

Final Draft
of the original manuscript:

Lillepaerg, J.; Georgopoulos, P.; Shishatskiy, S.:
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In: Journal of Membrane Science (2014) Elsevier

DOI: 10.1016/j.memsci.2014.05.039

Stability of blended polymeric materials for CO₂ separation

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Abstract:

Blend materials of Pebax[®] 1657 and low molecular weight poly(ethylene glycol)s were studied for their stability at temperature up to 90°C. It was found that a threshold of molecular weight exists at which leaching out of the low molecular weight compound from the polymer matrix becomes minimal. Poly(ethylene glycol) with methyl end groups having a molecular weight of 500 g/mol provides a blend material with a CO₂ permeability coefficient higher than in case of Polyactive[™]. PEBAX[®]/DM500 blend can be a cheaper alternative to tailor made Polyactive[™] in large scale production of thin film composite membrane.

Keywords

Gas separation; CO₂ capture, Polymer membrane; Polymer blend; Poly(ethylene glycol); Pebax[®]; Polyactive[™]

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1. Introduction.

Since the beginning of industrial revolution in 19th century which was accompanied with a wide use of fossil fuel like coal and later on oil and gas, Earth's atmosphere has accumulated large amounts of greenhouse gases. The increase of carbon dioxide concentration from 310 to 400 ppm in the last 50 years is considered to be responsible for 1 °C increase of the atmosphere temperature.[1,2] Reduction of carbon emission is considered as a major goal for the environment, in order to avoid drastic climate change which can occur if atmospheric temperature would rise for 2 °C.[3]

In 2010 electricity and heat production consumed 4840 million tons of oil equivalent (MTOE) of coal (46.5%), natural gas (22.8%) and oil (5.7%) as well as of nuclear (14.9%) and renewable energy (10.2%) [4]. Power generation is the most stable and stationary source of carbon dioxide emission and thus attracts attention as a candidate for carbon capture and storage (CCS).

Membrane separation of fossil fuel fired power plants off-gases has been extensively studied during the last decade and compared to other techniques such as cryogenic air separation, adsorption and absorption.[5–7] It is acknowledged that the implementation of a carbon capture technology in energy production will require significant investments, operational expenses and thus increase of energy cost.[5] Gas separation will be the most expensive part of the CCS process.

Three main strategies are studied for CCS: pre-combustion, oxyfuel and post-combustion.[8] For the pre-combustion (CO_2/N_2) and oxyfuel (O_2/N_2) ceramic membranes able to withstand high operating temperatures in the range of 800°C are considered, post-combustion (CO_2/N_2) separation is planned to be carried out using polymeric membranes.[9]

Post-combustion separation will deal with enormous feed flow rates equal or slightly above the atmospheric pressure with low nitrogen concentration not exceeding 15 vol.%. Off-gas is at 100% of relative humidity and contains up to 60 mg/m³ of solid impurities which will be accumulated on the frontal side of the membrane module if not removed. Small amounts of sulfur and nitrogen oxides present a significant challenge for the stability of the membrane especially at conditions when water could condense on the feed side of the membrane. [10] Nevertheless successful pilot tests of post-combustion membrane separation with polymeric membranes are reported. [11,12]

Modeling of the post-combustion membrane separation process gives an idea on required permeance, selectivity and by these also on the price of membrane. The most suitable membrane for single stage separation process would have about 8 m³(STP)/(m²h bar)

permeance, a selectivity CO_2/N_2 in the range of 140 and a price of 20 Euro/ m^2 in module.[13] The required membrane surface is strongly dependent on membrane permeance but according to calculations using parameters of existing membranes it will be about one million square meters for a 600 MW power plant. Low feed pressure requires a vacuum scheme of membrane use and thus process selectivity and energy demand will depend on the vacuum created on permeate side of the membrane and pressure losses inside the membrane module. The energy required for the separation is mostly determined by the selectivity of the membrane: in order to match the selectivity of the process to the high selectivity of the membrane a strong vacuum will be necessary.

