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The studies on novel magnetic polyimide inorganic-organic hybrid membranes for air separation

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ABSTRACT

This paper focuses on the preparation and characterization of a new type of polyimide magnetic inorganic-organic hybrid membranes and analysis of their potential application in synthetic air enrichment with oxygen. These hybrid membranes were based on linear (ODPA-MDA) and hyperbranched (ODPA-MTA) polyimide matrix and NdFeB magnetic microparticles. It was conducted the characteristics of their gas permeation, magnetic, thermal, mechanical and rheological properties. It was stated that the application of polyimides as polymer matrices and magnetic powders as fillers (especially with higher content and lower particle size) allowed to create unusual hybrid membranes with the improved gas transport and separation properties (coefficient's ***P***, ***D***, ***S*** and ***α***), mechanical and rheological parameters (***E***, ***G′***, ***G″*** and ***tan δ***) and the excellent thermooxidative stability. All this will allow for their future potential application in the separation of air.

1. Introduction

The intensive research on new materials with excellent chemical, mechanical and dielectric properties are currently being carried out. One of the most important classes of high-performance polymers became polyimides with many applications in electronics, aircraft industry, space exploration and polymeric separation technologies [1,2]. The usage of PIs in membrane technology is promising, because of their high selectivity in gas separation, chemical, thermal and mechanical resistance. Unfortunately such membranes have low gas fluxes, which could be enhanced by incorporation of inorganic materials, like, for instance, graphene, zeolites or silica [3–5]. Combination of organic and inorganic components provides the new materials with adjusted properties, obtained by control of composition, content and morphology of the filler addition, usage of different processing techniques or by modification of the polymer matrix. All these operations provide materials with excellent properties and suitable for usage in various applications, like: aerospace, sensors, microelectronics, photocatalysis, magnetic devices, batteries, electrochemical display devices, electrical-magnetic shields and microwave absorption materials, coatings, biomedical, and powder metallurgy, hydrogen recovery or carbon dioxide removal from the coal syngas or natural-gas [6–9]. This paper is the continuation of our earlier research on magnetic hybrid inorganic-organic membranes and their application in the enrichment of air with oxygen [10–12]. In this work, we are going to characterize the gas transport, magnetic, mechanical and rheological parameters of magnetic hybrid membranes based on polyimide matrices.

2. Experimental

2.1. Membrane synthesis and gas permeation analysis

The homogeneous LPI (linear polyimide), HBPI (hyperbranched polyimide) and heterogeneous magnetic membranes were produced on the basis of synthesized LPAA and HBPAA polyamic acids and the isotropic magnetic powders MQFP-B+(Nd-Fe-B) with various granulation ($d_m = 5$ µm, $d_m = 7$ µm, $d_m = 15$ µm and $d_m = 20$ µm – products of Magnequench company). These membranes were made by casting of magnetic powder dispersions (inorganic content ranging from 50.0 to 88.0 wt%) in LPAA and HBPAA solutions. The whole process was carried out in gradually increasing

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temperature (finally at 230 °C for 1 h) and in the external magnetic field. Gas (N_2, O_2 and synthetic air) permeability measurements were conducted for membranes before and after magnetization in impulse inducteur (magnetic field intensity of 2280 kA/m) on the low-pressure gas permeation analyzer IDP-2, furnished with a gas chromatograph PerkinElmer/GC Clarus 580, Arnel Model 4018 (measurement of the O_2 and N_2 concentration in permeate). Measurements were carried out at temperature of 25 °C. These flow-rate data and percentage of the air enrichment were used to evaluate the mass transport coefficients (***D***, ***P***, ***S*** and $\boldsymbol{\alpha}$), using Time Lag method [10–12].

2.2. Characterization of polyimide hybrid magnetic membranes

The membrane's characteristics included the examination of magnetic parameters, determined on the basis of magnetic hysteresis loops from a Lake Shore 7010 vibrating sample magnetometer (VSM). The magnetic field of 1600 kA/m (according to the producer's data) was applied to register the hysteresis loops and to get more than 90% of saturation magnetization [13]. The XRD, IR and TGA measurements were performed using the Rigaku MiniFlex II diffractometer with Cu Kα radiation, a Nicolet 740 spectrometer using either liquid samples (solutions of polyamic acids) or KBr pellets (solid polyimides) and a TG-750 Stanton-Redcroft (heating rate 10 °C min^{-1}). The mechanical and rheological measurements were carried out using static testing machine Zwick/Roell Z050 (range 50 kN force) and ARES rheometer from TA Instruments (dynamic mode at strain amplitude $\gamma = 0.5\%$ and variable angular frequency $\omega = 0.1–79.4$ Hz).

3. Results and discussion

3.1. Magnetic and gas transport properties of PI hybrid membranes

The gas transport coefficients of the selected magnetic hybrid PI membranes, evaluated using appropriate formulas [10–12] (the mean values of six measurements with standard deviations) are presented in Table 1.

The hysteresis loops of the magnetic polyimide hybrid membranes with various particle sizes and content of added magnetic fillers are shown in Fig. 1a and b. In turn the dependencies of coercivity on granulation and R and Ms on magnetic filler addition are shown in Fig. 1c and d.

