Polymer Networks with Antibacterial Activity by UV Photopolymerization

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ABSTRACT: The crosslinking by radical UV photopolymerization of mixtures of acrylic oligomers added with 2,4,4′-trichloro-2′-hydroxydiphenyl ether (TCDPE) allows to obtain polymer films which perform like hygienic coatings. The release of the bioactive compound from two types of acrylic networks obtained by UV crosslinking of polyfunctional monomers, namely, epoxy-based and urethane-based diacrylic oligomers, has been investigated. The photopolymerization process was influenced by biocide presence only at high biocide concentration, where the plasticizing effect of the biocide increased the double bond conversion. The kinetic curve of the photopolymerization was fitted by an Avrami-like equation and the release of TCDPE from the networks into solutions of ethanol–water of different compositions was discussed on the base of the Fick's diffusion equation. The antimicrobial activity of the UV photopolymerized film has been tested by putting the coatings in contact with two types of colony-forming bacteria, the *Escherichia coli* (Gram negative) and the *Staphylococcus aureus* (Gram positive). Strong hygienic performances toward the tested pathogens were observed for the urethane and epoxy films containing TCDPE in quantities as low as 0.1 wt %. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2334–2342, 2009

Key words: photopolymerization; networks; antibacterial; diffusion; swelling; coatings

INTRODUCTION

Synthetic macromolecules are suitable materials for the production of functional coatings able to control active molecule release for pharmaceutical[1] or hygienic[2] purposes. The coatings perform as functional coatings when they contain additives which can be released on the surface or into the surrounding environment to develop a specific activity. Additives with biocide activity can generate hygienic coatings when the biocide released from the bulk on the surface or into the surrounding medium reaches a concentration higher than minimum inhibitory concentration toward pathogen microorganisms.

A fast way to obtain functional coatings is to use the UV photopolymerization to form networks that contain the active substance dissolved in the crosslinked polymer. Besides the advantage of the intrinsic insolubility of the crosslinked polymer in the contacting liquids, there is the opportunity to modulate the swelling behavior that controls the diffusion rate and the release of specific active molecules. The swelling extent is influenced by the crosslink density and, in relation with the composition of the liquid contacting the polymer film, by the network chemical composition.

When UV photopolymerization is used to generate a functional crosslinked coating further benefits should be taken into account: the very fast conversion of the liquid into a solid, the easiness to copolymerize different monomers to obtain structures with designed properties, and a friendly system without volatile solvents that could be released in the environment.

The physical and chemical properties of the crosslinked film can be controlled through the selection of a suitable mixture of monomers and/or oligomers, the only limitation being the required presence of UV reactive chemical groups, namely, acrylic or methacrylic groups for polymerizations started by UV initiators with radical mechanism of action.[3]

In this article, we report about the use of acrylic bifunctional monomers, namely, diacrylic compounds based on epoxy or urethane oligomers, to obtain epoxy or urethane networks with different structure and crosslink density, containing a biocide able to hinder the growth of bacteria through inhibition or destruction of living cells.

At the present time, the hygienic performance of an antimicrobial agent present in a polymer matrix cannot be easily predicted or controlled. There is a

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lack of data about the quality and quantity of antimicrobial agent necessary to generate antimicrobial action either by the direct action of the surface or by the release into the media contacting the coating.

Moreover, the molecular diffusion in the bulk of the polymer toward the surface and from the surface to the environment leads to a concentration of the active constituent that is changing in time. The durability of the biocide action of a hygienic coating depends on the factors influencing the biocide migration in the bulk and into the environment of the polymer film.

In this work, the 2,4,4′-trichloro-2′-hydroxydiphenyl ether (TCDPE) was used as an antimicrobial. The TCDPE is a biocide agent commercially known as Triclosan®, a compound largely used as antiseptic additive into cosmetic products and soaps for hand scrubbing.

The experiments showed that this compound does not influence the UV photopolymerization up to concentrations that are two orders of magnitude higher than the concentration required to have hygienic properties. The kinetics of UV photopolymerization was described through an equation having the form of the equation used to fit the kinetics of polymer crystallization, i.e., the Avrami's equation.[4]

The release of TCPDE was evaluated by putting the film in contact with ethanol–water mixtures of different compositions and analyzing the TCDPE content of the solution at different times. The TCDPE release in time of the films based on the urethane and the epoxy diacrylic oligomers was analyzed taking into account the Fick's diffusion equations. The apparent diffusion coefficients evaluated by fitting the experimental data were in agreement with the extent of the observed swelling and crosslink density of the different polymer networks.

