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# Synthesis and behaviour of the polymer covering on a solid surface: 1. Attachment of the polymer initiator to the solid surface

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Attachment of the peroxide initiator of radical polymerization to the surface of various oxides due to the adsorption of reactive copolymers of peroxide monomer and maleic anhydride (PM–MA) was performed. Plateau adsorption amount of PM–MA depend mainly on the nature of the solvent. It was found that adsorption is irreversible with respect to the solvent. Measuring the exchange between the polymer in the adsorbed layer and in solution, with the aid of a labeled polymer, it was shown that adsorption is reversible with respect to the polymer. Studying the competitive adsorption of PM–MA with some other polymers showed that PM–MA, because of its high adsorption ability, could not be replaced by another polymer, but it could replace another polymer from the adsorbent surface. A wetting technique was used to assess the behaviour of the polymer covering formed with PM–MA.

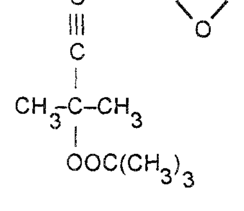
**(Keywords: peroxide copolymer; adsorption; polymer covering)**

## INTRODUCTION

Obtaining a relatively thin 10–1000 nm uniform polymer covering on the solid surface, including ultrafine powders, is useful for a wide range of pragmatic applications: stabilization of powder suspension[1,2], encapsulation[3,4], immobilization of ferments and catalysts[5,6], obtaining adsorbents[7], treatment of fillers and fibres for composites[8–12]. In our work we are especially interested in the problems of stabilization of ultrafine suspensions and the problem of formation of polymer layers on the filler's surface. These two problems are closely related to the problem of development of polymer composites. First, the polymer skin brings about the steric stabilization of the inclusions and causes uniform distribution of the filler in the polymer matrix (e.g. polymer particle filled composites, paints). On the other hand, the polymer skin on the filler surface can be considered as a preliminary synthesized interlayer which influences the mechanical behaviour of the composite[13]. Apart from possible pragmatic application this way seems to be very interesting for the investigation of the fracture mechanism of composites because it allows the control of properties of interlayers in a wide range.

Synthesis of the polymer skin on the solid surface requires fulfillment of a succession of stages: attaching an initiator, polymerization on the solid surface and evaluation of polymer covering features. We propose to publish a series of papers on the problems discussed above.

This paper deals with the problem of attaching the radical polymerization initiator to the solid surface. In our opinion adsorption of a reactive polymer is the most suitable technique for the immobilization of reactive components, in particular the initiator, on the solid surface. The copolymer (PM–MA) of peroxide monomer (PM) 5-tertbutyl-peroxy-5-methyl-1-hexen-3-yne and maleic anhydride was used in our experiments:



This copolymer satisfies the requirement of high adsorption ability, and can be synthesized easily. It is very suitable for investigations because of its solubility in organic solvents (toluene, alcohols, acetone) and water[14].

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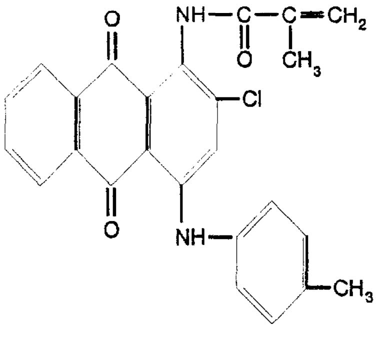
The most important requirements for the immobilization technique (indeed, apart from the attaching) may be listed as follows. First, the technique should be insensitive to the nature of the solid surface, therefore the same technique and initiator could be used for different matters. Secondly, the solid surface covered by the initiator should be wetted by the monomer solution well. The latter is very important especially for ultrafine powders. Finally, the surface concentration of the initiator should be taken into account. The choice of that depends on what value of grafted polymer is desirable to be grafted. It is important to estimate the amount of initiator which has to be immobilized and to take into account the smaller efficiency of the initiation reaction compared to the one in the bulk. In this paper we proved that these requirements could be met using a polymer initiator adsorption technique.

## EXPERIMENTAL

### Materials

A copolymer of PM–MA was obtained from solution radical polymerization[14]. A labelled copolymer (PM–MA–L) was obtained by adding a third comonomer-dye 1-methacryloyl-amino-2-chlorine-4-(p-tolyl)-aminoanthraquinol (MD):



All copolymers were purified by precipitation. Characteristics of the purified samples are given in *Table 1*. Polystyrene ($M_w \approx 100\,000$), polybutylacrylate ($M_w \approx 100\,000$) were synthesized by radical polymerization in solution. Polyethyleneglycol (PEG, industry product $M_n \approx 5000$) was used as received.