Due to the limitations of the separation process the membrane module should give as small resistance to the feed flow as possible, should have as large packing density as viable, and low production and installation costs. Most probably modules equipped with flat sheet membranes will be advantageous compared to hollow fiber modules because of the well-defined fluid dynamics in the module and effectiveness of membrane use. Additionally it has to be mentioned that today there are no hollow fiber membranes having a rubbery selective layer produced in pilot scale with permeances competing to flat sheet membranes.

Membrane materials having two transport mechanisms are under consideration for post-combustion application: i) active or facilitated transport, where specific interactions between CO_2 and membrane material provide fast CO_2 molecule “hopping” from one active center to another, thus enforcing high selectivity; ii) “passive” transport according to the solution-diffusion mechanism where polymers or organic compounds having affinity toward CO_2 provide a relatively moderate selectivity. Other approaches as membrane contactors [14], supported liquid membranes [15] most probably will not reach application stage in the near future.

Moderate selectivity of polymeric membrane materials for CO_2/N_2 separation is graphically presented as upper bound of Robeson plot [16] from which it is evident that CO_2/N_2 selectivity for polymers never exceeds 90. Active transport materials demonstrate significantly higher selectivity, e. g. 160 for samples prepared as membranes for pilot scale experiments [17,18]. Unfortunately these membranes still have relatively thick separation layers and thus low permeance of about $1 \text{ m}^3(\text{STP})/(\text{m}^2\text{h bar})$. It should be mentioned that when using advanced coating techniques and membrane preparation conditions permeance can reach about $10 \text{ m}^3(\text{STP})/(\text{m}^2\text{h bar})$ [19]. If active transport membranes would be stable against the post-combustion feed stream such membranes would be very competitive candidates for industrial separation systems.

Poly(ethylene glycol) (PEG) containing compounds are widely studied as materials for CO₂ selective membranes.[6] Combination of relatively high permeability and selectivity bring polymers containing ethylene glycol moiety to or above the present upper bound for CO₂/N₂ in the Robeson plot. Fine tuning of polymer composition, adjustment of block length, or blending with low molecular poly(ethylene glycol)s allow significant increase of permeability without decrease in selectivity.[20–23]

At least two TFC membranes based on PEG containing polymers have been examined in post-combustion CO₂/N₂ pilot scale separation. Polaris™ of MTR (Menlo Park, USA) and Polyactive™ TFC membrane of Helmholtz-Zentrum Geesthacht have been tested at power plants and showed stable results.[11,24] A 12 m² membrane module with Polyactive™ TFC membrane is currently tested in the off-gas separation system on a coal fired power plant within the frames of METPORE II project.

The requirement of cost reduction of the membrane separation system leads to use of cheap mass products for membrane preparation. Polyactive™ is a much more expensive polymer compared to Pebax® 1657. In case a Pebax® 1657 based membrane will have properties similar to Polyactive™ the choice of the polymer for the selective layer will be obvious.

As it was reported before, blend materials of Pebax® 1657 and poly(ethylene glycol) of different molecular weights and nature of end groups show very promising results for use as membrane selective layers.[25] Poly(ethylene glycol) functionalized POSS [26] and PDMS [23] give very promising gas transport property change to Pebax® when blended with it. Here we report on results of the blend stability. Blends of low molecular weight compounds and polymers are known to be unstable in time and leaching out of low molecular weight compounds is well known in e.g. rubber technology.[27–30] In our research we have studied blends having a high content of low molecular weight poly(ethylene glycol)s (LMWPEG) of different molecular weights and nature of end groups. Fast changes in blend structure were induced by heating to 90°C, the temperature exceeding possible application range, while measuring the gas transport properties of an about 100µm thick film of the material. Changes in the blends composition were studied by weighing, thermographic and calorimetric techniques. The threshold of the LMWPEG molecular weight was identified at which leaching out of LMWPEG is stopped.

