

Preparation, properties and potential applications of a photocurable varnish with pleasant limonene smell

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Photocurable materials which are obtained on the basis of urethane acrylate resins are often used in the industry for the production varnishes or protective coatings. The main disadvantage which is connected with the utilization of these varnishes is their unpleasant smell during the process of production and curing. This work presents the photocurable varnish which was obtained on the basis of aliphatic urethane acrylate and R-(+)-limonene. The utilization of this raw materials allows to obtain the smelling coatings. The aim of this work were the studies on the influence of limonene molecules on the mechanical properties of the UV-cured coatings. These studies showed that the coatings with limonene molecules retain their properties, and are characterized by the very good adhesion, cohesion and high gloss. These kinds of varnishes can be applied for preparation of appropriate protective coatings on the surface of wood, metals, and nail plates. These protective coatings have not only pleasure smell but also can have the bactericidal and fungicidal properties. The studies performed with *Escherichia coli* ATCC29425 and *Candida albicans* confirmed these properties.

Keywords: varnishes with limonene, smelling varnishes, urethane acrylate, UV-curing coating.

INTRODUCTION

UV-curable coatings represent a class of coatings which do not include or include low amount of volatile organic compounds and these materials have been widely used in many branches of industry¹. The main components of the UV-curable coating are: an oligomer, a monomer and a photoinitiator. The prepolymers or oligomers on the basis for example urethane acrylates have often very complex structures. UV-curable urethane acrylate oligomers with molecular weights ranging from 600 to 6000 g/mol and with functionalities ranging from 2 to 6 are commercially available². The studies on the improving of the performances of UV-curable coatings and adhesives by the utilization of polyurethane acrylates have been carried out by many researchers.

Polymethacrylates, which are obtained by the free-radical polymerization, exhibit a high transparency, a high weather resistance, and a low toxicity. However, their poor cohesive strength, a low thermal stability and a low abrasion resistance limit their applications, especially in comparison to two-phase composites. The properties of the methacrylate can be improved by combining them with other polymers such polyurethanes. Polyurethanes have many unique properties, such as a wide range of flexibility combined with toughness, a high abrasion resistance, a good chemical resistance, a high acid etch resistance, an excellent weather resistance, and a low temperature of curing^{2,3}.

Photocurable varnishes on the basis of urethane acrylate can be applied for preparation of appropriate surfaces on a glass, metal, wood, and even on the surface of the nail plates^{3,4}. One of the significant problems during the synthesis and the process of curing of varnishes is their intense, unpleasant smell. In case of coatings used in

the automotive and furniture industries smell is not as important as in case of their applications in cosmetics, where the unpleasant smell can have a negative influence on the human body. The aim of this work were the studies on the utilization of urethane acrylates and R-(+)-limonene for preparation of the smelling coatings. For the unpleasant smell of the photohardening varnishes are mainly responsible solvents and methacrylic acid. Methacrylic acid is used to increase the adhesion of the polymer coating utilized in nail plate surface formation. In order to remove the bad smell from the varnish essential oils can be used, but essential oils can significantly reduce useful properties of coatings, especially adhesion to the surface. This work presents the utilization of R-(+)-limonene for obtaining of photocurable coatings and their properties.

Limonene (4-isopropenyl-1-methylcyclohexene) belongs to a group of monoterpenes, which are widely distributed in nature. Limonene has a center of asymmetry at the C4 atom and therefore it may exist in the form of two enantiomers: R(+) and S(-) or as a racemic mixture (the name of limonene relates to all of these compounds). Limonene is a colorless, oily liquid having a boiling point in the range of temperatures 176–177°C. It is soluble in common organic solvents, but in water it dissolves very poorly (0.15 mmol/dm³ at 25°C). It is a fragrance compound, but its enantiomers differ in smell. R-(+)-limonene is a component of essential oil of orange, lemon, caraway, grapefruit and it is known as citrus scent, while the S(-)-limonene is present in the oil of spruce and fir, and it has a characteristic smell of trees and shrubs. Racemic limonene was found in the essential oil and bergamot camphor. D-limonene in the Code of Federal Regulations is generally recognized as a safe (GRAS) flavoring agent and can be used in common food items

