TRANSPORT OF GASES AND ORGANIC VAPOURS THROUGH MEMBRANES MADE OF POLY(AMIDE-IMIDE)S CROSSLINKED WITH POLY(ETHYLENE ADIPATE)

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Transport of permanent gases (N_2, O_2, CO_2) and of saturated organic vapours of benzene, toluene and methanol through membranes based on poly(ethylene adipate)-crosslinked poly(amide-imide)s was studied. The membranes containing more than 50 wt.% of non-polyimides showed higher permeability coefficients (by 2–3 orders) for the organic vapours than for the gases.

Keywords: Crosslinked poly(amide-imide)s; Membrane transport; Gas separation; Volatile organic vapour separation; Copolymers; Crosslinked polymers.

Membrane separation processes rank among new types of mass-separation techniques which have been applied in various technological processes. They also become important for separation of volatile organic compounds (VOC) from air. Separation of organic vapours from air by conventional methods such as absorption and adsorption has the disadvantage of being a discontinuous process requiring regeneration and thus shifting the problem of pollution from air to water and dumping grounds. Alternative thermal treatment at 700–1 000 °C requires additional energy and, in addition, generates toxic components[1].

Mass transport through a non-porous polymeric membrane is characterized by permeabilty, diffusion and solubility coefficients which depend particularly on the nature of both the membrane and the penetrant. The permeability in a polymer depends on the solubility and diffusivity of the permeating species in that polymer.

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Non-porous membranes prepared from elastomeric polymers having both low glass transition temperatures (T_g) and non-negligible sorption of some organic solvents were successfully tested for the preferential removal of organic vapours from air[1–3]. Many solvent-containing air exhaust streams are produced in high-temperature industrial ovens. Therefore, not only the membranes with high permeability and good selectivity but also with acceptable thermal and chemical stability are needed.

Aromatic polyimides (PI) rank among the most thermally (up to 200–250 °C) and chemically stable polymers[4]. Non-porous polyimide membranes show high separation factors (selectivity) for separation of mixtures of permanent gases but low permeability for both permanent gases and organic vapours[5]. Asymmetric membranes and hollow-fiber membranes based on polyimide and poly(ether-imide) materials were successfully employed in separation of organic vapours from permanent gases (air)[6,7].

The non-porous membranes based on linear poly(imide-siloxane) copolymers showed a considerable increase in the permeabilities to organic vapours in comparison with homopolyimides. Nevertheless, the results were irreproducible, probably due the irreversible changes of the polymer structure after penetration of the organic medium[5].

Stability of polymeric materials can be improved by crosslinking. From this point of view, it appeared useful to prepare membranes based on PI crosslinked with a suitable component (with a lower T_g than that of a homopolyimide) and to test their transport properties for organic vapours and permanent gases.

This work deals with transport properties of saturated organic vapours (benzene, toluene, methanol) and permeability to gases (nitrogen, oxygen, carbon dioxide) of isotropic non-porous membranes based on poly(ethylene adipate)-crosslinked poly(amide-imide)s.

EXPERIMENTAL

Chemicals

Pyromellitic dianhydride (PMDA) was heated overnight to 160 °C in vacuum before use. 4,4′-Oxydianiline (ODA) was used as received. 4-Methyl-1,3-phenylene diisocyanate-terminated poly(ethylene adipate) (TDI-PEA) with a number average molar mass M_n = 1 300 g mol^{-1} and phenol (all Aldrich) were used as received. 1-Methyl-2-pyrrolidone (NMP) (Merck) was distilled in vacuum over phosphorus pentoxide and stored in an inert atmosphere.

Synthesis of Polymeric Materials

Synthesis of Poly(amic Acid) PMDA-ODA

All glassware was dried in an oven at 120 °C for 3 h before use and the syntheses were carried out under an inert atmosphere.

The polyimide precursor, poly(amic acid) based on PMDA and ODA [PAA(PMDA-ODA)], was prepared by the reaction of equimolar amounts of the dianhydride and the diamine in NMP (solid content 10 wt.%) at room temperature for 24 h (ref.[4]).