2. Experimental

2.1. Materials

The Pebax[®] MH1657 (further Pebax[®]) was received in a pellet form from Arkema. The Polyactive[™] 1500PEGT77PBT23 (further Polyactive[™]) was purchased from PolyVation. PEG's having different end groups were obtained from Sigma-Aldrich: dimethyl ether DM250 (250 g/mol), DM500 (500 g/mol), divinyl ether DV240 (240 g/mol), diglycidyl ether DG526 (526 g/mol); PEG allyl ether A500 (500 g/mol), allylmethyl ether AM350 (350 g/mol), were gratefully received from Clariant SE. Ethanol and tetrahydrofuran (THF) from Th. Geyer (purity 99.9%) as well as high purity deionized water having conductivity 0.06 μ S cm⁻¹ were used as solvents.

2.2. Membrane preparation

Gas transport properties were determined for films having a thickness of approximately 100 μ m which were prepared by casting from polymer solution. A 3% solution of Polyactive[™] was prepared using THF as a solvent by stirring at 30°C for 2 h. Pebax[®] was dissolved in a mixture of ethanol/water (70/30 wt.%) by stirring at 80°C for 3 h in order to obtain 3 wt.% solution[25]. For preparation of Pebax[®] blended with LMWPEG's films the polymer solution was cooled down and then the respective amount of LMWPEG was added. The solution was vigorously stirred for at least 30 minutes. The solution was filtered and poured into the aluminum ring placed on a leveled Teflon[®] coated glass plate kept at 30°C. Ethanol/water solvent was evaporated during 36-48 hours. For dust protection the aluminum ring was covered with polyester non-woven. Polyactive[™] films were prepared by the same procedure except temperature was kept at 25°C and the aluminum ring was covered with a glass cup providing a small gap between the cup and the ring in order to allow slow evaporation of THF (at least 36 hours). After solvent evaporation obtained film membranes were evacuated overnight at 30°C in the vacuum hood equipped with turbomolecular pump.

2.3. Membrane characterization.

Films with a thickness from 88 to 135 μ m with deviation \pm 4-14 μ m were cast as described above. The films thickness was measured with a digital micrometer DELTASCOPE[®] FMP10. The weight of the films after drying under vacuum at 30°C was measured with an analytical balance XP/XS from Mettler Toledo.

2.3.1. Gas transport properties

The permeabilities of pure carbon dioxide, nitrogen, helium, oxygen, methane, and ethane were measured by a constant volume variable pressure technique [31] (time-lag) in the temperature range from 30 to 90 °C and for cooling down from 90 to 30 °C. The feed pressure was 600, 450 and 350 Torr, respectively, for consecutive measurements for all gases. The permeability coefficient P [$\text{cm}^3(\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$] of single gas was determined as [32]:

$$P = \frac{V_p l (p_{p2} - p_{p1})}{ART \Delta t (p_f - (p_{p2} + p_{p1})/2)}, \quad (1)$$

where V_p is the constant permeate volume [$\text{cm}^3(\text{STP})$], l is the film thickness (cm), A is the effective area of membrane (cm^2), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), Δt is the time for permeate pressure increase from p_{p1} to p_{p2} (s), P_f is the feed pressure (cmHg). The use of pressures instead of fugacities is justified since the absolute pressures involved are sufficiently low.