The antimicrobial activity of the photopolymerized coating was tested by contacting films containing the biocide with two types of colony forming bacteria, the *Escherichia coli* (Gram negative) and the *Staphylococcus aureus* (Gram positive). A concentration of 0.1% of TCDPE has shown to be sufficient to confer hygienic properties on the coatings toward the tested pathogens.

MATERIALS AND METHODS

The aliphatic urethane-diacrylate oligomer (EB 270, d_{25}: 1.100 g/mL, M_W: 1500) was supplied by UCB Chemicals, Belgium. The epoxy acrylate oligomer, the bisphenol-A-propoxylate diacrylate (BAPDA, PO/phenol: 2, d_{25}: 1.084 g/mL, M_W: 420), was supplied by Sigma Aldrich, Milano, Italy. The 2,4,4′-trichloro-2′-hydroxydiphenyl ether (TCDPE), the tripropylene-glycol diacrylate oligomer (TPGDA, d: 1.030, M_W: 300), and the pure ethanol were Sigma Aldrich's products. The UV photoinitiator, 2-hydroxy-2-methylphenyl-propanone (Darocur 1173) was a Ciba's product.

The UV spectra were collected by a double beam instrument Unicam UV2 Spectrometer. Real-time kinetics through infrared analysis were obtained by a Thermo Electron Corp. FTIR Nicolett 5700 instrument modified for the purpose. The dynamic mechanical analyses were performed by the thermal analyzer Reometric Scientific MK III.

Crosslinking of the oligomer film

Films with antibacterial properties were obtained by UV photopolymerization of the oligomer, Eb 270 or BAPDA, mixed with 40% (w/w) of TPGDA as a thinner, to obtain a mixture with a suitable viscosity to be layered with homogeneous thickness on a substrate. The mixtures, added with 3% (w/w) of Darocur and 0.1% (w/w) of TCDPE, were spread with a calibrated wire wound applicator on a glass plate in a layer 200 μm thick. The crosslinking was performed by submitting the liquid layer to UV irradiation with a Hg vapor lamp (25 mW/cm^2) under N_2 atmosphere. The layers were submitted to three repeated irradiations, for a total of 90 s, to obtain the maximum crosslink density of the sample, as evidenced by FTIR analysis. After the irradiation, the coated glass plates were used as samples for tests of antibacterial activity whereas the experiments of release of biocide were performed on the free films, detached from the glass plate.

Bioactivity of the surface

The biocide activity of the crosslinked polymers has been evaluated by spreading 100 μL of the bacterial suspension on an area of 10 cm^2 of the polymer film, supported on a glass surface and previously sterilized for 15 min in oven at 170°C.

Bacterial suspension of *Escherichia coli (E.C.)* or *Staphylococcus aureus (S.A.)* in the range 1.0 10^5–1.0 10^6 Colony Forming Units (CFU) per milliliter were used. The spread suspension was covered with an aseptic film of PET and, after 6–24 h of contact with the polymer coating, was washed with 35 mL of water. Three sample of 1 mL were allowed to grow in a Petri dish filled with agar at 35 ± 1°C and 90% relative humidity and the living colonies were counted after 24 h of incubation (*E.C.*) or after 48 h (*S.A.*).

The results were expressed as relative values CFU (%), that is the bacteria counted on the surface of the sample expressed as percentage of the bacteria counted on an aseptic glass surface submitted to the same procedure (control sample).

Biocide release in liquid media

The release of TCDPE has been tested in liquid water–ethanol mixtures by monitoring the biocide concentration by UV spectrophotometry. To follow the kinetics of the biocide release, the film was introduced in an optical quartz system filled with the liquid, mechanically stirred, and continuously monitored. A ratio (liquid volume)/(film surface area) of about 1.6 was maintained for all the experiments. The height and the area of the absorbance peak at the wavelength of 245 nm were evaluated to determine the TCDPE concentration.

Network swelling

The swelling of the crosslinked film was evaluated through the weight increase of samples immersed into liquids of different composition. The samples were dipped in the liquids at room temperature for 150 min, dried with blotting paper, and weighted. The swelling percentage was evaluated by the ratio between weight increase of the swollen film and the weight of the fully dried film.

Dynamic mechanic thermal analysis

The samples for the DMTA analysis were obtained by pouring the diacrylate mixtures into a polyethylene mold with dimensions 10 mm × 20 mm × 1 mm. After full curing by UV irradiation the crosslinked sample was extracted from the mold and the elastic (E') and the dissipative (E'') modulus were recorded as a function of the temperature in a tensile assembly operating at 1 Hz. The dissipation factor was evaluated as $\tan\delta = \frac{E''}{E'}$.

