Surface silylation of polymers in form of fibers and foils

Petr Exnar[1], Erika Heyduková[2], Jakub Wiener[2], Jan Grégr[1]
Technical University in Liberec,[1] Faculty of education,[2] Faculty of textile engineering

Annotation

Practical tests of silylation were conducted with samples of polyester and polyamide fabric and foils, cellophane and also glass for comparison. There were tested several methods of silylation by clear agents, by trimethylchlorsilane (TMCS) and 1,1,1,3,3,3 - hexamethyldisilazane (HMDS), their mixture and further their solutions. All of tested methods proceeded to certain intensity of surface silylation of tested material. Sequence of agent and method efficiency was different for every material. By reaction there were not observed degradation of samples except cellophane. However speed of reactions was by much slowly than literature shows.

Surface of all silylated samples was dipped by water and diiodmethane less than surface unmodified substrate. Calculations of surface energy from measured contact angles of water and diiodmethane on prepared samples acknowledged meaningful falling their values by silylation. From the practical view it means reduction of wettability of material.

Dye test of polyamide foils and fabrics acknowledged that silylated materials can be common dyed.

Key words: silylation, polymers, fibers, wettability, contact angle, surface energy.

Introduction

Technological progress produces not only new special materials but also special surface finish of common materials. It is for example special surface finish of textile with very effective properties where hydrophobic finish of surface layers plays also an important role [1].

Except raise of hydrofobicity silylation of nature materials should raise also their life and resistance [2].

From the practical view silylation agents can be divided into two big groups: halogensilanes and silazanes. For practical tests trimethylchlorsilane (TMCS) and 1,1,1,3,3,3 - hexamethyldisilazane (HMDS) were chosen as basic compounds of present groups. Low ability of HMDS which is main disadvantage of this application by some types of alcohols (e. g. tertiary alcohols) can be very raised by catalysis by iodine according to Karimi and Golshani [3]. Under these conditions silylation should proceed during a few minutes with 92 – 99 %.

Silylation has to run in perfectly waterless medium because otherwise silylation agent would first react with water. That is why perfectly dry inert solvents like hydrocarbons (for example cyclohexane, toluene) or halogenated hydrocarbons (for example dichloromethane) must be used. On the other hand own productive equipment for silylation technology is not potentially complicated and it is just practically composed of silylation bath, bath for rinsing balance of agent and drying for put a remainder of solvent out.

Experimental part

Practical tests of silylation [4] were conducted with samples of polyester fabric (PL) and nylon (PA), polyester and polyamide foils, cellophane and also glass for comparison. There were tested several methods of silylation by clear agents TMCS and HMDS, their mixture in mass quantity 1:2 and further their solution in cyclohexane or dichloromethane by laboratory temperature including catalysis by iodine. Silylation of polyester fabric and foil by

TMCS or HMDS in toluene on boil was made for comparison. All of used solvents were perfectly dried by molecular sieve 3A and every silylation experiments were conducted in a dry box. There was standard used reactionary time of 15 minutes at laboratory temperature. At choice series of experiments also kinetics of silylation reaction was watched. Temporal scale of 1, 2, 4, 8 and 16 minute was chosen for this purpose. At the end of silylation surplus of silylation agent was always put from the samples out by treble dipping of sample in corresponding solvent.

Variations in wettability of surfaces were quantified based on measurement of contact angle of distilled water and diiodmethane by means of image analysis LUCIA G 4.61. Acquired values of contact angles were used for determination of critical surface energy by Zisman, Girifalco and Good and values of surface energy components by Kaelble theory [5-8].

Changes of dyeing of polyamide materials (fabric and foils) in consequence of silylation were compared with standard after elaborating in dyeing bath of solution of Midlon red PRS with CH_3COOH. Dyeing was conducted at temperature of boiling water bath for 2 minutes.