The diffusion coefficient D ($\text{cm}^2 \text{ s}^{-1}$) is calculated from membrane thickness l (cm) and time-lag θ (s) determined graphically as intersection of the line drawn through the linear region of pressure increase curve to intersection with time axis:

$$D = \frac{l^2}{6\theta}. \quad (2)$$

Solubility coefficient S ($\text{cm}^3 (\text{STP}) \text{ cm}^{-3} \text{ cmHg}^{-1}$) and selectivity α (-) between two components A and B can be expressed by the following equation:

$$S = \frac{P}{D}. \quad (3)$$

Ideal selectivity of the material can be expressed as a ratio of permeability coefficients of two penetrants and as follows from Eq. 3 it consists of diffusion and solubility selectivity:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B}. \quad (4)$$

Since gas transport parameters show the exponential temperature dependence of an activated process [33] the Arrhenius equation was used to estimate activation energies of permeability E_P and diffusion E_D (kJ mol^{-1}):

$$P = P_0 \exp\left(-\frac{E_P}{RT}\right) \quad (5)$$

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \quad (6)$$

The change in enthalpy of sorption ΔH_s (kJ mol^{-1}) can be estimated as a difference between E_P and E_D [34]:

$$\Delta H_s = E_P - E_D$$

2.3.2. *Materials characterization*

For the characterization of the materials used for the blends as well as the finally produced thick membranes (LMWPEGs and commercial polymers Polyactive™ and Pebax®), spectroscopy and thermal analysis experiments were accomplished. ATR-FTIR spectroscopy experiments were conducted in order to verify the purity of the used materials. ATR-FTIR with diamond crystal was accomplished on a Bruker Alpha ATR-FTIR spectrometer. Thick membranes were directly measured and compared with the spectrum of the other solid or liquid materials. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed to characterize the material's thermal properties, especially in case of TGA there was done a direct comparison with the weighing on the analytical balance before and after the time-lag measurements.

DCS experiments were done with a calorimeter DSC 1 (Mettler Toledo), within the temperature measurement range from $-100\text{ }^\circ\text{C}$ up to $+280\text{ }^\circ\text{C}$ at a heating rate of 10 K/min .

TGA experiments were carried out on the TG 209 F1 Iris (Netzsch). The experiments were done at a temperature range from $25\text{ }^\circ\text{C}$ up to $500\text{ }^\circ\text{C}$, and heating rate of 10 K/min . The measurements were performed in nitrogen as protection gas.

3. Results and discussion

Development of a highly CO₂/N₂ selective membrane able to withstand environment of the coal power plant stack will allow modernization of existing power generation facilities resulting in reduction of CO₂ emission. The most promising materials for membranes to be used in post-combustion gas separation are polymers containing polyethers, namely poly(ethylene glycol) and poly(propylene glycol).[6,35] It was shown that such polymers can provide membranes with properties matching economic requirements of post-combustion separation. Realistic analysis of the separation process indicates that currently it is not possible to reach a CO₂ purity sufficient for transportation and storage in a one stage separation.[10] In case of a two stage separation process poly(ethylene glycol) based membranes can provide the necessary CO₂ purity. Properties of already developed Polaris™ and Polyactive™ membranes are fitting to the optimum region for industrial membrane application. [36]

TFC membranes having selective layers of PEG containing polymers are produced in pilot scale. The thickness of the Polyactive™ selective layer was determined to be in the range of 50-80nm.[37,38] The thinnest TFC membrane prepared from such a block copolymer had an effective thickness of the selective layer in the range of 30nm.[39] In both cases a multilayer structure of the TFC membrane is necessary in order to keep the material responsible for the target separation intact under operation conditions. In a multilayer arrangement the selective layer is packed between supporting and protective layers of PDMS or another “fast” and stable polymer. Exchange of substances between layers and decomposition of the selective layer should be avoided meaning that the blend material used to substitute Polyactive™ should be stable in time.