Preparation of PMDA-ODA–TDI-PEA Mixture[8,9]

A poly(amic acid) solution in NMP and a TDI-PEA terminated with phenol (Ph-TDI-PEA; prepared by heating TDI-PEA and PhOH in molar ratio 1 : 2 at 80 °C for 3 h) were mixed at room temperature for 2 h in various weight ratios.

Membrane Preparation

A solution of PMDA-ODA or a PMDA-ODA–Ph-TDI-PEA mixture in NMP was cast onto a glass plate with a casting knife. After evaporating the solvent, the films based on PMDA-ODA were thermally imidized at 150, 200, 300 and 330 °C for 1, 2, 1 and 0.5 h, respectively; the films based on PMDA-ODA–Ph-TDI-PEA mixtures at 150, 200 and 250 °C for 1, 2 and 1 h, respectively. The membranes tested were slightly opalescent films with a thickness of 20–50 μm.

Apparatus

The differential permeation method was used to determine the permeability coefficient. This method makes it possible to determine also the diffusion coefficient of the permeant in a polymer membrane from an asymptotic solution of the relevant diffusion equations[10,11].

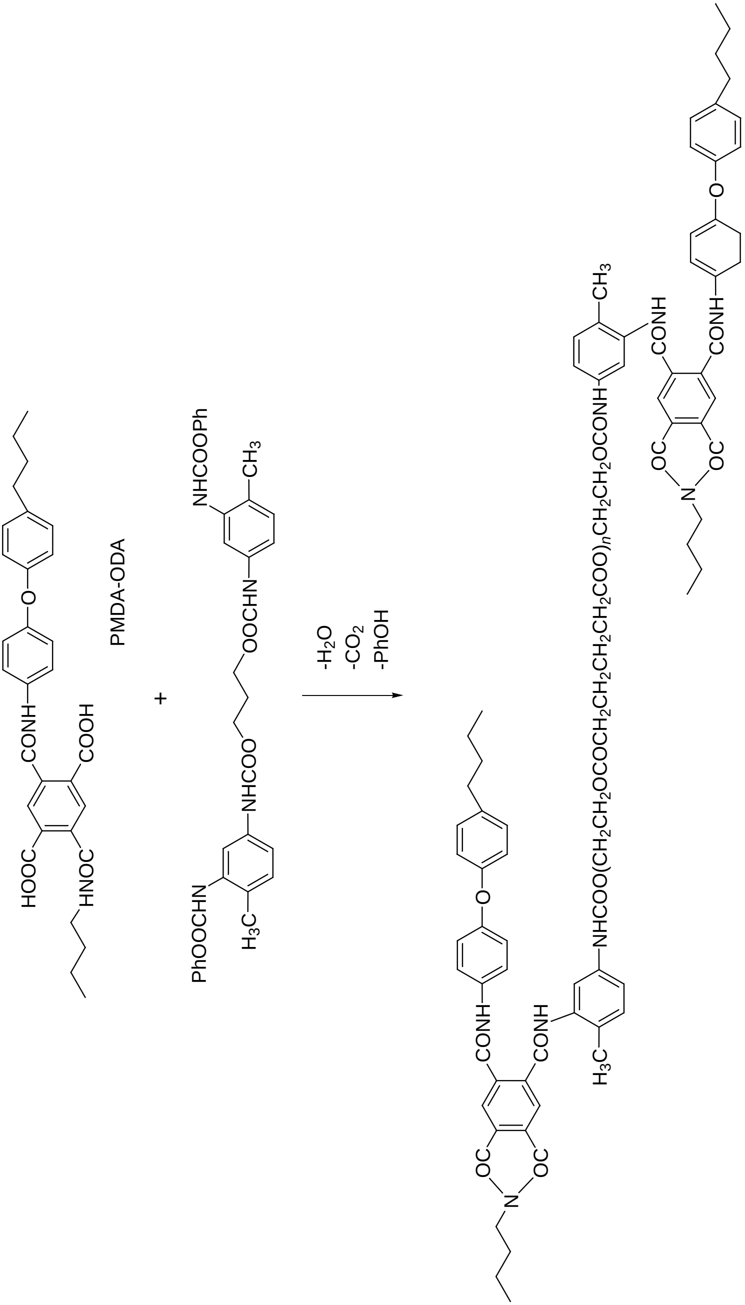
The sorption of an adsorbate by a membrane was evaluated using an apparatus consisting of a spiral quartz balance placed in a thermostatted glassjacket connected to a manometer[11].