It was stated (Fig. 1), that the saturation magnetization and remanence increased with the rise of magnetic filler addition. For the Ms, the dependency was linear. Value of coercivity depended mainly on a microstructure and composition of the magnetic powder. The remanence also depended to a small degree on the filler's microstructure. Comparing the measured magnetic parameters with values given by the producer it could be stated that they were within the manufacture's range. However, there are some differences (powder $d_m = 20$ μm), especially in the case of coercivity and Ms, which could be caused by influence of the polymer coating, polydispersity, bonding chemistry, shape anisotropy and surface morphology [14–16].

From the dependencies shown in Fig. 2 could be stated that the increase in magnetic filler content positively influenced the values of remanence and saturation magnetization Ms, and this in turn improved the gas transport and selectivity coefficients of analysed membranes (*D*, *P*, *S* and α). The exponential increase was observed

Table 1
Mass transport coefficients of pure and mixture of oxygen and nitrogen for various LPI and HBPI magnetic membranes.

Membrane	α O2/N2	N_2 pure				O_2 pure			
		$\bar{D}$	D_L	P	S	$\bar{D}$	D_L	P	S
		$\cdot 10^8$ (cm^2/s)		(Barrer)	$\cdot 10^4$(cm$^3_{STP}$/cm^{3}cmHg)	$\cdot 10^8$ (cm^2/s)		(Barrer)	$\cdot 10^4$(cm$^3_{STP}$/cm^{3}cmHg)
LPI	5.61	0.27 ± 0.03	0.25 + 0.03	0.05 ± 0.01	18.00 ± 1.34	0.90 ± 0.10	0.85 ± 0.10	0.28 ± 0.03	31.00 ± 2.17
LPI, 0.71g, MQFP-B+, d_m=7 μm	5.84	4.53 ± 0.54	4.46 ± 0.53	0.96 ± 0.09	21.30 ± 1.50	16.03 ± 1.92	19.30 ± 2.28	5.63 ± 0.56	35.11 ± 2.45
LPI, 0.94, MQFP-B+, d_m=7 μm	6.17	5.85 ± 0.70	5.66 ± 0.68	1.43 ± 0.14	24.46 ± 1.72	24.39 ± 2.92	28.85 ± 3.40	8.84 ± 0.83	36.23 ± 2.52
LPI, 1.18g, MQFP-B+, d_m=7 μm	6.52	7.67 ± 0.92	7.31 ± 0.87	2.07 ± 0.20	27.00 ± 1.89	36.43 ± 4.37	42.60 ± 5.01	13.51 ± 1.23	37.09 ± 2.59
LPI, 1.40g, MQFP-B+, d_m=7 μm	6.86	9.74 ± 1.27	9.17 ± 1.10	2.80 ± 0.23	28.72 ± 2.01	50.87 ± 6.10	59.11 ± 7.00	19.19 ± 1.13	37.72 ± 2.64
LPI, 1.70g, MQFP-B+, d_m=7 μm	7.38	13.17 ± 1.58	12.29 ± 1.47	4.00 ± 0.40	30.37 ± 2.12	76.73 ± 9.20	88.71 ± 10.25	29.52 ± 2.93	38.47 ± 2.69
LPI, 1.40g, MQFP-B+, d_m=5 μm	6.79	11.11 ± 1.33	10.46 ± 1.25	3.21 ± 0.32	28.86 ± 2.02	50.87 ± 6.10	59.11 ± 7.01	19.19 ± 1.13	37.72 ± 2.64
LPI, 1.40g, MQFP-B+, d_m=15 μm	6.54	8.43 ± 1.01	7.98 ± 0.95	2.35 ± 0.23	27.89 ± 2.00	34.99 ± 4.17	40.85 ± 4.90	13.03 ± 1.03	37.25 ± 2.61
LPI, 1.40g, MQFP-B+, d_m=20 μm	6.02	7.86 ± 0.94	7.46 ± 0.89	2.16 ± 0.22	27.52 ± 2.00	30.82 ± 3.62	32.83 ± 3.82	17.78 ± 1.73	57.68 ± 4.03
HBPI	5.82	0.44 ± 0.05	0.40 ± 0.05	0.11 ± 0.01	25.00 ± 1.75	1.48 ± 0.17	1.60 ± 0.19	0.64 ± 0.06	43.00 ± 3.01