3.1. Gas transport properties of pristine polymers

Detailed studies of the properties of Pebax® and Polyactive™ were performed by A. Car et al [40]. As reported, Pebax® and Polyactive™ have high CO₂ selectivities over N₂ and H₂. Their CO₂ permeability can be improved by adding LMWPEG without affecting the selectivity. Both of these commercially available polymers contain flexible, rubbery PEG segments, which amount to 60 wt% for Pebax® and 77 wt% for Polyactive™, respectively. The glass transition temperature T_g of PEG blocks was measured at -53°C and at -49°C, respectively, which relates to the difference in molecular weight distribution of blocks in these two polymers and thus their packing ability since both polymers are reported to have blocks of similar weight.[23]

Samples of thick films were prepared with a thickness of about 100 μm according to the method described for tests of the gas transport properties in the temperature range 30 – 90 $^{\circ}\text{C}$. This temperature range was chosen in order to control stability of the material at temperatures higher than at possible operation conditions of stack where the temperature can be as high as 65 $^{\circ}\text{C}$. High temperature was expected to provoke undesired changes within the blend materials under study which could occur during operation under industrial conditions. Gas transport experiments under heating and cooling done with pristine Pebax[®] and Polyactive[™] gave results comparable to results reported earlier [21]. Several films of Pebax[®] having thicknesses varying from 8 to 140 μm were carried out to prove reproducibility of the film preparation technique. In each case, the difference of permeability data on heating and cooling was less than 2%. The standard deviation for each measurement point of permeability for e.g. a film having thickness of 107 μm was not more than 0.07%. The number of permeability measurements of and, accordingly, the diffusion of the gas at each temperature ranged from 3 up to 5 times. Although the film thickness can vary up to $\pm 5\mu\text{m}$, the large number of thickness measurement points assured obtaining an average thickness which will result in values of permeability and diffusion coefficient matching to films of other thicknesses and to values reported in literature [41].

The presence of water in Pebax[®] based membranes obtained from water-ethanol solution was controlled by ATR – FTIR experiments. It was found that the symmetric and asymmetric stretching vibrations of water (ν_3 , H-O-H), a peak which is very broad, at approximately 3700 cm^{-1} , was very weak although it is well known that a broad and strong peak is expected when even a small amount of water is incorporated into the sample. Additionally no further peak at 1500 cm^{-1} due to the water bending vibration (ν_2) was found which confirms complete solvent evaporation during membrane preparation.

In Fig. 1 are presented the Arrhenius plots of permeability, diffusion and solubility. It can be seen that for all gases temperature dependence is linear according to the Arrhenius equation (Eq. 5 and 6). Determination of the hydrogen diffusion coefficient represents an obvious difficulty because of very small time-lag values, the error of $D(\text{H}_2)$ determination can reach 25% which results in a rather significant deviation from linearity in the case of the hydrogen solubility coefficient.

Table 1 summarizes the permeability, diffusion, solubility coefficients and their activation energies for Pebax[®] and Polyactive[™] as well as of two blend materials. Permeability coefficients of all gases except hydrogen for Polyactive[™] are approximately 2.3 times higher than those for Pebax[®] due to higher content of more regular PEG in the Polyactive[™] and,

probably due to the difference in chemical structure of the hard blocks (poly(butylene terephthalate) in Polyactive and Nylon 6 in Pebax[®]). Hydrogen permeates 3.6 times faster through Polyactive[™] compared to Pebax[®] which arises from the relatively high solubility coefficient of hydrogen in Polyactive[™]. Solubility coefficients of Polyactive[™] are generally higher than those of Pebax[®], but the same behavior is not observed for the diffusion coefficients.

3.2. Polymers blended with low molecular weight PEGs

As shown by W. Yave et al. [41], the addition of poly(ethylene glycol) may increase 4-5 times the permeability of the blend material for carbon dioxide, with almost no selectivity decrease. The best result at a temperature of 30 °C was achieved for films containing 40 % of PEG.

In order to assess stability of blend materials of Pebax[®] and LMWPEG and to confirm the possibility to use such blends as materials for the selective layer of thin film composite membranes, thick films of Pebax[®] were made with the addition of LMWPEG's having molecular weights from 250 up to 550 g/mol. Samples were tested at heating from 30 to 90 °C and then cooling again to 30°C. It was found that all curves of temperature dependence obtained at heating stage are not matching the Arrhenius equation. Comparison of permeability data at 30 °C after sample cooling with the data published in the work of Yave et al [41], revealed strong deviation of the permeability values in the range from 30 to 80% in case of various LMWPEGS.