Kinetics of UV curing

The kinetics of the cure was followed by measuring the acrylic double bond content of the film by means of a real-time infrared spectroscopy apparatus. A film of the liquid mixture, about 10 μm thick, was placed on a Si plate and FTIR spectra were collected during the UV irradiation. The 1640 cm^{-1} band, assigned to acrylic double bond, was used as analytical band and the 1725 cm^{-1} band, assigned to carbonyl groups, was used as a reference band. The quantitative analysis of the d.b. content in the film was performed on the basis of the area A of the selected bands, in absorbance units, and the double bond conversion z_{db}, at the time t, was obtained by the equation

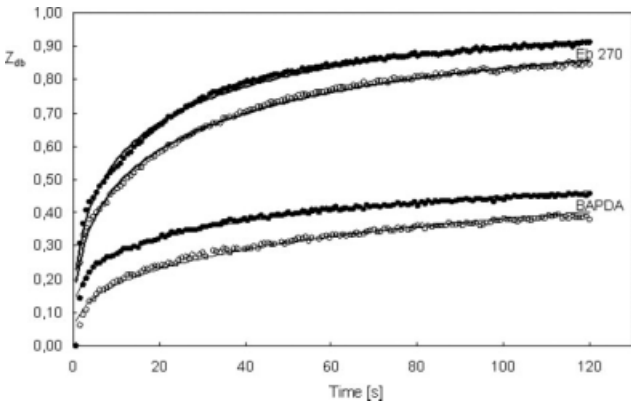

Figure 1 Kinetics of FTIR acrylic double bond conversion during UV irradiation of pure diacrylate oligomer films (○) or containing 10% of TCPDE (●). Line: fitting of the experimental points through the Avrami's equation. Parameters for the Avrami equation: Pure resins: EB 270 (k = 0.239, n = 0.437); BAPDA (k = 0.0938, n = 0.354). TCDPE added resins: EB 270 (k = 0.290, n = 0.446); BAPDA (k = 0.188, n = 0.248).

$$z_{db}(t) = \frac{A_{1640}(t)}{A_{1640}(t_0)} \frac{A_{1725}(t_0)}{A_{1725}(t)}$$

where t_0 is the starting time of the UV irradiation.

RESULTS AND DISCUSSION

Kinetics of UV photopolymerization

A fast rate of disappearance of acrylic double bonds was observed at the beginning of the UV irradiation of the oligomer films based on BAPDA or on EB 270 but a high fraction of acrylic groups remains in the films also if completely dried after a long period of irradiation.

As can be seen in Figure 1, the maximum of acrylic double bond conversion at high irradiation times is about 0.85 for the pure EB 270 resin and about 0.40 for the pure BAPDA resin.

The limited conversion evidences that, when the polymer network formation was in progress, the mobility of the reacting species, i.e., the propagating radicals and the acrylic oligomers, was reduced up to the point where all the reactive groups were immobilized in the bulk of the material and the polymerization reaction stopped. In other words, the reacting system undergoes a phase inversion by conversion of the initial microgels dispersed in the reacting liquid, into a polymer network matrix encompassing the reactive functionalities. When the glass transition temperature of the network, T_g, becomes higher than the reaction temperature, the reactive groups became wrapped in a stiff molecular structure and the polymerization stops.[5]

The high difference between the observed values of the maximum double bond conversion of the two pure resins can be explained taking into account that it is the reaction of each acrylic group that generates a branching of the growing chain, i.e., a crosslink of the growing network, that hinders the molecular mobility. The observed limit conversion values of 0.85 and 0.40 correspond to a relatively lower difference in the crosslinking density. Taking into account the properties of the liquid oligomers, the crosslinking density, at the observed conversion, are 2.3 10^{-3} moles/ml and 3.2 10^{-3} moles/ml for the BAPDA and EB 270, respectively.

The higher value of crosslink density reached at the gel point for the urethane-acrylic resin can be ascribed to the longer chain of the oligomer that allows a higher mobility of the reactive group at the end of the side chains connected to the network. The evaluation of the molecular structure of the oligomers in a linear conformation by a computational method[6] gives a head-to-tail length of 20.9 Å for the BAPDA and 112.1 Å for the linear urethane made by hexamethylene diisocianate and ethylene glycol (EB 270).

Moreover, the reactive group mobility is increased by the high flexibility of the methylene chains of the aliphatic urethane-acrylate oligomer, compared with the stiff moiety of bisphenol-A that connects the terminal acrylic groups of the epoxy-acrylate oligomer.

The presence of the biocide (TCDPE) in the film does not modify the rate of the photopolymerization when the concentration of biocide is in the order of some units percent. A sensible influence on the kinetic behavior has been observed only at high concentrations of biocide, as can be seen in Figure 1 where the photopolymerization kinetics of EB 270 and BAPDA systems, pure or containing a 0.1 weight fraction of TCDPE, are compared.