such as fruit juices, soft drinks, baked goods, ice creams, and puddings. Limonene can be also obtained by dimerization of isoprene and by racemization of enantiomers at 250°C. It is also obtained by thermal isomerization of α -pinene and camphene, and from natural rubber during pyrolysis. On an industrial scale, R-(+)-limonene is produced in the amount of 73 000 tons/year. The main source of this compound are orange peels, which are a waste from the orange juice industry. The content of R-(+)-limonene in orange oils obtained from orange peels is very high and amounts to 97%⁵. R-(+)-limonene found many applications in syntheses of new generation polymeric materials and also in syntheses of many useful intermediates for organic syntheses. Among others, R-(+)-limonene was used in the copolymerization with methyl or butyl methacrylate^{5,6} and N-vinylpyrrolidone⁷ and it was applied in polymerization with castor oil⁸. Moreover, R-(+)-limonene was applied in epoxidation with hydrogen peroxide. The obtained epoxide compound was used in polymerization with carbon dioxide^{8,10}. Limonene has the antibacterial properties. It is also used as insecticide for cotton fabrics (it shows high activity against mosquitoes)¹¹. Another interesting application of limonene is its utilization as the component of new polymers for food packing. Polymers derived from renewable resources (with limonene) are now considered as promising alternatives to traditional petro-polymers (renewable and biodegradable materials)¹². Limonene has also applications in medicine. D-limonene has been tested for carcinogenicity in mice and rats. Although initial results showed that d-limonene increased the incidence of renal tubular tumors in male rats, female rats and mice in both genders showed no evidence of any tumor. Subsequent studies have determined how these tumors occur and established that d-limonene does not pose a mutagenic, carcinogenic, or nephrotoxic risk to humans. In humans, d-limonene has demonstrated low toxicity after single and repeated dosing for up to one year. The molecule of limonene is sensitive to oxygen, and in air it is converted to hydroperoxides that rapidly degrade forming numerous potent allergens including perillyl alcohol, carveol acetate, and carveone¹³. Limonene can be conveniently formulated with surfactants to form environmentally friendly water-base formulations with lower flammability, lower odor and VOC suitable for treating contaminated surfaces in many industrial environments (cleaners for concrete, marine vessel, print inks and for adhesive removal)¹⁴.

The aim of this work were the studies on the preparation of smelling coatings on the basis of urethane acrylate and the reduction of their unpleasant smell during the process of synthesis and curing by addition of R-(+)-limonene. The process of hardening of the varnish with limonene was performed by the evaporation of the solvent – the method which was described previously^{14,15}. The photocurable smelling coatings are definitely new direction in the coating technology. The aim of this work was also examination of the bactericidal and fungicidal properties of the obtained coatings.

EXPERIMENTAL

Raw material

The following raw materials were used during these studies: aliphatic urethane acrylate (Genomer 4230, Rahn), 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, BASF), trimethylolpropane triacrylate (TMPTA, BASF), R-(+)-limonene (98%), methacrylate acid (BASF), and butyl acetate (BASF).

The synthesis of the photocurable varnishes

The synthesis of the first photocurable varnish was carried out at the ambient temperature. The compounds were mixed in round-bottom flask by mechanical stirring (100 min⁻¹) in the dark. At first, the photoinitiator (5 wt%) was mixed with TMPTA monomer, methacrylate acid, and butyl acetate until the homogenous solution was obtained. After that the appropriate amount of urethane acrylate (75 wt%) was added and the obtained mixture was stirred. The stirring was performed at the same rate and at the increased temperature (60°C) for 0.5 hour (PR29). The second synthesis of photocurable fragrance varnish (PR29LIM) was carried out at the ambient temperature and also in the dark. This synthesis was performed the same as the first synthesis, and only one difference was an addition of R-(+)-limonene in the amount of 1 wt%. After addition of urethane acrylate (75 wt%) the mixture was stirred at the same rate and at the temperature of 60°C for 0.5 hour.

1-hydroxycyclohexyl phenyl ketone is a highly efficient non-yellowing photoinitiator, which is used to initiate the photopolymerization of chemically unsaturated pre-polymers, e.g. acrylates in combination with mono- or multifunctional vinyl monomers¹⁶. It is soluble at the temperature of 20°C in amount of 43 g/100 g of solution in trimethylolpropane trisacrylate (TMPTA)^{17,18}. At the first stage, Irgacure 184 absorbs a quantum of radiation, which causes formation of two radicals (Fig. 1).

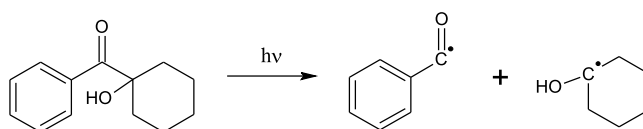


Figure 1. The formation of free radicals from Irgacure 184 photoinitiator

1-hydroxycyclohexyl radical reacts with the unsaturated bond of the acrylate group to yield radical derived from an acrylate group¹⁹. At a later stage the chain reaction is continued, which increases the molecular weight of the oligomer molecules (Fig. 2).