It is known that low molecular weight compounds have a tendency to leach out from the polymer matrix. [30] On the assumption that there is a leakage of LMWPEG from the polymer matrix, new samples of Pebax[®] blended with LMWPEG of different molecular weight were prepared and gas transport properties were measured in the heating mode from 30 to 90 °C and cooling mode from 90 to 30 °C. The weight and thickness of samples was determined before and after the gas transport measurements.

For all measured samples discrepancies between results obtained during the heating and cooling parts of experiments were observed. The greatest deviation has been found in case of LMWPEG additives with the lowest molecular weights, such as PEG DM250 and PEG DV240. Lowest deviation was observed for films with LMWPEG additives having molecular weights of 500 g/mol and above. Temperature dependencies of permeability and diffusion coefficients typical for all studied materials are presented on Fig. 2 for Pebax[®] blended with DM250, DM500 and DV240. For comparison purposes and since the aim of the work is the

preparation of a material having properties superior to Polyactive™, the curves for pristine Pebax® and Polyactive™ are given. It can be seen that for all studied materials the first permeability coefficient obtained during the heating part at 30°C is higher than for pure polymers. But during the temperature increase the curve doesn't follow an exponential curve as expected for activated processes. In case of DM250 the CO₂ permeability coefficient is gradually decreasing with temperature and for DV240 the curve has a turning point at 50°C. At the same time the temperature dependence of the diffusion coefficient shows an exponential increase with temperature. In case of DM500 the heating and cooling parts are close to each other. Such behavior as presented on Fig. 2 has led us to the conclusion that blend samples undergo severe changes in structure and composition during the temperature treatment associated with gas transport experiments. The fact that LMWPEG with different molecular weights respond differently to such treatment has forced the conclusion that samples are losing LMWPEG during experiments. The process of mass loss is not momentary as it can be seen from two points for heating and cooling parts taken at 90°C. The difference between them is related to the fact that there was some time gap between two parts of experiment and during this time samples were losing LMWPEG and changing properties. Since the thickness of the sample cannot be determined when the film is fixed in the measurement cell and appropriate permeability and diffusion coefficients cannot be recalculated to the real state of the sample, the points at 90°C have different positions. The curves for the permeability and diffusion coefficients corrected to the thickness change are presented on the Fig.2 as well. It can be seen that all of them are lower than the not corrected curves and for LMWPEG having a molecular weight of app. 250 g/mol they are mostly similar to the curve of pure Pebax®.

The weight of each sample was determined before and after the gas transport experiment. Assuming that the density of the rubbery material blended with the LMWPEG of the same nature will not change drastically with the loss of LMWPEG, the thickness can be recalculated proportionally to the weight loss.

Fig. 3 presents the data of weight loss and of permeability at 30°C before and after heating experiments for the blend samples. As expected, the higher molecular weight PEGs are not leaching out from the blend under these experimental conditions while PEGs having molecular weights of 240, 250, and 350 g/mol are mostly lost from the film. Permeability coefficients decay correspondingly to the weight loss and reach the level of Pebax® for the PEG with lowest molecular weight.

TGA experiments carried out on pure Pebax[®] and LMWPEGs with molecular weights of 250 and 500 g/mol, as well as on the thick films of their blends confirmed the data obtained from weighing. During the heating from room temperature to 600°C LMWPEG was losing the mass in one step and Pebax[®] in two steps which is attributable to the presence of two sorts of blocks in the multiblock copolymer. No evidence of water or other volatile solvent was observed and there was no remaining mass at the end of the measurement. It is worth to be mentioned that the degradation temperature of the low molecular weight substances is much lower compared to the one of the commercial polymers. TGA experiments (Fig. 4) carried out for the membranes with the LMWPEG DM250 showed significant differences in the content of LMWPEG before and after gas transport experiments quantitatively confirming the observation of film weight loss.