The higher level of double bond conversion observed in the presence of a relatively high content of TCDPE can be ascribed to the plasticizing effect of the solubilized molecules.

As a consequence of the plasticizer, the material becomes softer and more flexible, the mobility of the network increases and the crosslinking reaction could be enhanced. The analysis of the dynamic mechanical spectra of the cured materials gives evidences in agreement with this hypothesis.

From Figure 2, where the DMTA thermograms of tan δ of the cured EB 270 and BAPDA resins are reported, it is clear that the temperature of the maximum of tan δ decreases when the cured materials contains the biocide. The maximum of tan δ indicates the main transition of the networks, namely, the T_g of the material.

In agreement with a stiffer network structure, the BAPDA shows a T_g of 99°C, higher than the 79°C

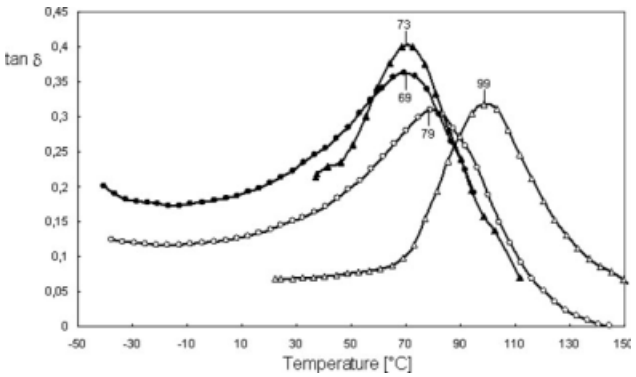

Figure 2 Values of tan δ at different temperatures as obtained by DMTA analysis of the cured samples. (○): EB 270, (●): EB 270 added with 10% of TCDPE, (△): BAPDA, (▲): BAPDA added with 10% of TCDPE.

showed by the EB 270. Moreover, the decrease of the T_g to 73°C and to 69°C, in the presence of 10% of TCDPE, for the BAPDA and the EB 270, respectively, gives an evidence of the plasticization of the network caused by the dissolved biocide.

Model for kinetics of UV photopolymerization

It was found that a suitable model to fit the data of UV photopolymerization of the studied system is the model based on the Avrami equation proposed for the thermal curing of polyfunctional oligomers.[7,8]

The Avrami theory, originally developed to describe the kinetic process of polymer crystallization, can be applied to fit the kinetics of UV photopolymerization on the assumption that the UV crosslinking proceeds through formation of microgels that grow during the reaction like the crystal seeds during the crystallization. There is a phenomenological analogy between the UV crosslinking and the polymer crystallization. On one side, the radical formation and the growing of the chemical network by polymerization of the diacrylate oligomers can be assimilated to the nucleation and growing of a polymer crystal. On the other side, a crystallization process can be considered a process that physically bonds different macromolecules through crystalline domains that, like a chemical crosslink, generates a polymer network.

The parameters of the Avrami's equation

$$\ln(1 - \alpha) = -k \cdot t^n$$

when used to describe the UV photopolymerization process, with analogy to the original model for crystallization, assume the following new meanings: α becomes the relative conversion of double bonds, t the cure time, k the kinetic constant of the chemical process, and n a value related to the mechanism of microgels formation and growing.

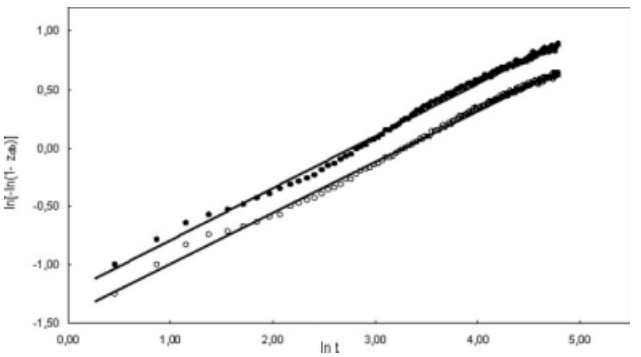

Figure 3 Avrami's plots of experimental UV photopolymerization kinetic data of resin Eb 270 added with 10% of TCDPE (●) and without additive (○).

As in the classical use of the Avrami equation, the n and k parameters can be deduced from the experimental kinetic data introduced in the equation

$$\ln[-\ln(1-\alpha) = \ln k + n \cdot \ln t$$

that allows to obtain the value of the constant k from the intercept and the value of the exponent n from the slope of the plot of $\ln[-\ln(1-\alpha)$ versus $\ln t$.

