Influence of polyethylene glycol concentration on morphology of polypropylene membranes

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This work studied the influence of polyethylene glycol (PEG) concentration on the polypropylene membranes morphology. Polypropylene membranes were modified with argon plasma and then immersed in PEG solution with various concentration between 50-80%. Changes of membranes morphology were observed by scanning electron microscope, Fourier transform infrared spectroscopy and contact angle measurements.

Key words: membrane modification, polyethylene glycol, polypropylene membrane

IIntroduction

Membrane Processes

Membrane processes are a large group of techniques for the separation of gases and liquids mixtures. Membrane is defined as the continuous phase, separating two fluids, which is a barrier for the flow of contaminants. It can be used for particle separation with dimensions from a few microns to a few nanometers (Ceynowa, 2009).

There are a lot of different approach for dividing membrane processes. The most common one is based on the type of driving force [2]. This division includes processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis (Ceynowa, 2009).

A major problem connected with membrane techniques is microbial contaminations. These impurities may be the source of infections, diseases and even deaths. This problem is particularly dangerous in the food industry, medicine and the pharmaceutical industry. Moreover there is the problem of biofilm formation on the membrane surface which is called biofouling. During biofouling biological contaminants significantly reduce the effectiveness of membrane separation. It is mainly associated with the formation of a filter cake on the membrane surface and clogging of the pores (Ceynowa, 2009).

Membrane modification

During membrane modification surface properties can be changed. The phenomena of adsorption and adhesion of undesirable substances on the membrane surface can be prevented. New functional layer can be created by grafting of suitable functional groups (Ulbricht, M. , 2006) (Yu, Zhang, Wang, Brash and Chen, 2011).

Polymers used for membrane manufacturing are typically of hydrophobic nature. Grafting hydrophilic macromolecules may have a beneficial effect on the membrane filtration process. For many applications, the introduction of functional groups having a charge may be the first choice. The negative surface charge of the membrane will have a beneficial effect on the separation of biological pollutants, since most proteins exhibit a negative charge (Ulbricht, M. , 2006).

Plasma treatment for membrane surface activation

Plasma is the fourth state of matter containing ionized gas molecules. Significant portion of the molecules are electrically charged (Bryjak, M., Janecki, T.,Gancerz, I. and Smolińska, K., 2009).

Plasma surface modification (PSM) has become very popular among the available methods of surface modification. The last decade was crucial in understanding the mechanism of plasma processes. Often, the plasma modification is only a first stage in the polymer grafting or immobilisation of biomolecules (Kotra, K., Piątkiewicz W., 2013).

The purpose of plasma modification is to obtain a specific surface properties such as mechanical strength, adhesion, surface conductivity and biocompatibility. During such a modification the polymer surface is cleaned, etched and cross-linked (Kotra, K., Piątkiewicz W., 2013).

By applying different gases, such as argon, oxygen, nitrogen, fluorine, carbon dioxide and water vapor, specific surface properties for a particular application can be obtained. For example, oxygen plasma can increase the surface energy, while fluorine plasma can reduce this energy. Often different functional groups responsible for the increase in the hydrophilicity of the material are introduced into polymer surface (Kotra, K., Piątkiewicz W., 2013).

For technological applications, including surface modification, low temperature plasma is used. A particular advantage of processes using „cold" plasma is a large number

of process variables which may be controlled over a wide range. The most important parameters which can be almost freely chosen are pressure, structure of the electromagnetic field, geometry of discharge, the characteristics of the feed gas. Characteristics of the power and geometry of the electrodes determine the type of electrical discharge (Kotra, K., Piątkiewicz W., 2013).

Polyelectrolytes
Polyelectrolytes are polymers having positively or negatively ionized functional groups. They dissociate in aqueous solutions. The properties of polyelectrolytes depend on many factors (Dobrynin and Rubinstein, 2005).

Their unique properties are used in a number of technological and industrial areas. Polyelectrolytes represent a large part of the biological molecules, for example polypeptides, glycosaminoglycans or DNA (Banerjee, I., Pangule, R. and Kane, R., 2011).

Materials and method

Materials
Polypropylene (PP) capillary membranes with diameter 300 µm and wall thickness 150 µm were purchased from the Polymem® company. Polyethylene glycol (PEG) with average molecular weight 200 kDa was supplied by Fluka.

Experimental setup
Plasma modification process was carried out in a Dionex Series 2000 Plasma Processing Reactor supplied with argon gas as illustrated in Fig. 1. Membrane was placed in the field of RF plasma inside heat resistant cylinder-shaped chamber.