PM and MD were synthesized in the Department of Organic Chemistry Technology of Lvivska Polytechnica State University. Styrene, butylacrylate (industry products) were purified by distillation in residual pressure. Maleic anhydride (reagent grade) was used as received. Powders $TiO_2$ (industry pigment, $s = 1.0\,m^2/g$), ZnO (industry pigment, $s = 0.6\,m^2/g$), $Al_2O_3$ (reagent grade, $s = 0.1\,m^2/g$), and quartz powder prepared by milling of quartz glass ($s = 0.22\,m^2/g$) were treated by 2-propanol and dried at 120°C in a residual pressure of 10 mm of Hg. The specific surface at the powders ($s$) is given in brackets. The value of the latter was evaluated by sedimentation analysis technique. The reason for this choice of the technique will be discussed in a following paper. It is known that the surface of the pigment is usually covered by different oxides, but in our experiments we did not consider the specific nature of the surface. Different powders were used to vary the nature of the surface and particle size. Solvents (reagent grade) were used as received.

**Table 1** Characteristics of reactive copolymers

| Copolymer | Composition (% mol) PM | MA | MD | Molecular mass $M_n$ | $M_w$ |
|---|---|---|---|---|---|
| PM–MA | 52.5 | 47.5 | – | 2800 | 3200 |
| PM–MA–L | 52.2 | 47.3 | 0.5 | 3000 | 4800 |

### Adsorption experiment

The adsorption of the copolymer was performed by adding 10 ml of polymer solution to 2.5 g of powder, followed by agitation for 0.5 h. The suspension was then centrifuged and the concentration of the copolymer in the solution was determined by u.v.-visible spectra measurements for the labelled copolymer near the 450 nm band, or by measuring the refractive index (for the unlabelled copolymer). Adsorption isotherms were computed using the change of the copolymer concentration in the solution due to adsorption (the concentration of the copolymer before the contact with adsorbent was preliminary measured by the same technique). Simultaneously, following the centrifuge, the powder was separated, dried and the value of the copolymer on the surface of the particles was evaluated by pyrolysis at 500°C. Statistical error estimation showed very close values for these two methods of analysis. The relative error was not more than 10%.

### Contact angle measurement

Plates of glass, quartz, titanium, zinc and aluminium foil were used. The plates were preliminary heated at 400°C (300°C for Zn) for 2 h. It was assumed that the surface of these metal foil plates was covered by a corresponding oxide skin. The adsorption was performed by keeping the plate in contact with polymer solution for 0.5 h. Then the plate was washed with the same pure solvent three times. Each washing was performed with new pure solvent. Then the plate was dried at ambient temperature. A drop (0.001 ml) of double distilled water was put on the plate surface with a microlitre syringe. Diameter ($d$) and height ($h$) of the drop were measured by cathetometer. The contact angle value was computed as $\tan(\Theta/2) = 2h/d(\Delta\Theta = 1°)$.

## RESULTS AND DISCUSSION

### Regularities of the adsorption

The adsorption kinetics of PM–MA were investigated (*Figure 1*). The main amount of PM–MA adsorbs within 10 min. This period of quick adsorption is followed by a period of slight changes of the adsorption value ($A$). Adsorption equilibrium seems to be reached after 0.5 h. Most of the obtained isotherms of adsorption–desorption of PM–MA on the surface of different adsorbents were ordinary Langmuir-type isotherms (*Figure 2*). The adsorption was investigated in a wide range of polymer concentrations including the concentration of polymer chains cross-over region ($c^*$). In the case of PM–MA at high concentration ($c^* = 7.6\%$, acetone) the isotherm shows no difference in shape (*Figure 3*). *Figure 2* show a slight temperature dependence on plateau adsorption amount. This is usual

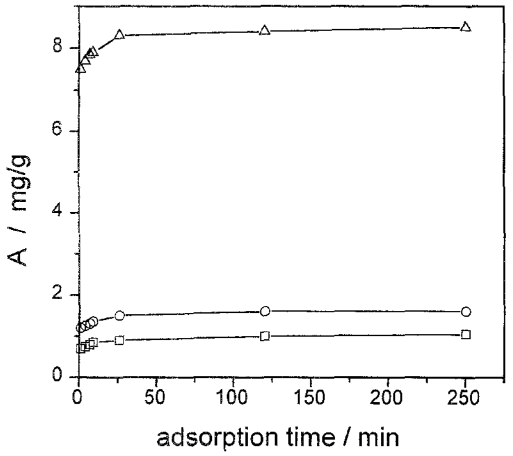


**Figure 1** Dependence of PM–MA adsorption on (△) $TiO_2$, (□) $Al_2O_3$ and (○) quartz powder from dioxane (293 K) on time