Dynamic thermogravimetric measurements were performed in air with a DuPont 990 Thermal Analyzer, module 951 (heating rate 10 °C min^{-1}).

RESULTS AND DISCUSSION

Polymeric materials based on the poly(amide-imide)s (PAI) with poly(ethylene adipate) (PEA) crosslinks were prepared. The theoretical amount of PEA was 0 (PAI-PEA 100/0), 20 (PAI-PEA 80/20), 50 (PAI-PEA 50/50), 60 (PAI-PEA 40/60) and 80 wt.% (PAI-PEA 20/80). The starting precursors were the polyamic acid based on pyromellitic dianhydride and 4,4′-oxydianiline (PMDA-ODA) (Scheme 1) and 4-methyl-1,3-phenylene diisocyanate-terminated poly(ethylene adipate) (TDI-PEA) with M_n = 1 300 g mol^{-1}.

The remaining isocyanate groups in TDI-PEA were end-capped with phenol to prevent their premature reaction when mixing both components


PMDA-ODA
HOOC
COOH
CONH
HNOC
O
+
PhOOCHN
NHCOOPh
H3C
CH3
NHCOO
OOCHN
-H2O
-CO2
-PhOH
OC
N
CONH
NHCOO(CH2CH2OCOCH2CH2CH2CH2COO)nCH2CH2OCONH

SCHEME 1

(see Experimental). Phenol was released in the course of thermal treatment of thin layers (10^{-1} mm) prepared from the reaction mixture on glass supports and the deprotected isocyanate groups of TDI-PEA reacted with the carboxylic groups of PMDA-ODA under the formation of amide groups (Scheme 1).

The obtained materials were analysed by IR spectroscopy. The absorption bands corresponding to the amide groups (at *ca* 1 680 cm^{-1}), methylene groups (2 950 cm^{-1}) and urethane groups (3 350 cm^{-1}) became more distinct with the increasing content of the PEA crosslinks (these bands were not observed in the spectrum of PAI-PEA 100/0).

Resistance of these materials to selected solvents (methanol and benzene) was evaluated by their weight change after immersion for 60 days into the medium. The weight loss (25 wt.% in methanol and 11 wt.% in benzene) was found for PAI-PEA 20/80 only. In this case, the system contains less carboxylic groups than isocyanate groups and a part of the poly(ethylene adipate) crosslinker remains unreacted in the system (polyamide crosslinked with PEA (polyamide : PEA = 25 : 75 wt.%) was in fact obtained).

The temperature corresponding to the 10 wt.% weight loss in the course of thermooxidative degradation decreased with increasing content of PEA in the materials (from 600 °C for PAI-PEA 100/0 to 330 °C for PAI-PEA 20/80). All the materials showed no weight losses up to 270 °C.

Our main attention was paid to the study of transport properties of the membranes made of these polymeric materials. The transport of saturated vapours of benzene, toluene and methanol and permanent gases (nitrogen, oxygen and carbon dioxide) was monitored. By using a differential permeameter modified for monitoring transport properties of mixtures organic vapour–permanent gas, it was found that the presence of a permanent gas did not almost influence the permeability coefficients of organic vapours. Therefore, transport properties of gases and vapours could be monitored separately (such a procedure is experimentally easier). The accuracy of the measurements was ±5%.