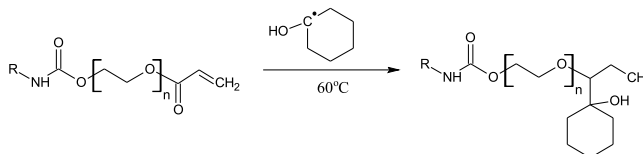


Figure 2. Free radicals polymerization of urethane acrylate using photoinitiator

Isolation of R-(+)-limonene

R-(+)-limonene used for the synthesis of the varnish was obtained by the distillation. To the three-necked flask with the capacity of 5000 ml, equipped with heating

coil, dropping funnel and condenser, early cut orange peels were introduced. Then, water was added to the reactor. The orange oil distillation was continued until the increase of the organic phase in the distillate was observed. In the last step, the obtained distillate was cooled in order to remove water from the distillate. The obtained oil was analyzed by coulombometric method (water content) and also its purity was checked by the gas chromatography method.

Coatings formation

The deposition of the 120 μm thick photoreactive varnish layer was performed on the adhesive films using the special applicator. After layer coating butyl acetate was evaporated. After evaporation of low molecular weight solvent, the distance between molecules of acrylic components become close, significantly restricting molecules mobility²⁰. After the application of varnish layer the irradiation of this sample was started under UV-lamp for 60 s with intensity of $I = 10\text{--}12 \text{ mW/cm}^2$. The distance from UV source ($\lambda = 350\text{--}400 \text{ nm}$) to crosslinked photoreactive layer was 5 cm.

Characterization of the varnishes

The varnishes were analyzed with help of the following instrumental method: NMR, FTIR spectroscopy and TGA. FT-IR spectroscopy was used for monitoring of the disappearance of various functional groups during the synthesis of the varnish with limonene. ^1H and ^{13}C NMR spectroscopy were used for determination of the structures of the synthesized varnish which was based on urethane acrylate containing limonene. ^1H NMR spectrums were recorded on a BRUKER DPX 400 spectrometer at 400 MHz with tetramethylsilane as the standard. ^{13}C NMR spectra were recorded on the same instrument at 100 MHz. All spectra measurements were carried out in CDCl_3 . Thermal stabilities of varnishes were recorded on TG 209 F1 LIBRA NEZTSCH. Measurements were recorded in the range of temperatures from 20° to 500°C with an increase of 10°C/min.

RESULTS AND DISCUSSION

NMR studies

The comparative analyses of the ^1H and ^{13}C NMR spectra of varnish samples with and without limonene shown that limonene is not incorporated into the polymer structure. The position of the signals in ^1H NMR spectra at: 1.73, 4.7 and 5.4 ppm as well as signals in ^{13}C NMR spectra at: 20.8, 23.5, 27.9, 30.6, 30.8, 41.1, 108.4, 120.6 and 150.3 ppm were typical for limonene in CDCl_3 solution. It indicates that limonene is located between polymer chains. Other signals of the limonene in ^1H and ^{13}C spectra's were overlapped by other groups of the polymer.

FT-IR studies

The reaction was also monitored with help of the FT-IR spectroscopy. The FT-IR spectrums of the varnish with and without limonene are shown in Figure 5. For the sample of PR29 it is visible the more accentuated $\text{R-CH}_2\text{-R}'$ stretching band around of 2950 cm^{-1} . Generally, to certify the curing of the acrylates, the absorbance bands of acrylate at 1635 , 1410 and 810 cm^{-1} are used. The characteristic absorption of urethane acrylate at 1635 cm^{-1} was used to determine the extent of the polymerization in these studies. PR29LIM sample shows other absorption band at 1509 cm^{-1} ($\text{C}=\text{C}$).

Thermal stability

The measurement results of the thermal stability of paint samples exhibit weight changes in the range of 20–180°C what suggest the breakdown of limonene and auxiliary components like TMPTA used for the synthesis of the photocurable coatings. For the thermal stability of the sample PR29LIM and PR29 there are no large differences. Limonene addition to the paint composition does not cause large changes in the thermal stability of the resulting product (Figs. 6–8). The resulting coatings are stable at the temperatures to which they are subjected to a hardening process.