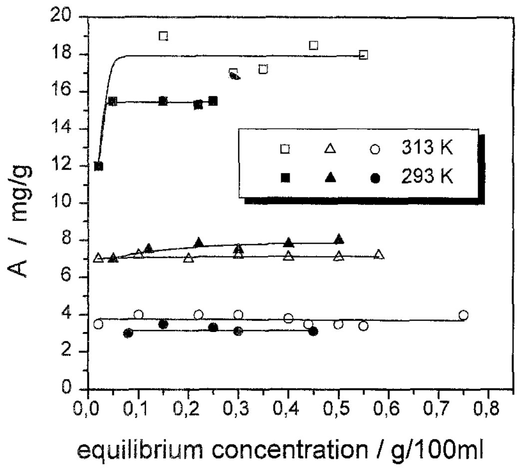


**Figure 2** Adsorption isotherms of PM–MA from toluene on the surface of (□, ■) $TiO_2$, (△, ▲) ZnO and (○, ●) quartz powder

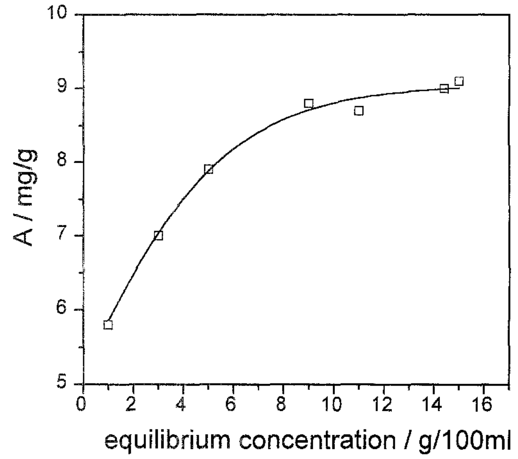


**Figure 3** Adsorption isotherm of PM–MA from acetone (293 K)

behaviour for polymer adsorption, but these relationships should be considered if the adsorption and polymerization experiments are carried out at different temperatures.

The effect of solvent and adsorbent nature on the adsorption amount was investigated. The plateau adsorption values on the surface of various adsorbents from the same solvent are close. The plateau adsorption amount on the same adsorbent from various solvents is substantially different (*Table 2*). *Figure 4* shows a relationship between the parameter being proportional to characteristic length of the macromolecule chain in the solution, and adsorption value (due to the Flory equation[15]). It was found that the adsorption of polymer is irreversible with respect to the solvent. To prove this the adsorption–desorption isotherm (*Figure 5*) was used. It will be clear from undermentioned data that it means apparent irreversibility being caused by molecular mass inhomogeneity of polymer (different fractions show different adsorption ability), and the dependence of conformation of the adsorbed macromolecule on the adsorption value.

**Table 2** Plateau adsorption values of PM–MA–L on the surface of various adsorbents from various solvents (293 K)

| Solvent | Intrinsic viscosity $[\eta]$ ($dl\,g^{-1}$) | A ($mg\,m^{-2}$) $SiO_2$ | $TiO_2$ | ZnO |
|---|---|---|---|---|
| Toluene | 0.07 | 11 | 14.3 | 11.7 |
| 2-Propanol | 0.09 | 8.7 | 9.8 | 8.0 |
| Acetone | 0.13 | – | 6.0 | – |
| 1,4-Dioxane | 0.13 | 8.0 | 9.5 | 10.0 |

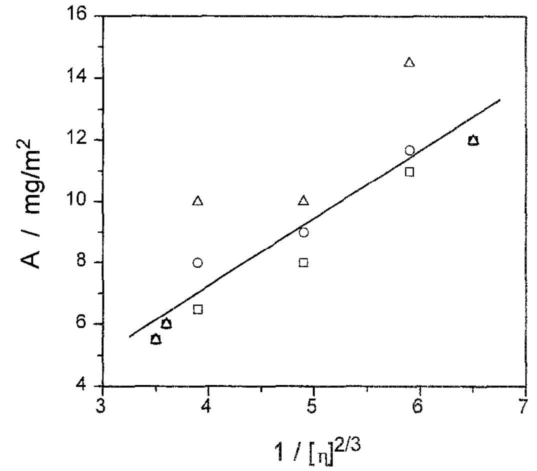


**Figure 4** Dependence $A - 1/[\eta]^{2/3}$ for PM–MA adsorption from various solvents: (○) quartz, (□) ZnO, (△) $TiO_2$ (293 K)

