials* **2020**, *30*, 2003062. https://doi.org/10.1002/adfm.202003062

[4] Ngo T.D., Kashani A., Imbalzano G. *et al.*: *Composites Part B: Engineering* **2018**, *143*, 172. https://doi.org/10.1016/j.compositesb.2018.02.012

[5] Li J., Wu C., Chu P.K. *et al.*: *Materials Science and Engineering R* **2020**, *140*, 100543. https://doi.org/10.1016/j.mser.2020.100543

[6] Javaid M., Haleem A., Singh R.P. *et al.*: *Advanced Industrial and Engineering Polymer Research* **2021**, *4*, 312. https://doi.org/10.1016/j.aiepr.2021.07.005

[7] Deng Y., Li J., He Z. *et al.*: *Journal of Applied Polymer Science* **2020**, *137*, 49294. https://doi.org/10.1002/app.49294

[8] Wang N., Wang X., Lang J. *et al.*: *Polymers* **2021**, *13*, 2039. https://doi.org/10.3390/polym13132039

[9] Li S., Cui Y., Li J.: *Journal of Applied Polymer Science* **2021**, *138*, 50525. https://doi.org/10.1002/app.50525

[10] Li S., Duan W., Zhao T. *et al.*: *Journal of the European Ceramic Society* **2018**, *38*, 4597. https://doi.org/10.1016/j.jeurceramsoc.2018.06.046

[11] Yang Z., Shan J., Huang Y. *et al.*: *Journal of Applied Polymer Science* **2020**, *138*, 49881. https://doi.org/10.1002/app.49881

[12] Kim D.S., Seo W.H.: *Applied Polymer Science* **2004**, *92*, 3921. https://doi.org/10.1002/app.20422

[13] Li S., Sun D., Li A. *et al.*: *Applied Polymer Science* **2021**, *138*, 49859. https://doi.org/10.1002/app.49859

[14] Kwak R., Park H.H., Ko H. *et al.*: *ACS Macro Letters* **2017**, *6*, 561. https://doi.org/10.1021/acsmacrolett.7b00233

[15] Endruweit A., Johnson M. S., Long A.C.: *Polymer Composites* **2006**, *27*, 119. https://doi.org/10.1002/pc.20166

[16] Xiang H.P., Wang X.W., Ou Z.R. *et al.*: *Progress in Organic Coatings* **2019**, *137*, 105372. https://doi.org/10.1016/j.porgcoat.2019.105372

[17] Seidler K., Griesser M., Kury M. *et al.*: *Angewandte Chemie International Edition* **2018**, *57*, 9165. https://doi.org/10.1002/anie.201803747

[18] Xiang H., Wang X., Lin G. *et al.*: *Polymers* **2017**, *9*, 552. https://doi.org/10.3390/polym9110552

[19] Wang H., Yan Y., Tian L.: *Composites Communications*, **2022**, *36*, 101355. https://doi.org/10.1016/j.coco.2022.101355.

[20] Rau D.A., Forgiarini M., Williams C.B.: *Additive Manufacturing* **2021**, *42*, 101996. https://doi.org/10.1016/j.addma.2021.10199.

[21] Lee W.J., Jo Y.H., Yilmaz B., *et al.*: *Journal of Dentistry* **2023**, *135*, 104598. https://doi.org/10.1016/j.jdent.2023.104598

[22] Hata K., Ikeda H., Nagamatsu Y. *et al.*: *Polymers* **2021**, *13*, 4435. https://doi.org/10.3390/polym13244435

[23] Lyu Y., Wen X.L., Wang G.L. *et al.*: *Composites Science and Technology* **2022**, *218*, 109167. https://doi.org/10.1016/j.compscitech.2021.109167

[24] Bharadwaja K., Rao S.S., Rao T.B.: *Materials Today: Proceedings* **2021**, *45*, 3343. https://doi.org/10.1016/j.matpr.2020.12.653

[25] Yadav P.S., Purohit R., Kothari A.: *Materials Today: Proceedings* **2019**, *18*, 5530. https://doi.org/10.1016/j.matpr.2019.07.666

[26] Liu G.L., Chen Y.T., Shi H.L. *et al.*: *Carbon* **2022**, *200*, 116. https://doi.org/10.1016/j.carbon.2022.08.052

[27] Malaki M., Hashemzadeh Y., Tehrani A.F.: *Progress in Organic Coatings* **2018**, *125*, 507. https://doi.org/10.1016/j.porgcoat.2018.07.034

[28] Malaki M., Hashemzadeh Y., Karevan M.: *Progress in Organic Coatings* **2016**, *101*, 477. https://doi.org/10.1016/j.porgcoat.2016.09.012

[29] Elsami R., Bagheri R., Hashemzadeh Y., Salehi M. *Progress in Organic Coatings* **2014**, *77(7)*, 1184. https://doi.org/10.1016/j.porgcoat.2014.04.007

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