Figure 3 reports the plot of the kinetic data obtained in the photopolymerization of the EB 270 resin, pure or added with TCDPE, according to the mentioned equation. In the legend of Figure 1 are reported the values of the Avrami parameters evaluated by fitting of the experimental values.

As can be seen in Figure 1, where the experimental data and the theoretical curves are compared, a good fitting of the experimental kinetics of acrylic double bond conversion during the UV photopolymerization can be obtained by application of the Avrami's equation.

Biocide release from the cured films

The release of the biocide, in the liquid contacting the crosslinked film added with TCDPE, has been studied by experiments of extraction with water–ethanol mixtures. The results obtained by using liquid mixtures containing ethanol in the range 50–95%, in contact with crosslinked films containing a weight fraction of 0.001 of TCDPE, are reported in Table I for the two types of networks.

The extracted quantity of biocide and the rate of extraction from the two networks are quite different: higher initial rates are showed by the urethane-acrylate network but higher quantities at longer times are extracted from the epoxy acrylic network. In either cases, the extraction data after a long contact time evidence the presence of a repartition equilibrium of the TCDPE between the network and the liquid phase.

In the case of the EB 270, the extracted TCDPE does not show a regular behavior with the liquid composition: as it can be seen in Figure 4, the quantity of biocide released from the network increases with the ethanol contained in the liquid mixture up to a content of 85% but at higher contents a decrease of the extracted biocide is observed.

Instead, as showed in Figure 5, the biocide release from the BAPDA cured film shows a continuous increase of the extracted TCPDE with the increase of ethanol in the mixture.

This can be assumed as a regular behavior if it is considered that the TCDPE is quite insoluble in water and highly soluble in ethanol.

TABLE I
Concentration of TCPDE (mg/L) in Water–Ethanol Solutions After Different Periods of Contact with Crosslinked Films Containing 0.1% of TCDPE Film Based on Urethane-diacrylic oligomer (EB 270) or Epoxy-diacrylic oligomer (BAPDA)

		Ethanol/water volume ratio					
Resin	Time (h)	50/50	65/35	75/25	85/15	90/10	95/5
EB 270	0.5	1.06	1.52	2.63	6.62	4.81	0.22
EB 270	1	1.40	2.39	4.84	9.77	7.41	0.36
EB 270	1.5	1.42	2.99	5.92	11.2	9.69	0.37
EB 270	2	1.45	3.42	6.65	13.1	10.6	0.37
EB 270	2.5	1.44	3.60	6.67	13.2	11.2	0.38
BAPDA	8	–	0.726	0.950	1.29	1.91	3.07
BAPDA	24	–	1.54	3.50	5.16	5.83	7.67
BAPDA	32	–	2.15	4.85	6.50	7.55	9.70
BAPDA	48	–	3.07	6.38	8.90	10.5	12.5
BAPDA	56	–	3.69	7.24	9.63	12.3	13.7
BAPDA	72	–	4.85	8.41	10.55	14.7	16.4
BAPDA	80	–	5.22	9.08	10.9	15.8	17.2
BAPDA	96	–	5.28	9.94	11.3	16.6	17.8
BAPDA	104	–	5.25	10.1	11.5	16.6	17.9
BAPDA	120	–	5.25	9.94	11.5	16.6	17.9

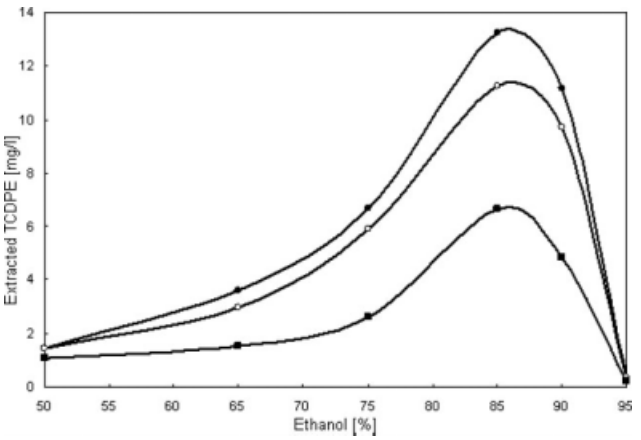

Figure 4 Extracted biocide for different contact times between EB270 films with 0.1% of TCDPE and ethanol/water mixtures. Contact time (h): (■) 0.5, (○) 1.5, (●) 2.5.

The different behavior in the extraction process from the urethane and the epoxy networks suggests that, more than the solubility of the TCDPE in the liquid of extraction, the interaction of the extracting liquid with the networks is the factor controlling the release.

The swelling can be a suitable measure of the interaction between the liquid and the polymer network.

Figure 6 reports the observed swelling of the two cured materials in the presence of water–ethanol mixtures.