Results and discussions

All of tested methods proceeded to certain intensity of surface silylation of tested material. Sequence of agent and method efficiency was different for every material. Modified surface was dipped in all cases less than unmodified substrate. Difference in silylation degree among clear agents (TMCS, HMDS) and their solutions was unmeaningful therefore it is practically and priced more advantageous solutions of agents used. Obtained results evaluation showed that silylation passed by much slowly than literature shows [3]. It is documented on pictures number 1 to 4 for contact angle by distilled water and diiodmethane. There is evidently seen, that silylation proceeded yet after 8th minute. At sample of cellophane occurred there during reaction first to falling and then to rising of cos θ. It can be explained by influence of longer effect of silylation agent and gradual degradation of surface of cellophane foil. Tested samples of polyester fabric and foil kept also hard silylation conditions of boil in toluene under aftercooler for 45 minutes.

Contact angles of distilled water and diiodmethane measured by means of image analysis were used for determination of critical surface energy of modified materials [5-8]. The critical surface energy γ_C of measured materials was quantified by Zisman, Girifalco and Good theories. Two liquids constituted model series therefore just two values of critical surface energy for each material were acquired by means of simpler theory of Girifalco and Good. By means of Kaelble theory valuation of disperse γ^d_{SV} and polar γ^p_{SV} component of surface energy and resulting surface energy γ_{SV} for all types of substrates and surface modifications was conducted. In a table 1 there are shown examples of counted values of surface energies for polyester foil.

Values of surface energy counted on the basis of different theories differ. However this resulted from the all counted values of surface energy that surface modifications have influence on energetic parameters of surface all of tested materials. Modified surfaces of materials showed less values of surface energy than unmodified substrates, which correspond to a presumed reaction of agents with surface OH-groups. If value of surface energy is lower then less nonreacted groups on surface of substrate occur. From the practical point of view it means falling of wettability of material.

During dyeing test of polyamide foils and fabrics modified by method of silylation there was found that fall of satiety of dyeing of modified samples was not mostly too expressive. There was not too marked barrier effect and dye could not pass through surface layer. Own effect of silylation considerable presented only in a case of dyeing of polyamide fabrics modified by means of oneself HMDS when modified surface impeded penetration of dye. So we can presume that modified fabrics and polymers of this way can be common dye.

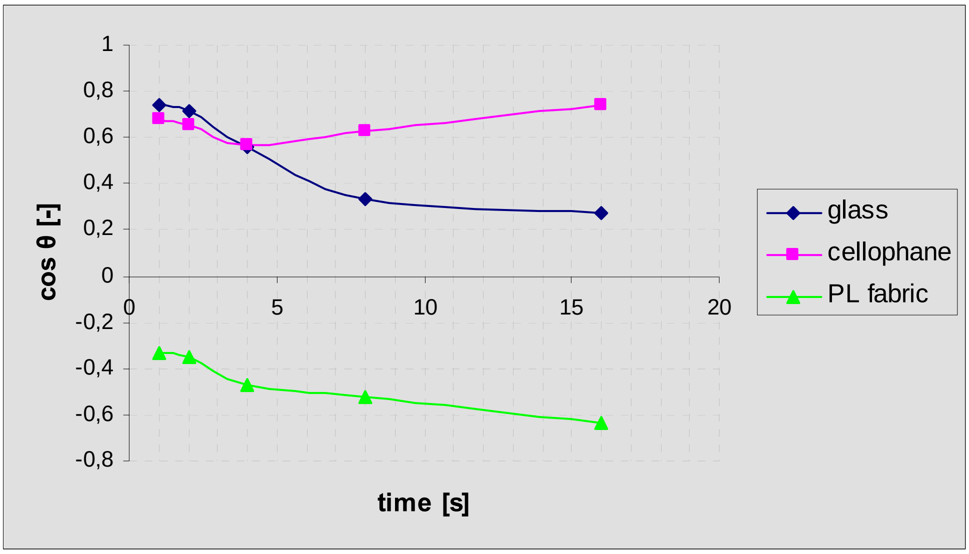

Fig. 1: Graphic dependence of cos θ of distilled water on time by silylation using HMDS