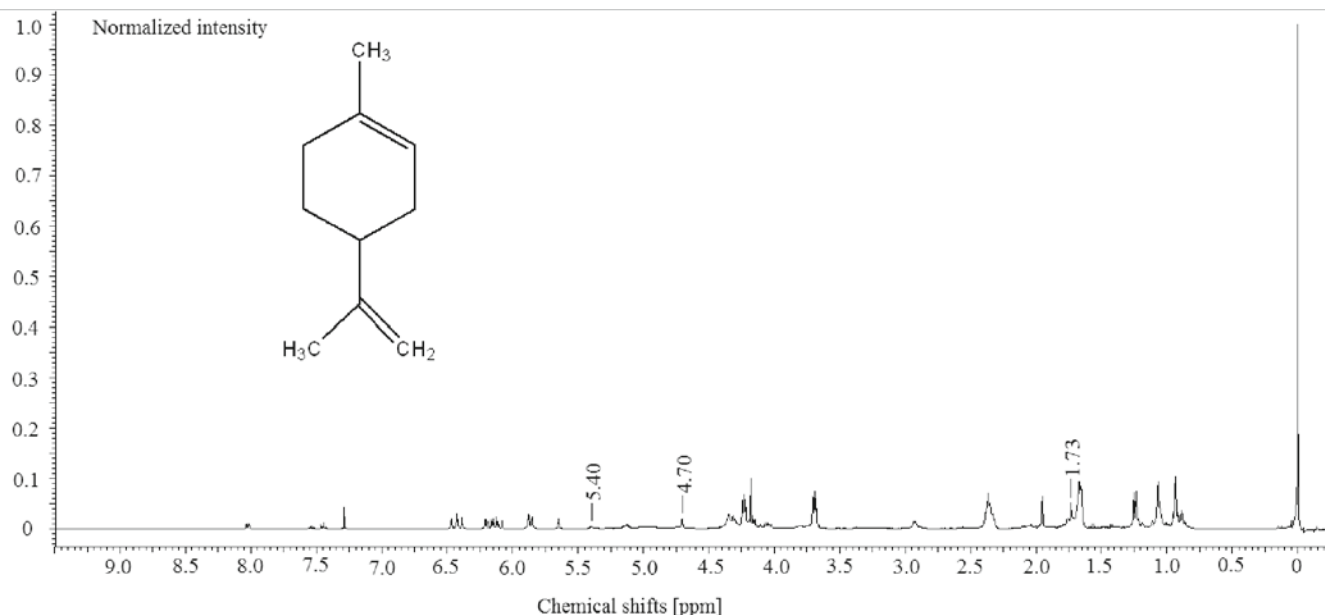


Figure 3. ^1H NMR of the varnish with R(+)-limonene (PR29LIM)

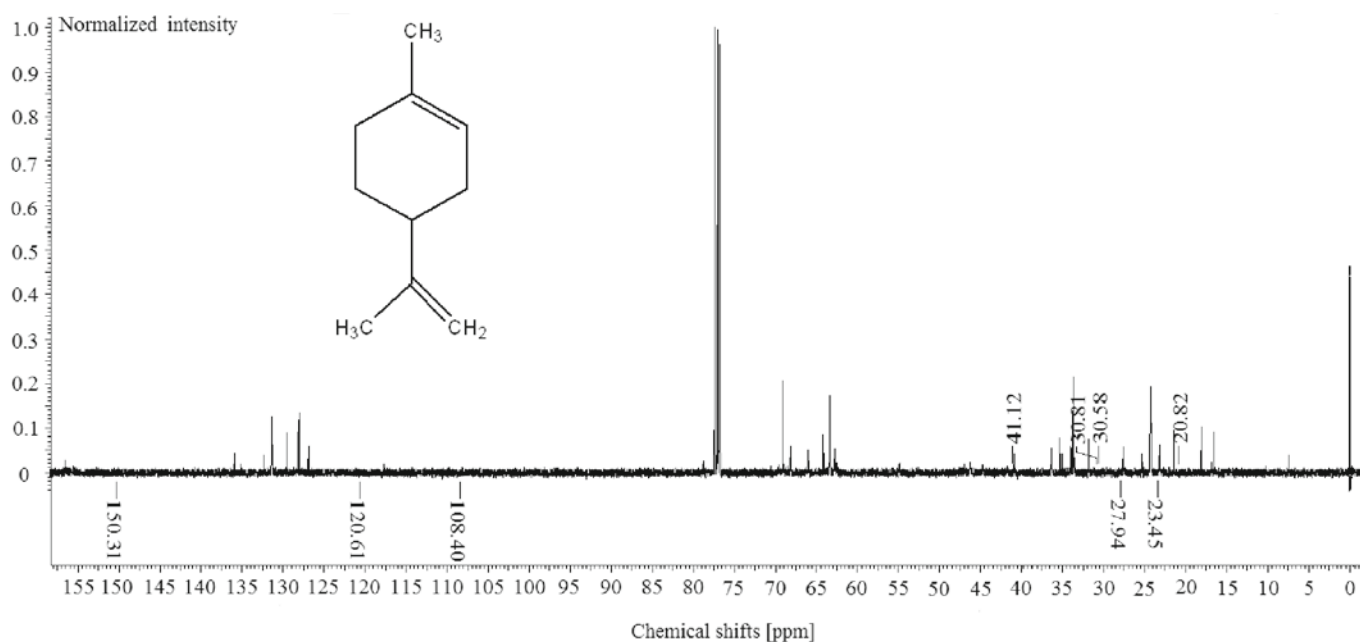


Figure 4. ¹³C NMR of the varnish with R(+)-limonene (PR29LIM)