Membrane modification
PP membranes were cut into 150 mm long pieces. Before plasma modification membranes were rinsed in ethanol to remove any impurities from the surface and pores, Then rinsed in water and dried in a vacuum oven for 60 minutes.

Modification process was conducted in a plasma reactor unit Dionex Series 2000 Plasma Processing Reactor in argon atmosphere under pressure of 3.5 Pa and temperature around 25-27 ^{0}C. Various combinations of plasma powers (25 or 50 W) and exposure times (60, 180 or 240s) were used.

After plasma treatment, samples were modified with polyelectrolyte. The activated membranes were placed in the previously prepared polyethylene glycol solution with various concentration between 50-80% and stirred for 2 hours while maintaining a constant temperature of 60^{0}C. At the end, each sample was washed for 5 minutes in distilled water to remove non-polyethylene glycol chains.
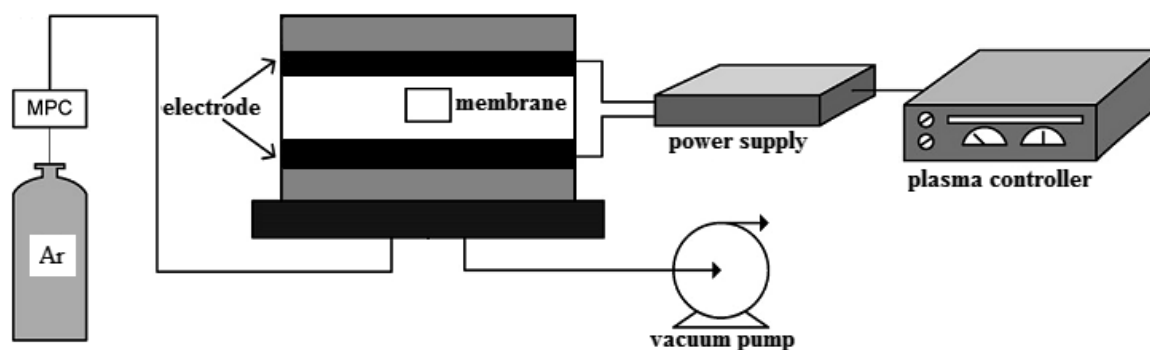

Fig. 1. Plasma reactor unit with argon supply (Kochan J., Wingents, T., Wong, J.E., and Melin, T., 2010).
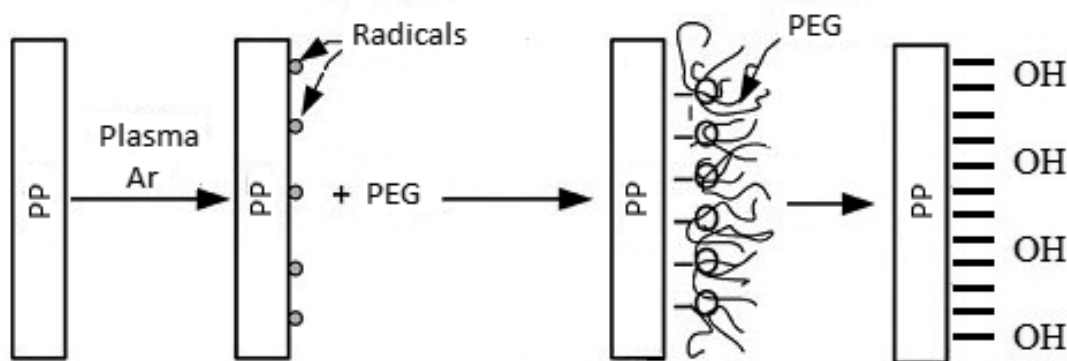