The summary of the weight loss [wt%] for films of Pebax[®] originally containing 40 wt% LMWPEGs of different molecular weight is shown below:

DV240	DM250	AM350	A500	DM500	DG526
38	32	32	10	7	9

It was also found that thicker Pebax[®] based membranes (about 200µm) are losing less LMWPEG due to diffusion restrictions. Since the aim of the work was to find limits of blend stability it was decided to focus on membranes where leaching out could occur during the time frames of a standard program for a gas transport experiment. At the same time the thickness of the sample should be big enough to obtain statistically relevant data on weight loss for blends containing various LMWPEGs. From numerous experiments it was found that the thickness of about 100 µm (this corresponds to approximately 10-20 thousand times the radius of gyration of a PEG chain) ensures good and reproducible results of all tests.

Blend films based on Polyactive[™] show behaviors similar to those based on Pebax[®] in the heating cycle of the gas transport experiment but have poorer mechanical properties and break when cooled from 90 to 60°C. The data obtained for Polyactive[™] based blends were considered as not reliable and are not reported.

The leaching out of LMWPEG depends on their molecular weight, the film thickness and on the duration effects of the gas flow. The threshold for weight loss was found between Mw 350 and 500 g/mol, the minimum weight loss was observed for LMWPEG A500 but DM500

and DG 526 are of interest for further experiments on thin film composite (TFC) membrane formation.

Since the leakage of LMWPEGs with a molecular weight of 500 g/mol was minimal and curves of gas transport properties were linear in Arrhenius coordinates, it was possible to determine the activation energies for permeability, diffusion and solubility and calculate activation energies of selectivity for some gas pairs. The data for the gas transport properties at 30°C at the end of the cooling cycle of the gas transport experiments of blends containing DM500 and A500 can be found in Table 1. The presence of LMWPEG in blends have only a small effect on ideal CO₂/N₂ selectivity (Fig. 5), the fact confirming that PEG blocks of both Pebax[®] and Polyactive[™] are controlling the gas transport in block copolymers and that LMWPEG is dissolved in PEG of a copolymer leaving the hard blocks intact. DSC experiments have confirmed this observation. The selectivity for both pure polymers and two blend materials are very close to each other but selectivity of Polyactive[™] decays faster with the increase of temperature. It can relate to more loose packing of Polyactive[™] which is evident from diffusivity selectivity. Values of CO₂/N₂ diffusion and solubility selectivities of all Pebax[®] based materials are close to each other.

The DSC experiments were carried out for Pebax[®], LMWPEGs DM 250 and DM500 and their blends. Blend films were tested before and after gas transport experiments. All the characteristic temperatures were calculated from the second heating cycle. The analysis of the thermographs (Table 3) showed that the LMWPEGs have a glass transition temperature (T_g) approximately at -50°C, which was very weakly observed to the low molecular weight, although several DSC experiments were conducted with various heating rates to acquire better resolution. The melting point temperature (T_m) was: for the DM250 -20 °C and for the DM500 +13 °C. Crystallization temperature (T_c) was acquired from the first cooling of the DSC measurement and it was estimated at -40 °C and -1 °C for the DM250 and DM500, respectively. Pristine Pebax[®] before and after time-lag measurement gave the same values of thermal transitions: T_g of poly(ethylene glycol) (PEG) block -40 °C, T_c of PEG block -30°C, T_m of PEG block 16 °C, T_c of polyamide (PA) at 160 °C and T_m of PA block ~205 °C. For the blended membranes based on Pebax[®] with DM250 and DM500 DSC experiments showed significant shifts in T_c and T_m of PEG block. More in detail, PA melting was not influenced at all by the presence of DM250 and minor shift from 205 to 200 in T_m was observed in case of DM500. Such shift can indicate some incomplete phase segregation between DM500 and Nylon 6 during sample preparation and therefore some minor presence of PEG in PA. Furthermore, for DM250 and DM500, DSC of the unused membranes showed a T_m shift of