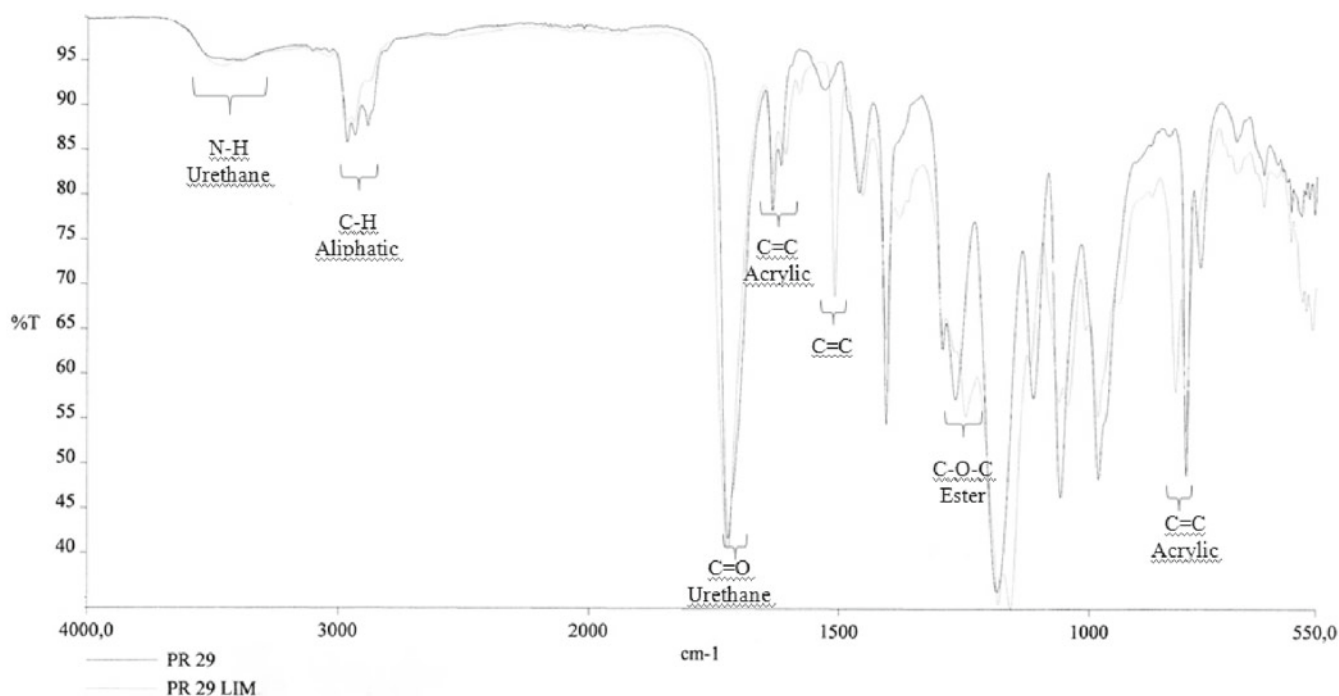


Figure 5. FT-IR spectrum of the varnish based on urethane acrylate (PR29) and varnish based on urethane acrylate with limonene (PR29LIM)

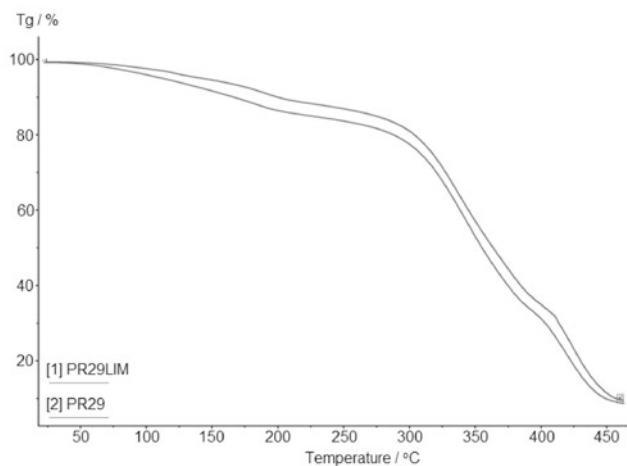


Figure 6. TGA thermogram curves of varnishes based on urethane acrylate (PR29LIM – with limonene)