Fig. 2. Mechanism of polypropylene membranes modification with polyethylene glycol (Narębska, P.)
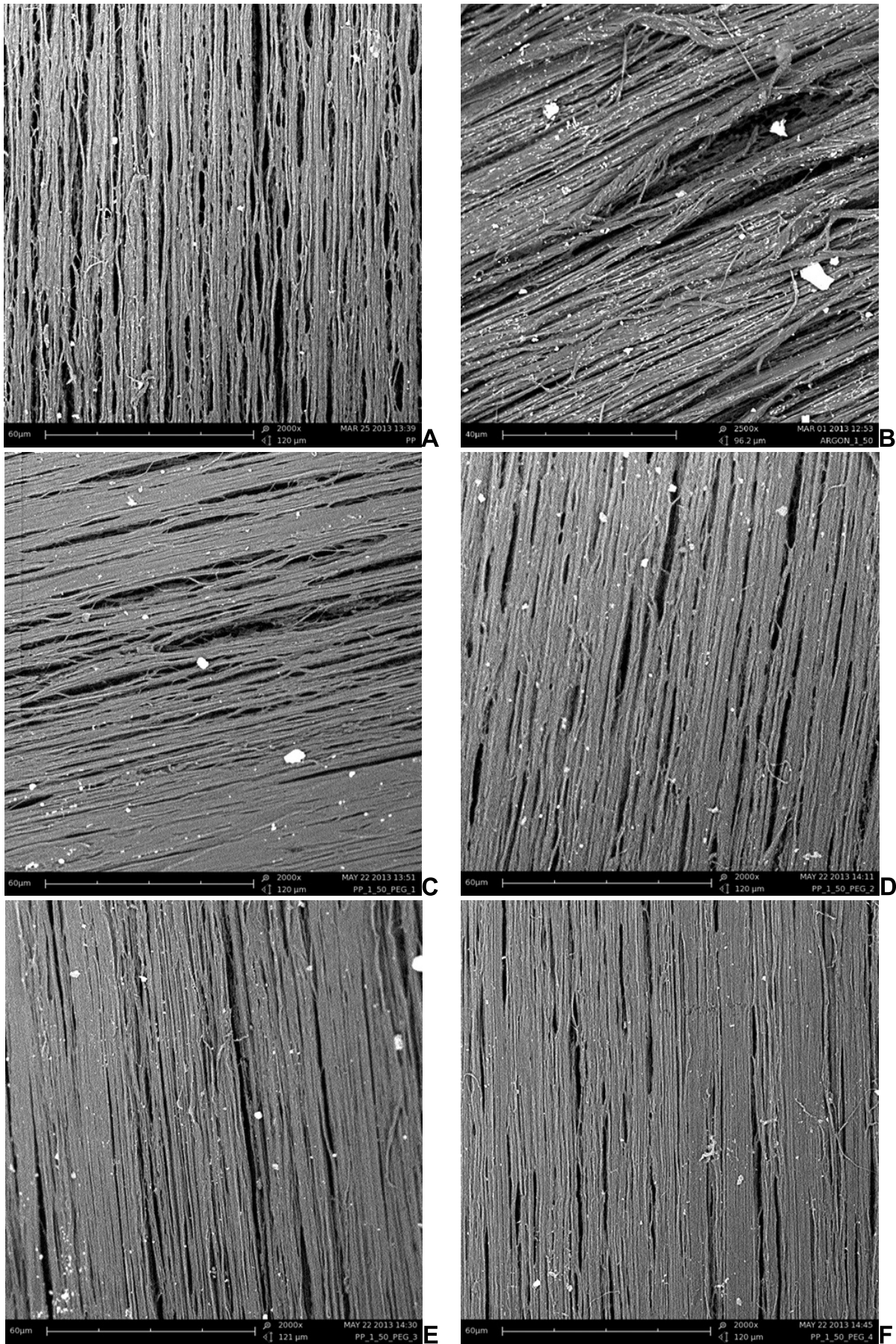
Fig. 3. Morphology of the PP membranes (A) - non-modified, (B) - plasma modification (60s, 50W), (C) – modification with 50% PEG, (D) – modification with 60% PEG, (E) – modification with 70% PEG, (F) – modification with 80% PEG.

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Membrane characterizations

Membrane morphology study

The surface morphology of the membranes were characterized by scanning electron microscopy (SEM). All samples were dried in vacuum for 12h at room temperature. The scanning of surface image was conducted at an accelerating voltage of 10 kV.

Fourier transform infrared spectroscopy (FTIR) study

To investigate the chemical structures of PP unmodified membranes and membranes modified with polyelectrolytes, Nicolet 6700 FT-IR was used. Each spectrum was obtained by cumulating 32 scans at a resolution of 4 cm^{-1}.

Water contact angle

Membrane hydrophilicity was studied by measuring contact angles (Krüss Processor Tensiometer K12) of the membranes at 25°C. PP capillary membranes were immersed into water and tested 5 times. The average of measured values was taken as its water contact angle.

The Wilhelmy-method was used to determine surface tension of water and contact angle.

Results and discussion

Morphology of the modified PP membranes

The membrane surface morphologies were presented by SEM images. The images below show membranes modified with plasma power of 50W within 60 seconds time process.