The permeability coefficients of both organic vapours and permanent gases were dependent on composition of the material. Membranes based on PAI-PEA 80/20 and PAI-PEA 50/50 showed similar behaviour to the membrane based on PAI-PEA 100/0. Their permeabilities were very low and it was not possible to determine the corresponding coefficients. On the contrary, the permeability coefficients were reliably determined for membranes with higher PEA contents (PAI-PEA 40/60 and PAI-PEA 20/80). The permeability coefficients of organic vapours were by 2 to 3 orders of magnitude higher than those of gases (Table I).

The diffusion and sorption coefficients are also summarized in Table I. The diffusion coefficients were calculated using data obtained by the differential permeation method[10]. Due to the low (but measurable) permeability of permanent gases even through the PAI-PEA 40/60 and PAI-PEA 20/80 membranes, the diffusion coefficients were not calculated. Sorption of permanent gases in these materials is also very low and it was not possible to determine sorption coefficients by using an apparatus employed in this work.

The diffusion and sorption coefficients of all organic penetrants are higher for the PAI-PEA 20/80 membrane in comparison with the PAI-PEA 40/60 membrane. Both segmental mobility – influencing a free volume (reflected in the diffusion coefficient) – and solubility of organic penetrants (reflected in the solubility coefficient) increase with increasing PEA content. In accord with that, the permeability coefficients for PAI-PEA 20/80 are higher in comparison with PAI-PEA 40/60 (permeability coefficient is proportional to both diffusion and sorption coefficients[11]). Nevertheless, the permeability coefficients, *P*, are higher than those calculated by means of the relation $P = DS$, where D is the diffusion coefficient and S the solubility coefficient. It seems that the relation is not valid in this case.

TABLE I
Transport parameters of permanent gases and organic vapours in polymeric membranes

Gas/ vapour	PAI-PEA 40/60			PAI-PEA 20/80		
	10^{16} P mol Pa^{-1} m^{-1} s^{-1}	10^{13} D m^2 s^{-1}	10 S mol m^{-3} Pa^{-1}	10^{16} P mol Pa^{-1} m^{-1} s^{-1}	10^{13} D m^2 s^{-1}	10 S mol m^{-3} Pa^{-1}
Carbon dioxide	5.6	–	–	15.1	–	–
Oxygen	2.5	–	–	3.2	–	–
Nitrogen	0.7	–	–	2.1	–	–
Benzene	2 169	3.18	1.70	[a]	–	3.73
Toluene	3 039	2.60	1.03	12 760	7.50	5.05
Methanol	5 434	13.00	1.50	18 270	27.90	2.87

[a] Too high to be measured. *P*, *D* and *S* are the permeability coefficient, diffusion coefficient and the solubility coefficient, respectively.

Separation factors (selectivities) organic vapour–permanent gas are summarized in Table II. They were calculated as the ratio of permeability coefficients of the corresponding media. Selectivities reach values of 10^2–10^3. The highest selectivities were obtained for a mixture of combination of organic penetrant and nitrogen, the lowest for organic penetrant–carbon dioxide mixture.

Using membranes PAI-PEA 20/80 and PAI-PEA 40/60, higher[3,6] or comparable[2] separation factors for organic vapour–permanent gas mixtures were obtained compared with results found in the literature. A very important property of these membranes is their resistance to penetrants. The membrane based on PAI-PEA 40/60 appears the most suitable for the purpose. In multiple organic vapour–permanent gas cycles, permeation coefficients varied within the accuracy of measurement (±5%).

The treatment of data obtained with a sorption apparatus will be discussed in detail in a forthcoming publication.

TABLE II
Separation factors for organic vapour–permanent gas mixtures

Gas/vapour mixture	PAI-PEA 40/60			PAI-PEA 20/80		
	N_2	O_2	CO_2	N_2	O_2	CO_2
Benzene	3 099	868	387	–	–	–
Toluene	4 341	1 215	542	6 033	3 988	845
Methanol	7 763	2 173	970	8 700	5 709	1 210

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