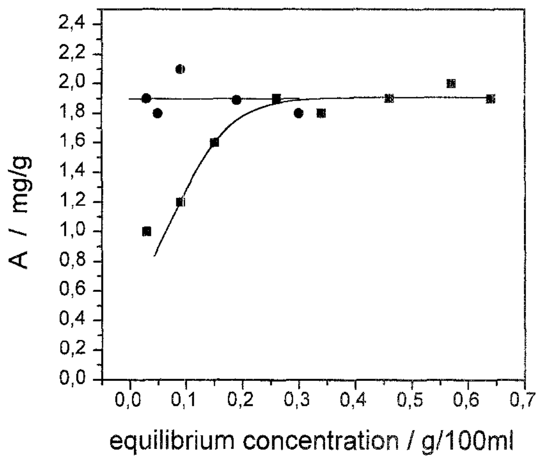


**Figure 5** Adsorption (■)–desorption (●) isotherms of PM–MA–L from 1,4-dioxane (293 K)

For the pragmatic consideration (immobilization of the initiator) it is important to know whether it would be easy to take the adsorbed PM–MA off the solid surface with the aid of a solvent. Such an experiment was performed. PM–MA was adsorbed on the powder surface from 1,4-dioxane. Then the sample of powder was washed by a pure portion of the solvent and kept in the solvent for 2 h. The sample was then dried in vacuum and the amount of PM–MA on the surface was determined by pyrolysis. The washing and change of the solvent by a new portion of solvent was carried out repeatedly (*Table 3*). The obtained data showed that even if repeated many times the treatment caused no change in the value of adsorbed PM–MA.

### *Dynamics of the adsorption layer*

Using PM–MA and labelled PM–MA–L copolymers the exchange between adsorbed copolymer and copolymer in the solution (*Table 4*) was investigated. In the first experiment the adsorption of both copolymers separately and in the mixture (1 : 1) was measured. In the second experiment the powder ZnO with adsorbed PM–MA–L was contacted with the solution of unlabelled PM–MA. In the third experiment the powder with adsorbed PM–MA was contacted with the solution of PM–MA–L. In both latter cases the concentration of polymer solution is adjusted to provide equal amount of the polymer in solution and on the surface. The total value of the adsorption ($A$) and adsorption of the labelled copolymer ($A_L$) was evaluated in all experiments.

*Table 4* shows that $A_L$ in the first experiment is equal to $1/2A$. This means that the adsorption ability of both copolymers is close. The second experiment shows that the unlabelled copolymer expels approximately 30% of labelled copolymer. The third experiment shows that the labelled copolymer expels 30% of unlabelled copolymer. Consequently, 60% of the adsorbed polymer exchanges into polymer in solution, but 40% is irreversibly adsorbed. But, this irreversibility could also be apparent and explained by molecular inhomogeneity. If some portion of the copolymer is adsorbed preferentially this means that the system adsorbent–adsorbate–solvent in the second and third experiments occurs to be enriched with most the adsorption-active portion by the preliminary adsorbed copolymer.

**Table 3** Dependence of $A$ (mg g$^{-1}$) for PM–MA on number of washing by pure solvent (1,4-dioxane)

| | Number of washings | | |
|---|---|---|---|
| Adsorbent | 1 | 2 | 10 |
| Quartz powder | 2.0 | 2.0 | 2.0 |
| $TiO_2$ | 11.2 | 11.0 | 11.0 |
| ZnO | 6.0 | 6.0 | 6.0 |

**Table 4** Exchange of PM–MA and PM–MA–L between adsorption layer and solution in 2-propanol (293 K)

| | $A$ (mg g$^{-1}$) | | |
|---|---|---|---|
| Experiment | PM–MA + PM–MA–L ($A$) | PM–MA–L ($A_L$) | $A_L/A$ |
| Mixture of PM–MA and PM–MA–L (1 : 1) | 4.6 | 2.30 | 0.50 |
| PM–MA replace PM–MA–L | 4.6 | 3.30 | 0.72 |
| PM–MA–L replace PM–MA | 4.6 | 1.47 | 0.32 |

Some aspects of the dynamics of the PM–MA adsorption layer were investigated by contact angle technique. The plate surface was covered by adsorbed polymer. The contact angle of wetting of the plate by water was measured following the extraction of the plate from polymer solution and drying. The first measurement was followed by contact of the plate with another solvent. Then the procedure was repeated again. The sequence of treatment by solvent was different in two series of experiments. The data are shown in *Tables 5* and *6*. Arrows show the succession of the treatment by solvents.