The PEG concentration were between 50 and 80 wt%. Results for other plasma parameters are analogous.

Presented results show that the modification by argon plasma affected PP membrane morphology. The membrane surface had been damaged while plasma modification. There are visible cracks of the surface. Moreover, membrane surface seems to be peeled off. Such changes may indicate higher water permeability and surface porosity.

Pictures C-F show impact of different PEG concentration on membranes structure. It can be deduced that the surface structure is more dense for higher PEG concentrations. Moreover, based on SEM pictures, it can be concluded that the membranes surface were covered by PEG. Unfortunately it is not possible to determine the quantity of the grafted polyelectrolyte.

Chemical structures on membrane surface

The chemical structures of the modified and non-modified membranes were shown by FTIR images on Fig. 4..

Based on data above, it appears that there is change in number of OH$^-$ groups (3600-3000 cm^{-1}). However, in present study only qualitative analysis was performed. Thus, it can be only stated that modification with polyelectrolytes took place.

Presented results show also that length of plasma modification affect on future polyelectrolyte modification. The longer plasma modification the lower PEG grafting.

Even though PEG is the most commonly used substance to impart protein resistance to a surface, it has a tendency to auto-oxidize and form aldehydes and ethers in the
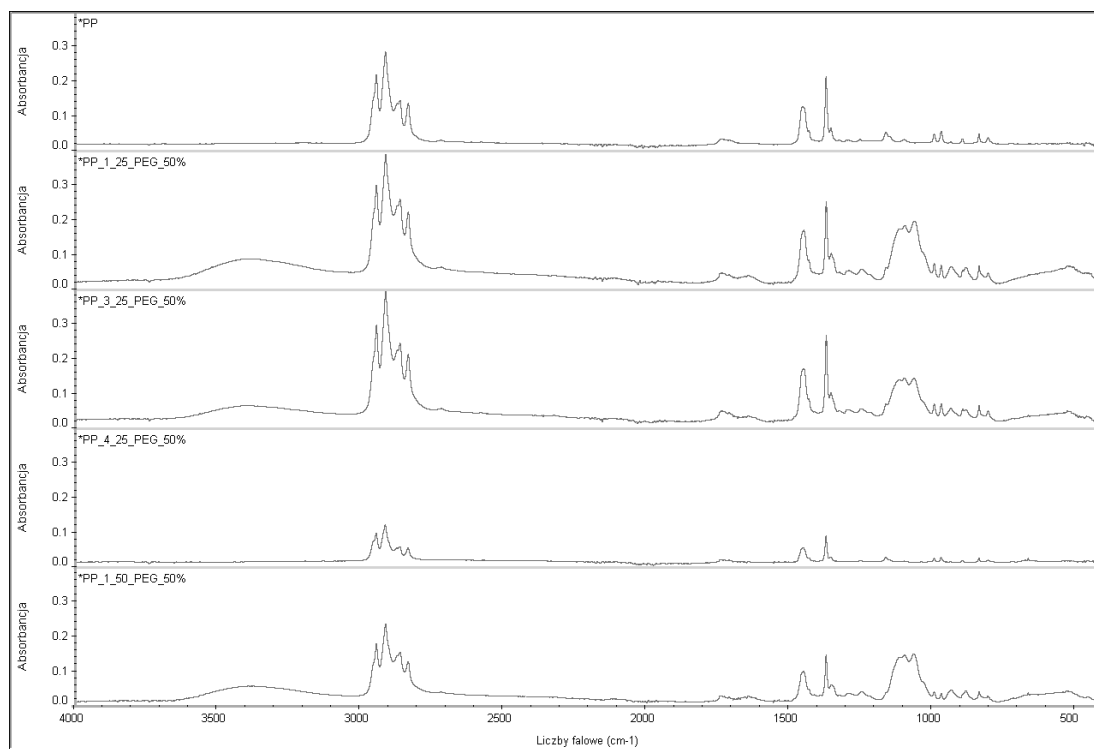

Fig. 4. FTIR results for 50% of PEG concentration and different plasma conditions