HBPI, 0.75g, MQFP-B+, d_m=7μm	5.75	9.31 ± 1.12	8.47 ± 1.02	2.96 ± 0.23	31.79 ± 2.22	28.63 ± 3.43	32.14 ± 3.75	17.01 ± 1.63	59.42 ± 4.15
HBPI, 0.98g, MQFP-B+, d_m=7μm	5.86	12.27 ± 1.47	10.99 ± 1.32	4.43 ± 0.43	36.09 ± 2.52	41.29 ± 4.83	45.01 ± 5.30	25.97 ± 2.55	62.90 ± 4.36
HBPI, 1.21g, MQFP-B+, d_m=7μm	6.02	15.86 ± 1.90	14.03 ± 1.68	6.33 ± 0.59	39.95 ± 2.78	57.90 ± 6.83	62.27 ± 7.10	38.11 ± 3.75	65.82 ± 4.60
HBPI, 1.43g, MQFP-B+, d_m=7μm	6.20	19.70 ± 2.36	17.28 ± 2.07	8.57 ± 0.83	43.53 ± 3.04	77.72 ± 9.21	83.39 ± 9.90	53.12 ± 5.01	68.34 ± 4.78
HBPI, 1.74g, MQFP-B+, d_m=7μm	6.50	25.42 ± 3.05	22.14 ± 2.65	12.44 ± 1.21	48.94 ± 3.42	112.72 ± 13.50	121.92 ± 13.60	80.89 ± 8.02	71.76 ± 5.02
		N_2 in air				O_2 in air			
LPI	3.25	0.36 ± 0.04	0.29 ± 0.03	0.08 ± 0.01	22.00 ± 1.54	0.89 ± 0.10	0.82 ± 0.09	0.26 ± 0.02	29.00 ± 2.03
LPI, 0.71g, MQFP-B+, d_m=7 μm	5.63	10.67 ± 1.28	11.27 ± 1.35	2.11 ± 0.19	19.81 ± 1.38	39.39 ± 4.72	43.34 ± 5.20	11.89 ± 1.11	30.19 ± 2.11
LPI, 0.94, MQFP-B+, d_m=7 μm	6.05	15.96 ± 1.81	16.98 ± 2.01	3.26 ± 0.31	20.41 ± 1.42	62.51 ± 7.50	67.86 ± 8.14	19.71 ± 1.87	31.53 ± 2.20
LPI, 1.18g, MQFP-B+, d_m=7 μm	6.46	23.19 ± 2.68	24.78 ± 2.87	4.82 ± 0.41	20.79 ± 1.45	95.74 ± 11.44	103.11 ± 11.99	31.16 ± 3.05	32.55 ± 2.27
LPI, 1.40g, MQFP-B+, d_m=7 μm	6.85	31.35 ± 3.66	33.59 ± 3.90	6.59 ± 0.59	21.01 ± 1.47	135.55 ± 16.00	145.37 ± 17.40	45.15 ± 4.43	33.31 ± 2.33
LPI, 1.70g, MQFP-B+, d_m=7 μm	7.44	44.85 ± 5.28	48.16 ± 5.57	9.51 ± 0.83	21.20 ± 1.48	206.74 ± 23.88	220.97 ± 24.40	70.75 ± 7.00	34.22 ± 2.39
LPI, 1.40g, MQFP-B+, d_m=5 μm	6.79	35.94 ± 4.21	38.52 ± 4.42	7.56 ± 0.68	21.03 ± 1.47	153.73 ± 18.06	164.82 ± 18.68	51.31 ± 5.06	33.38 ± 2.33
LPI, 1.40g, MQFP-B+, d_m=15 μm	6.50	26.34 ± 3.16	28.19 ± 3.38	5.51 ± 0.49	20.91 ± 1.46	108.8 ± 13.0	116.9 ± 14.0	35.8 ± 3.08	32.91 ± 2.30
LPI, 1.40g, MQFP-B+, d_m=20 μm	5.00	24.14 ± 2.80	25.82 ± 3.09	5.04 ± 0.53	20.87 ± 1.46	93.0 ± 11.1	100.1 ± 12.0	25.2 ± 2.11	27.07 ± 1.89
HBPI	4.10	0.45 ± 0.05	0.44 ± 0.05	0.12 ± 0.01	26.00 ± 1.82	1.43 ± 0.17	1.67 ± 0.20	0.49 ± 0.05	34.00 ± 2.38
HBPI, 0.75g, MQFP-B+, d_m=7μm	5.99	22.90 ± 2.74	25.65 ± 3.00	5.12 ± 0.53	22.36 ± 1.56	83.9 ± 10.0	86.8 ± 10.4	30.7 ± 3.02	36.57 ± 2.55
HBPI, 0.98g, MQFP-B+, d_m=7μm	6.12	34.22 ± 4.10	38.35 ± 4.60	7.81 ± 0.68	22.83 ± 1.60	125.7 ± 15.1	129.3 ± 15.5	47.8 ± 4.45	38.08 ± 2.66
HBPI, 1.21g, MQFP-B+, d_m=7μm	6.30	48.65 ± 5.56	54.81 ± 6.37	11.39 ± 1.07	23.42 ± 1.64	179.0 ± 21.5	183.7 ± 22.0	71.8 ± 7.08	40.09 ± 2.80
HBPI, 1.43g, MQFP-B+, d_m=7μm	6.50	65.27 ± 7.53	74.17 ± 8.80	15.73 ± 1.49	24.11 ± 1.69	240.7 ± 28.9	246.7 ± 29.0	102.3 ± 9.77	42.49 ± 2.96
HBPI, 1.74g, MQFP-B+, d_m=7μm	6.83	93.15 ± 11.01	107.64 ± 12.51	23.55 ± 2.21	25.28 ± 1.77	344.5 ± 41.0	353.2 ± 41.7	160.7 ± 15.89	46.66 ± 3.26