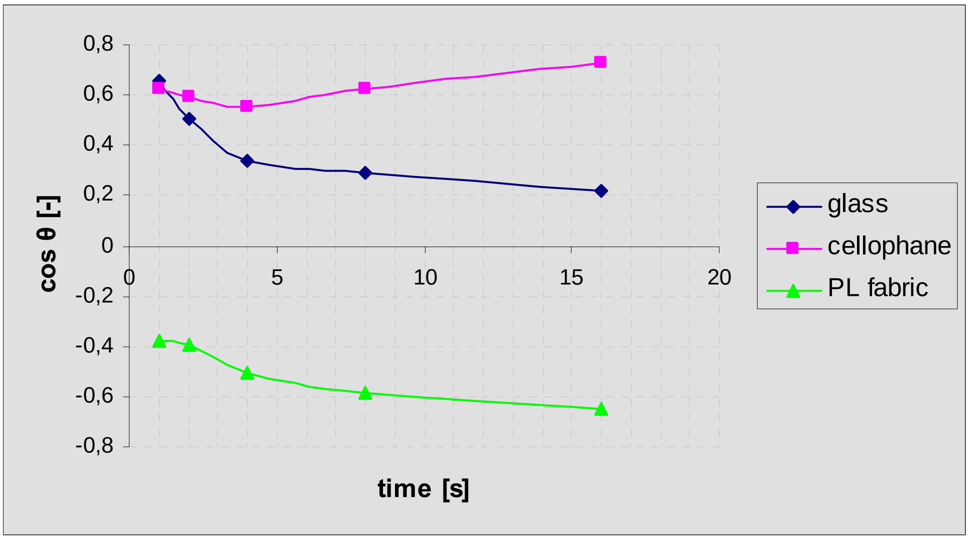

Fig. 2: Graphic dependence of cos θ of distilled water on time by silylation using TMCS

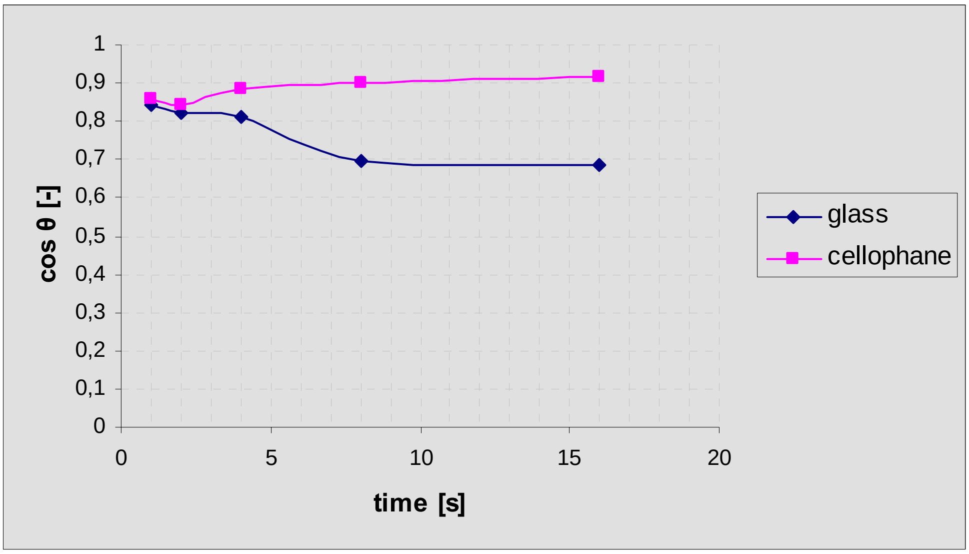

Fig. 3: Graphic dependence of cos θ of diiodmethane on time by silylation using HMDS (PL fabrics showed zero contact angles)