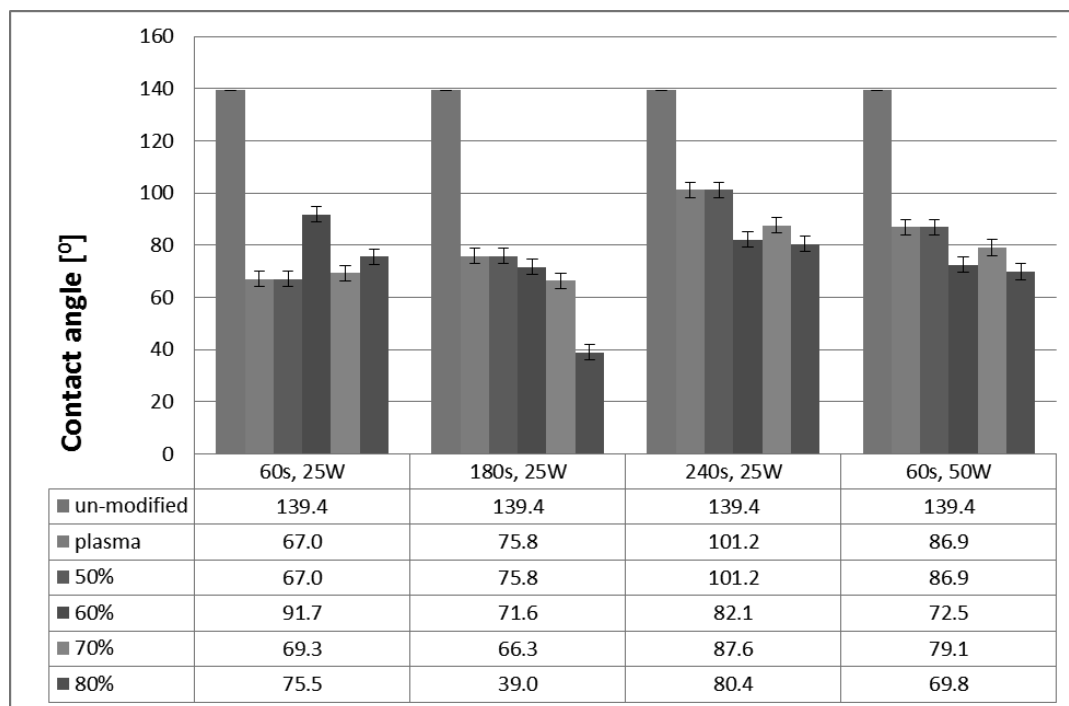|	60s, 25W	180s, 25W	240s, 25W	60s, 50W
■ un-modified	139.4	139.4	139.4	139.4
■ plasma	67.0	75.8	101.2	86.9
■ 50%	67.0	75.8	101.2	86.9
■ 60%	91.7	71.6	82.1	72.5
■ 70%	69.3	66.3	87.6	79.1
■ 80%	75.5	39.0	80.4	69.8

Fig. 5. Contact angle results for all plasma conditions and PEG concentration

presence of oxygen, which causes the surfaces to lose their protein resistance ability (Banerjee, I., Pangule, R. and Kane, R., 2011). This phenomenon can be observed by small change in 1700 cm⁻¹ what indicating the presence of carbonyl groups in aldehydes.

Contact angle of the modified membranes
Obtained results are shown in Fig. 5.

Based on data above, it can be concluded that contact angle depends on plasma modification parameters. It can be observed that plasma modification time has influence on contact angle. The most hydrophilic membrane was obtained for 60s of plasma modification. Higher hydrophilicity can be obtained by shortening the time of the modification and reduction in plasma power.

Correlation between PEG concentration and contact angle cannot be deduced from presented results.

Result for 180 seconds, 25W and 80% PEG concentration is not reliable because the sample could not be dried and was constantly.

Conclusions

Morphology of the membranes surface was changed by PEG and argon plasma modification. In case of all modified membranes there where some visible changes in membrane surface observed under scanning electron microscope. It appears that the membrane surface had been damaged while plasma modification. It can be observed that the surface structure is more dense for higher PEG concentrations. Such changes may indicate changes in water permeability and surface porosity.

Moreover, different plasma conditions affects on degree of grafting of polyelectrolyte. Based on FT-IR data, it appears that there is change in number of OH⁻ groups (3600-3000 cm⁻¹). Moreover, there is small change in 1700 cm⁻¹ what may indicate the presence of carbonyl groups in aldehydes created by PEG auto-oxidation.

Contact angle results show that higher hydrophilicity can be obtained by shortening the time of the modification and reduction in plasma power. However, correlation between PEG concentration and hydrophilicity cannot be deduced from presented results.

It is necessary to carry out the same research on different types of membranes and find a method to correlate the fundamental parameters of membrane surface modification.

Acknowledgment

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