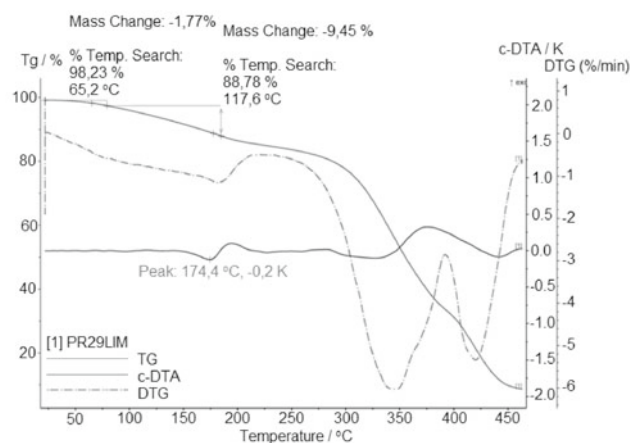


Figure 7. TG and DTG curves of UV cured urethane acrylates for PR29LIM sample

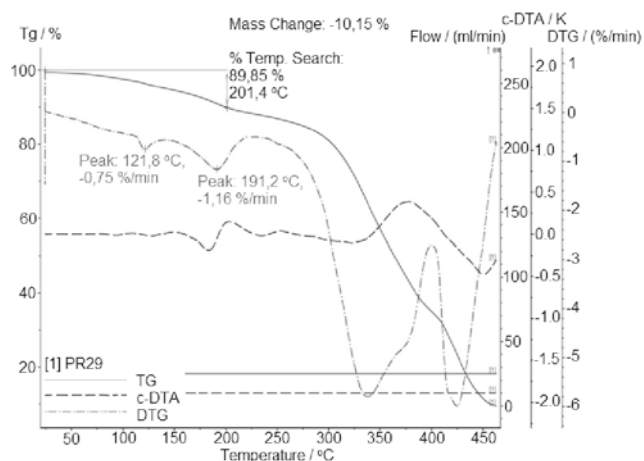


Figure 8. TG and DTG curves of UV cured urethane acrylates for PR29 sample

The curing of varnishes

The varnish layers with the different thickness from 0.25 to 1 mm, but with the same area (25 cm²), are cured under UV light. As the UV-curing of acrylate coatings is generally carried out in the presence of air, oxygen inhibition has always been a key issue. Indeed, the free radicals formed by the photolysis of the initiator are rapidly scavenged by O₂ molecules to yield peroxy radicals. These species are not reactive towards the acrylate double bonds and can therefore not initiate or participate in any polymerization reaction. They usually abstract hydrogen atoms from the polymer backbone to generate hydroperoxides. Moreover, this premature chain termination modifies the mechanical properties of the film¹⁷. During the film curing as a result of oxygen inhibition at the surface the unreacted monomers layer is formed, which is next removed with ethanol. Overcoming this unwanted reaction has turned into a major challenge. In order to the estimation the amount of the unreacted polymer the ratio of the weight of the cured layer to the total weight of the layer before UV-curing was calculated – Table 1.

Figure 9 presents the mass ratio of the cured polymer to the total weight of the film after UV curing depending on the layer thickness.

The changes of the curing temperature depending on the UV-curing time

It was measured the curing temperature of varnish layers with a thickness of 1 mm. The temperature sensors have been immersed in the polymer coating during the UV irradiation. The results of the changes of the curing temperature during the full cycle of the UV lamp lighting (120 seconds) are shown in Figure 10.

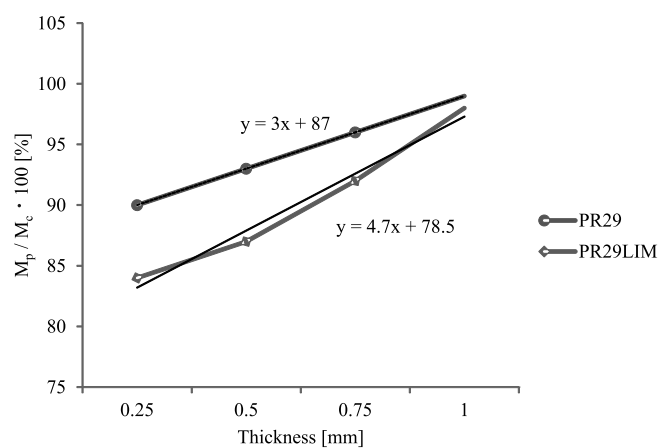


Figure 9. The mass ratio of the reacted polymer to the total weight of the cured film depending on the layer thickness