Obtained data show that if the adsorption is carried out using a good solvent (dioxane for PM–MA) the subsequent treatment by a poor solvent (toluene) will cause no change of contact angle despite the fact that $\Theta$ for the plate obtained by the adsorption from toluene is lower (see magnitude of $\Theta$ in second rows of both tables). If PM–MA is adsorbed on the plate surface from the poor solvent (toluene), the subsequent treatment by the good solvent (dioxane) will effect the change of $\Theta$ to the value close to the one on the plate being obtained, due to the adsorption from dioxane. The subsequent treatment effects no change of the angle. Consequently, the property of the surface covered by PM–MA is caused by the adsorption conditions and subsequent treatment. Using the best solvent from the rank it is possible to save the structure of the layer in these solvents in spite of subsequent treatment by other solvents from this rank.

### *Competitive adsorption*

If adsorbed PM–MA is used as an initiator of graft polymerization it is necessary to consider the fact that ungrafted polymer could be formed due to the polymerization in the bulk. This ungrafted polymer potentially

**Table 5** The contact angle of water on modified by PM–MA plate surface as a function of the sequence of treatment by solvents

| | The solvent | | |
|---|---|---|---|
| Material of the plate | 1,4-Dioxane→ | Toluene → | 1,4-Dioxane |
| Glass | 21 | 22 | 22 |
| Quartz | 37 | 38 | 38 |
| $Al_2O_3$ | 70 | 70 | 70 |
| $TiO_2$ | 85 | 87 | 86 |
| ZnO | 100 | 100 | 99 |

**Table 6** The contact angle of water on modified by PM–MA plate surface as a function of the sequence of treatment by solvents

| | The solvent | | | |
|---|---|---|---|---|
| Material of the plate | Toluene → | 1,4-Dioxane → | Toluene → | 1,4-Dioxane |
| Glass | 20 | 38 | 40 | 40 |
| Quartz | 33 | 37 | 37 | 38 |
| $Al_2O_3$ | 73 | 75 | 74 | 74 |
| $TiO_2$ | 60 | 90 | 90 | 90 |
| ZnO | 75 | 100 | 100 | 100 |

**Table 7** Plateau amount of PM–MA–L adsorption from the mixture with competitive polymer on the surface of quartz powder from 1,4-dioxane (293 K)

| Competitive polymer | *A* (mg g$^{-1}$) |
|---|---|
| – | 1.8 |
| Polystyrene | 2.5 |
| Polybutylacrylate | 3.4 |
| PEG | 3.4 |

**Table 8** Adsorption amount of PM–MA–L on the adsorbents initially covered by competitive polymer (2-propanol, 293 K)

| | *A* (mg g$^{-1}$) | | |
|---|---|---|---|
| Competitive polymers | $SiO_2$ | ZnO | $TiO_2$ |
| – | 1.9 | 4.8 | 9.8 |
| Polystyrene | 2.2 | 5.6 | 9.3 |
| Polybutylacrylate | 1.7 | 5.4 | 15.6 |
| PEG | 1.9 | 4.8 | 8.7 |

could displace PM–MA from the surface if it has higher adsorption ability. To assess this situation the cooperative adsorption of PM–MA–L from mixtures with a series of polymers which potentially could be grafted to the solid surface (*Table 7*) was investigated. This table shows that adsorption of PM–MA–L from mixtures with polystyrene, polybutylacrylate and polyethyleneglycol is higher compared to the adsorption value from pure solvent.

In the second experiment the surfaces of different adsorbents ($SiO_2$, $TiO_2$, ZnO) were initially covered by various polymers by adsorption from solution. Then the adsorbent brought into contact with PM–MA–L solution and the adsorption value of the copolymer was measured. It turned out that PM–MA–L displaced the preliminary adsorbed polymers (*Table 8*).

### *Effect of the solvent and agitation*

It turned out that the nature of a solvent affects the adsorption not only due to the effect of chain conformation but also due to the dispersity of the adsorbent. It is very important for the ultrafine powders. In line with this consideration, the solvent and agitation have similar effects on adsorption. It turned out that consideration of the problem requires a special experiment which will be discussed in a following paper.

## CONCLUSION

It was found that the adsorption process of the reactive copolymer on a solid surface is a suitable way to immobilize the initiator of radical graft polymerization. Using the characteristic features of apparent irreversibility of PM–MA adsorption, one can prepare coverings of reactive polymer sufficiently resistant to further treatment (solvent, competitive polymer, temperature). On the other hand, the equilibrium and reversible process of adsorption permits reproducibility in obtaining specimens of solid matter with immobilized initiator layers of a given structure.

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