As can be seen, the swelling and the extraction curves show a similar pattern as functions of the liquid composition. The film based on the Eb 270 oligomer has a maximum of swelling in a range of liquid composition that include the maximum of TCDPE extraction whereas the film based on the BAPDA shows values of swelling lower but continuously increasing with the ethanol content of the liquid mixture.

The swelling data agree with the predictions based on the difference between the solubility parameters of the network and of the liquid mixture. In the case of EB 270, this difference reaches a minimum with an ethanol content in the range 85–90%, the same range in which the maximum of biocide extraction is observed.

The same concept applied to the BAPDA networks explains the increasing amount of released biocide with the ethanol content of the liquid. The solubility parameter of the network, evaluated on the base of dispersive, polar an hydrogen contributions,[9] results of 15.8 $J^{0.5}$ $cm^{-1.5}$ and the solubility parameter of the water–ethanol mixture is in the range 47.8 (pure water) – 26.5 (pure ethanol) $J^{0.5}$ $cm^{-1.5}$. As a consequence, the minimum of the difference between the solubility parameters of the network and of the liquid mixture is reached with pure ethanol. In other words, the BAPDA network has the maximum of affinity with ethanol and this compound causes the maximum swelling of the network.

Model for biocide release

The release data reported in Table I have been interpreted on the base of Fick's diffusion laws under the assumption that the TCDPE is the only compound allowed to diffuse in the system, the crosslinked film contains a uniform distribution of TCDPE, the total amount of TCDPE in the system remains constant as diffusion proceeds and a monodimensional diffusion phenomena occurs.

The last assumption can be justified by considering that the film has a thickness of about 200 μm and an area of several cm^2. With a surface/thickness ratio very high, the mass transfer from the polymer

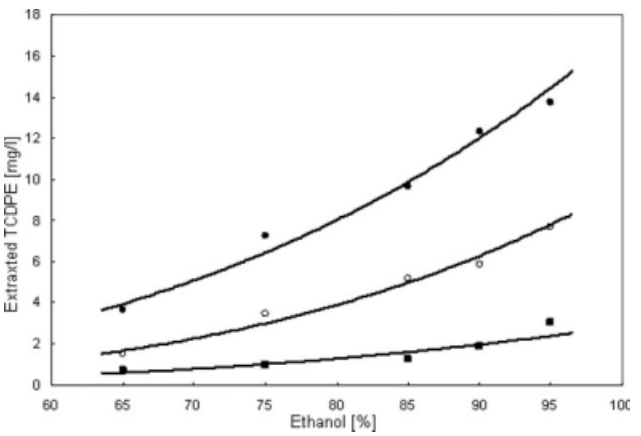

Figure 5 Extracted biocide for different contact times between BAPDA films with 0.1% of TCDPE and ethanol/water mixtures. Contact time (h): (■) 8.0, (○) 24, (●) 56.

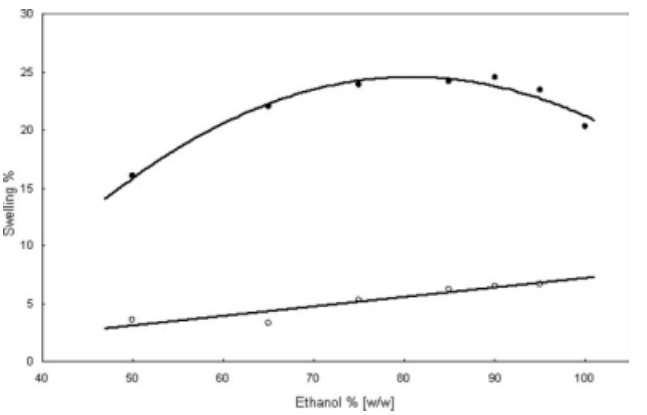

Figure 6 Swelling of EB 270 (●) and BAPDA (○) cured films in the presence of water–ethanol mixtures with different compositions.