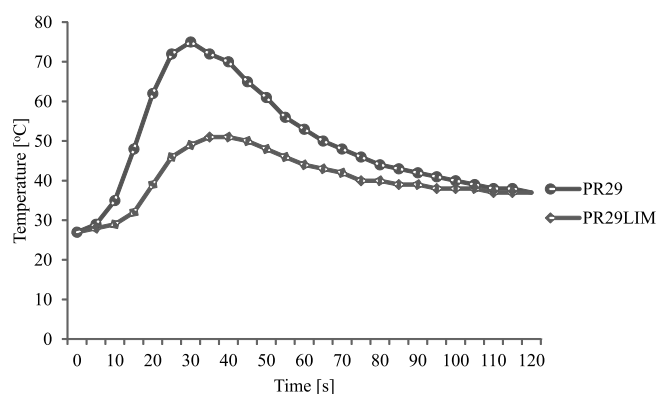


Figure 10. The curing temperature as the function of the curing time

Mechanical properties test

Organoleptic friability test of the cured polymer layers was made with the utilization of the layers with the thickness of 0.25 to 1 mm. The obtained results are shown in Figure 11. The smell of the cured polymer layers was maintained up to 7 days and it was observed the decrease of the smell of limonene during this time.

Biostatic properties of the urethane acrylate varnish with limonene

The biostatic properties of the urethane acrylate varnish modified with R-(+)-limonene also were studied. The resulting compositions (PR29 and PR29LIM) were treated with *Escherichia coli* ATC C29425, *Candida albicans* and *Trichophyton rubrum*, the molds frequently met in the human environments. The samples were plated on TTC – tergitol agar (Biocorp, Poland). The plates were incubated for 24 h at the temperature of 37°C and the colony-forming units (CFUs) were then counted.

Table 1. The comparison of the mass of the reacted polymer depending on the thickness of the layer

Varnish	Thickness [mm]	M _c – Total mass [g]	M _p – Reacted polymer mass [g]	M _p /M _c · 100 [%]
PR29	0.25	0.448	0.404	90
	0.5	0.800	0.744	93
	0.75	1.188	1.142	96
	1	1.540	1.520	99
PR29LIM	0.25	0.414	0.384	84
	0.5	0.862	0.746	87
	0.75	1.214	1.116	92
	1	1.616	1.578	98

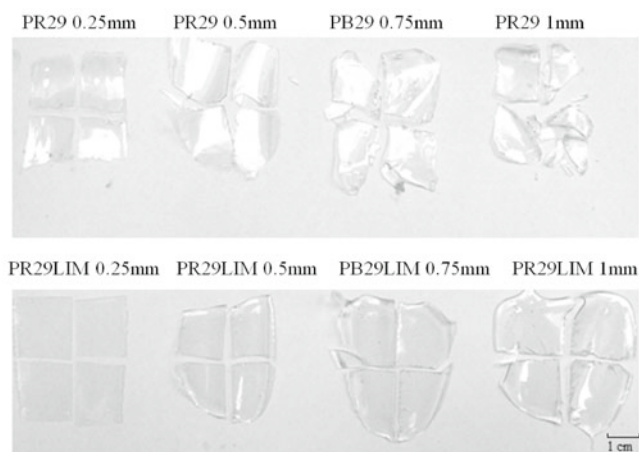


Figure 11. Organoleptic research on the friability

The studies with *Escherichia coli* ATC C29425 were performed by the disc method in Petri dish with a diameter of 10 cm. On the discs the limonene varnish in the amount of 5 μ l/disc was placed. Around the limonene varnish the area of the growth of the bacteria's was not observed (Fig. 12). It confirms the bactericidal and biostatic properties of limonene.

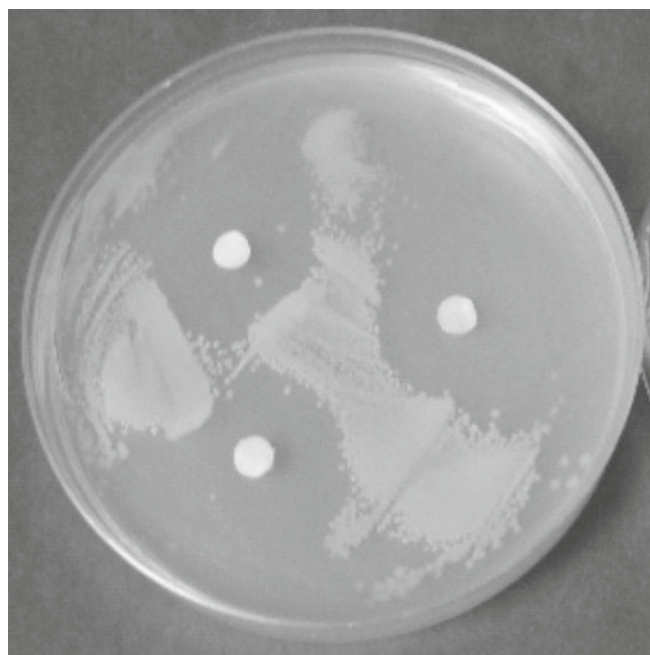


Figure 12. The studies on the resistance of limonene to *Escherichia coli* ATC C29425