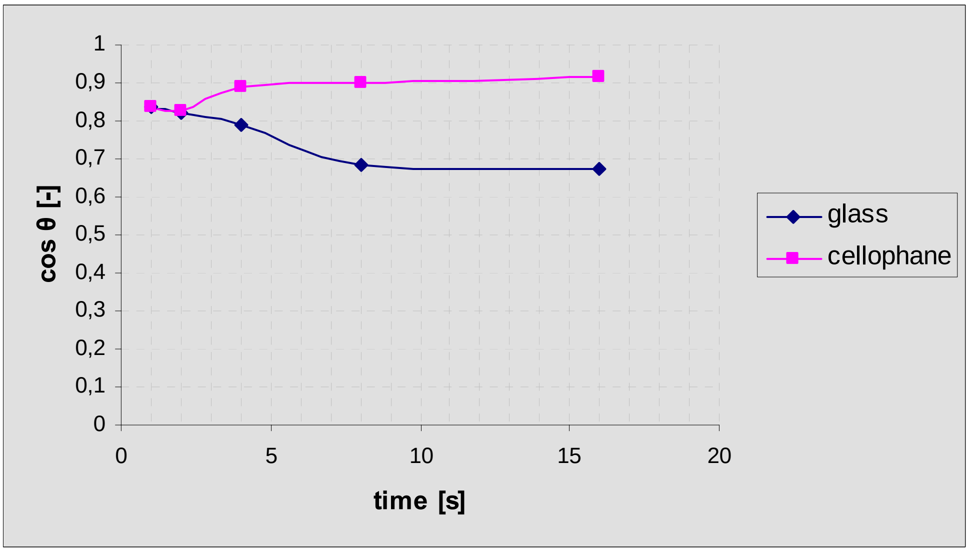

Fig. 4: Graphic dependence of cos θ of diiodmethane on time by silylation using TMCS (PL fabrics showed zero contact angles)

Table 1: Resulting values of surface energy for modified surface of PL foil (notes in text)

agent	time[min]	Girifalco + Good		Zisman	Kaelble		
		γ_C (CH_2I_2)	γ_C (H_2O)	γ_C	γ^d_{SV}	γ^p_{SV}	γ_{SV}
unmodified sample		44,6	42,5	42,9	44,6	11,7	56,3
HMDS	15	37,7	24,0	40,2	37,7	3,4	41,1
TMCS	15	36,7	22,6	39,5	36,7	2,9	39,7
HMDS + TMCS	15	37,5	15,6	43,0	37,5	0,5	38,0
TMCS in cyclohexane	15	38,6	24,3	41,2	38,6	3,3	41,9
HMDS in cyclohexane	15	37,5	21,5	41,0	37,5	2,4	39,8
H + T in cyclohexane	15	38,4	22,1	41,7	38,4	2,4	40,8
TMCS + triethylamine	16	42,9	30,2	44,3	42,9	5,2	48,1
HMDS- aftercooler	45	41,7	28,3	43,5	41,7	4,5	46,2
TMCS- aftercooler	45	40,2	26,1	42,4	40,2	3,8	44,0

Conclusion

During surface silylation of polyester and polyamide materials there was found that using of clear agents HMDS and TMCS as silylation agents did not acquit and it is more advantageous their dissolving in a form of solution. However the speed of reactions is also conspicuously slower in a case of using of catalytic amount of iodine in comparison with results published in literature [3]. High level of silylation was reached until reaction time of about 16 minutes.

Except cellophane, which showed symptoms of surface degradation after long time of operating of silylation agents, other materials were resisting to a reaction conditions. Tested samples of polyester fabric and foil kept also hard silylation conditions of boiling in toluene under aftercooler for 45 minutes.

Surface of all silylated samples was dipped in all cases less than unmodified substrate. Calculations of surface energies from measured contact angles of water and diiodmethane on prepared samples confirmed that their values fell meaningful after silylation. From the practical point of view it means reduction of wettability of material.

Dyeing test of polyamide foils and fabrics confirmed that silylated materials can be common dyed.

Literature

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