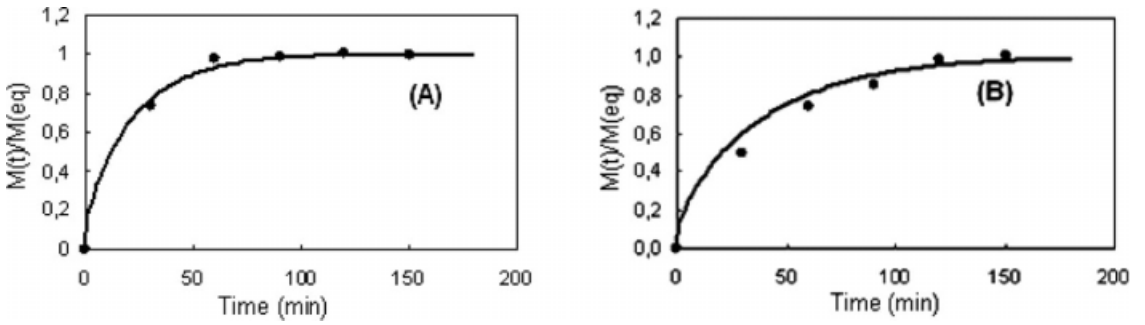

Figure 7 Comparison between experimental (points) and theoretical (line) values of TCDPE release from EB 270 cross-linked films. Ethanol fraction (w/w): (A) 0.50 and (B) 0.85.

to the liquid occurs near exclusively through the flat surfaces. In other words, only the diffusion along the axis perpendicular to the flat surface of the film, the *x*-axis, has to be considered, the diffusion along the axis parallel to the surface and the mass transfer through the border-limiting surfaces being negligible.

Along the *x*-axis, assuming a value of 2 L for the thickness of the film and a value of 2a for the thickness of the solution, the film occupies the space $-L \leq x \leq +L$ and the solution occupies the space $(-L - a) \leq x \leq -L$ and $L \leq x \leq (L + a)$.

The initial concentrations of the TCDPE in the solution and in the film are zero and C_0, respectively. In the stirred system, the diffusion in the liquid-polymer boundary layer can be considered faster than the diffusion in the bulk of the polymer film. In this system, the TCDPE concentration along the *x* axis could be described by the Fick's diffusion equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

where *C* and *D* are, respectively, the concentration and the apparent diffusion coefficient of TCDPE in the film.

If the concentration of solute at the interface liquid-polymer is assumed to be the same as in the liquid bulk, the following conditions at $t = 0$ can be set:

$C = C_0$ in the film, that is for $-L \leq x \leq L$

$C = 0$ in the solution, that is for $(-L - a) \leq x \leq -L$ and $L \leq x \leq (L + a)$.

The rate at which the solute leaves the film through the surfaces at $x = \pm L$ is always equal to that at which it enters the solution. The flux, at $t \neq 0$, can be evaluated by the Fick's equation:

$$a\frac{\partial C}{\partial t} = \pm D\frac{\partial C}{\partial x} \quad \text{for} \quad x = \pm L$$

The above reported system of differential equations can be solved by use of the Laplace transform and the following equation can be obtained[10]:

$$M_t = M_\infty \left(1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} e^{-\frac{Dq_n^2}{l^2}t}\right)$$

were M_t and M_∞ are the uptakes of TCDPE by the liquid at the time *t* and after an infinite time respectively, α is the ratio between the volumes of solution and film, and the q_n values are the positive roots of

$$\tan q_n = -\alpha \cdot q_n$$

The Figure 7, where the experimental and theoretical values of the equation in the form

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} e^{-\frac{Dq_n^2}{l^2}t}$$

are reported, shows agreement between the experimental values and the theoretical ones obtained by fitting the TCDPE release data of EB 270 with Fick's equation.

By this fitting, for mixtures of ethanol/water in the range between 50/50 and 95/5, an apparent diffusion coefficient in the range 1.2×10^{-8}–2.8×10^{-8} $cm^2\ s^{-1}$ was obtained.

The TCDPE release from BAPDA networks, reported in Table I, evidences a rather different behavior. As can be seen in Figure 8, where the data of the BAPDA release reported in Table I have been fitted with the same equation, a clear difference exists between the prediction based on Fick's equations and the observed release.

The experimental relative release data show a near linear increase in time up to the asymptotic region, where equilibrium between the liquid and the solid film is reached.

The linear increase has to correspond to a constant flux of TCDPE from the film into the solution through the solid–liquid interface and, in a diffusion controlled system, should be the consequence of a constant driving force, i.e., a constant difference of concentration between the solution in the film and the external solution.

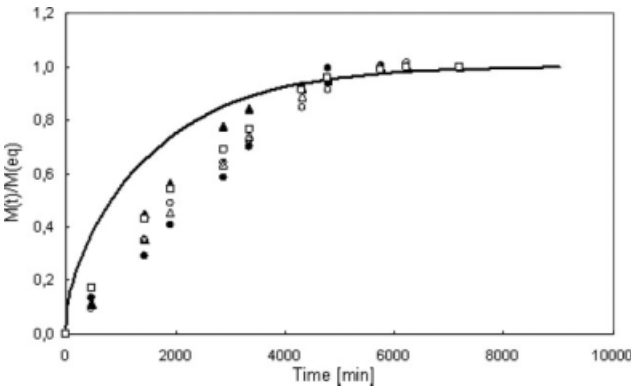

Figure 8 Comparison between experimental data (points) and theoretical values (line, $D = 4\ 10^{-10}$ cm^2 s^{-1}) for TCDPE release from BAPDA crosslinked films. Ethanol fraction (w/w): (○): 0.65; (■): 0.75; (□): 0.85; (▲): 0.90; (△): 0.95.