Also the studies which confirm the fungicidal properties of the varnish with limonene were performed. In these studies *Candida albicans* were used. In case of the PR29 varnish utilization fungi's grow on the whole area of the culture even under the surface of the varnish was observed (Fig. 13). For the PR29LIM varnish the lack of the grow area of *Candida albicans* under the surface of the varnish was observed (Fig. 14).

Studies with *Trichophyton rubrum* did now show good results, because varnish surface was overgrown with colonies of fungus.

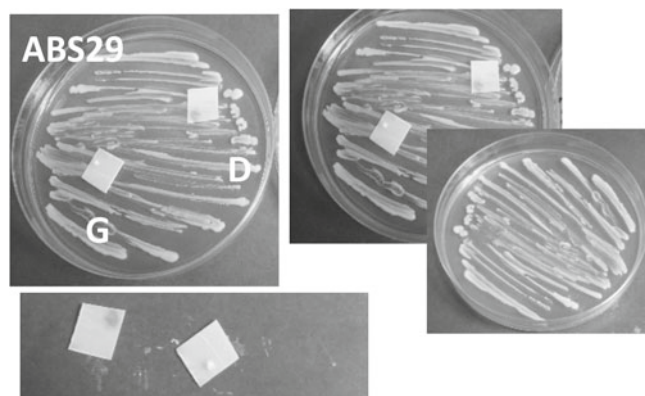


Figure 13. The PR29 varnish on the ground with ABS and on the medium with culture of *Candida albicans*

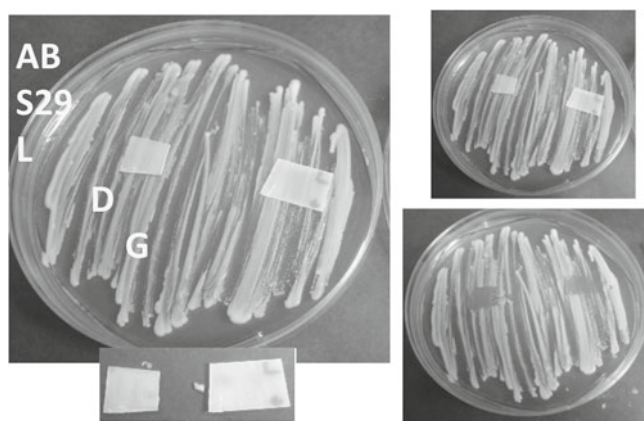


Figure 14. The PR29LIM varnish on the ground with ABS and on the medium with culture of *Candida albicans*

CONCLUSION

Both varnish layers with limonene before and after curing have a pleasant fruity scent. The varnish layer is colorless, transparent and flexible, and the smell of the cured film was maintained for 7 days. In comparison to the varnish without limonene, lacquers with limonene is characterized by the increased resistance to the fragility, which is the advantageous feature taking into account the utilization of this lacquers as the photocurable coatings for the surface wood, metals, and others for example nail plates. The mass ratio of the reacted polymer to the total weight of the layer in both cases generally increases with increasing the layer thickness, but in case of the varnish with limonene it is lower. The varnish with limonene is characterized by significantly lower curing temperature. Photocurable varnishes have the good thermal stability and the addition of R(+)-limonene improved their mechanical and thermal properties. The addition of limonene causes changes in the thermal stability and mechanical properties. Limonene gives varnishes the pleasant citrus scent. It can be proposed that limonene is present in this varnish in the "encapsulated" form between the polymer chains so that after curing the coating retains its aroma. Limonene does not react with urethane acrylate or trifunctional acrylate monomer. This kind of coatings is characterized by resistance to atmospheric factors. Thus, it can be successfully applied as the coating which can protect against wind and high or low temperatures. The coatings with limonene can have also bactericidal and fungicidal properties, so they can be used among others for the protection of wood. The

possible application can be also the protective coatings for fruits that can protect against sunlight, the weather conditions and fungi or bacteria. Another possible utilization of this kind of coatings can be the application of them on the side ships. These coatings would protect against microorganisms. Summarizing, varnishes with limonene can have a lot of applications in: cosmetics and medicine (protective and therapeutic varnishes), the chemical industry, shipbuilding, and horticulture.

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