A way to explain this phenomenon is to suppose a dual mode model of existence of TCDPE in the film, as has been ascertained the case of gas sorption into glassy polymers. In this case, below the T_g, the total absorbed concentration in the polymer is the summation of two contributes: the solute dissolved in the polymer following Henry's law and the solute filling the Langmuir-type microvoids of the glassy state.[11]

Analogously, in the BAPDA network, with the higher T_g and the higher crosslink density, a double distribution of the TCDPE dissolved in the film can be assumed: a fraction of the molecules is dissolved in the solvent that swells the polymer, and the other fraction is adsorbed on the glassy domains of the network. During the release process, the dynamic equilibrium between the molecules adsorbed on the network and the molecules solubilized in the internal liquid causes a continuous desorption of TCDPE from the network that replaces the loss for transfer into the external solution. As a consequence, the TCDPE released into the external liquid is continuously replaced by desorption of the TCDPE from the network into the inner solution and the driving force for the diffusion is leveled.

TABLE II
CFU Mean Values of *Escherichia coli* (*E.C.*) and *Staphylococcus aureus* (*S.A.*) Strains Spread on Sterilized Glass Substrate (Control) and on EB 270 Crosslinked Film Doped with the TCDPE (Coating)

Bacteria	Contact time (h)	TCDPE 0.1% (w/w)		TCDPE 0.5% (w/w)	
		Control	Coating	Control	Coating
E.C.	0	100	100	100	100
E.C.	3	435	58	386	30
E.C.	6	547	56	464	0
E.C.	8	–	6	–	0
E.C.	24	–	0	–	0
S.A.	0	–	100	–	–
S.A.	1	–	56	–	–
S.A.	1.75	–	48	–	–
S.A.	2	–	25	–	–
S.A.	24	–	0	–	–

TABLE III
CFU Mean Values of *Escherichia coli* Strain Spread on EB 270 Crosslinked Film Submitted to a Continuous Washing with Water

Contact time (h)	Washing time: 24 h; TCDPE: 0.5%		Washing time: 48 h; TCDPE: 0.1%	
	Control	Coating	Control	Coating
0	100	100	100	100
3	622	0	276	0
6	530	0	801	0

Biocide activity of the cured films

The biocide activity of the polymer surface toward *Escherichia coli* and *Staphylococcus aureus* strains, expressed as CFU obtained from vital count percentage, is reported in Table II.

As can be seen, in the case of *E.C.* the increase of TCDPE content increases the biocide activity of the polymer surface. A low concentration as 0.1% is sufficient to destroy the bacteria capacity to grow on the polymer surface either for the Gram-positive or the Gram-negative bacteria.

To evaluate a possible decrease of bioactivity by the gradual and continuous loss of the biocide content of the film in contact with a liquid, some experiments of bioactivity were performed after the treatment of the doped film surface with a continuous flux of water.

The results, shown in Table III, do not evidence a decrease of the biological activity of the surface after the treatment.

This phenomenon can be attributed to the very low solubility of TCDPE into water and to the high affinity of the biocide with the polymer that hinders the loss of biocide.

Moreover, the data suggest that the bioactivity of the TCPDE could be played on the surface by direct contact of the microorganism with the doped polymer surface, rather than by transfer of the TCDPE into the liquid suspension of bacteria.

CONCLUSIONS

Crosslinked films obtained by UV photopolymerization of diacrylate oligomers added with TCDPE perform like hygienic coatings and show bactericide activity toward either Gram negative (*Escherichia coli*) or Gram positive (*Staphylococcus aureus*) bacteria. A high antimicrobial activity was observed at low

concentration of TCDPE and the antimicrobial activity of the film is substantially conserved also after a continuous water washing of the surface.

With an additive concentration sufficient to explicate the bactericidal activity, the UV photopolymerization kinetics is not influenced by the presence of TCDPE and can be fitted by a two parameter equation having the form of the Avrami's equation.

The TCDPE can be released from the film into aqueous solutions of ethanol. The rate of extraction shows a dependence from the composition of the liquid and is related to the structure and the swelling of the polymeric network.

The release of TCDPE from urethane-diacrylate networks can be explained on the bases of Fick's diffusion equations whereas the release from epoxy-diacrylate networks shows a behavior that suggests different retaining conditions of the TCDPE molecules in the polymer network.

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