approximately 5 °C lower for the poly(ethylene glycol) block, leading to a value of +10 °C, lower than the initial +15 °C referring to the Pebax[®] measurement. In contrast to that, membranes which were measured in time-lag with the temperature program, sustained a stable T_m value for the PEG block, at 15 °C. The same results are obtained from the cooling cycles for the T_c of the PEG block which is shifted also approximately 10 °C, at -30 °C, in contrast to the membrane after being examined with time lag measurements, where the Pebax[®] PEG block T_c was stable at -20 °C. These results are leading to the explanation that the low molecular weight PEG was leaching out from the membrane during the heating cycle of time-lag measurement, since these membranes after time-lag measurements maintain the thermal characteristics only for the Pebax[®] giving strong proof to what was already observed for the gas properties measurements.

4. Conclusions

Gas transport parameters of Pebax[®], Polyactive[™] and blend materials of Pebax[®] with LMWPEGs of different molecular weight have been studied in a wide temperature range exceeding possible application temperature. It was found that blends with LMWPEGs having molecular weight less than 500 g/mol are unstable at elevated temperatures, tend to lose most of low molecular weight component and thus cannot be chosen as materials for the selective layer of TFC membranes. LMWPEGs form stable blends with Pebax[®] in which equilibrium fraction of low molecular weight component is between 30 and 33 wt%. The blend of Pebax[®] and PEG DM500 has properties superior to Polyactive[™].

TGA experiments have confirmed the leaching out of the LMWPEG from the Pebax[®] matrix. DSC studies have shown that LMWPEGs are dissolved in the PEG domains of the multiblock copolymer.

The data obtained during gas transport experiments at temperatures from 30 to 90 °C will allow quality control of TFC membranes to be developed. Results obtained on blend stability are to be studied further when blend materials will be implemented as a selective layer of multilayer TFC membranes.

It is planned to test successful membrane materials developments on pilot scale within the scope of the METPOERE II project funded by the German Ministry of Economics and Technology.

Acknowledgements

The authors would like to thank Volker Abetz, , Torsten Brinkmann, Volkan Filiz, Silvio Neumann and Carsten Scholles for their technical support and valuable discussions. This work was financially supported by the project from the Helmholtz Association of German Research Centres through the Helmholtz Portfolio MEM-BRAIN.

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Figures captions:

Fig. 1: Arrhenius plot of gas transport properties for pure gases measured for thick films of Pebax[®] MH1657 [(—◆—) CO₂, (—▶—) C₄H₁₀, (—▼—) H₂, (—△—) CH₄, (—□—) N₂, (—○—) O₂].

Fig. 2: CO₂ permeability and diffusivity for pure Pebax[®] MH1657 and its blends with LMWPEG [(—◆—) Pebax[®] MH1657 heating, (—◇—) Pebax[®] MH1657 cooling, (—■—) Pebax[®]-PEG DM250 heating, (—□—) Pebax[®]-PEG DM250 cooling, (—●—) Pebax[®]-PEG DM500 heating, (—○—) Pebax[®]-PEG DM500 cooling, (—▲—) Pebax[®]-PEG DV240 heating, (—△—) Pebax[®]-PEG DV240 cooling, (—×—) Polyactive[™]].

Fig. 3: CO₂ permeability and weight loss of the blends of PEBAX 1657 and LMWPEGs.

Fig. 4: Representative TGA thermograph for the degradation of Pebax and its blend with DM250 before and after time-lag measurement.

Fig. 5: Ideal permeability selectivity $\alpha_P(\text{CO}_2/\text{N}_2)$: [(—◆—) Pebax[®] MH1657, (—×—) Polyactive[™] 1500, (—●—) Pebax[®]-PEG DM500 heating, (—○—) Pebax[®]-PEG DM500 cooling].

Fig.1:

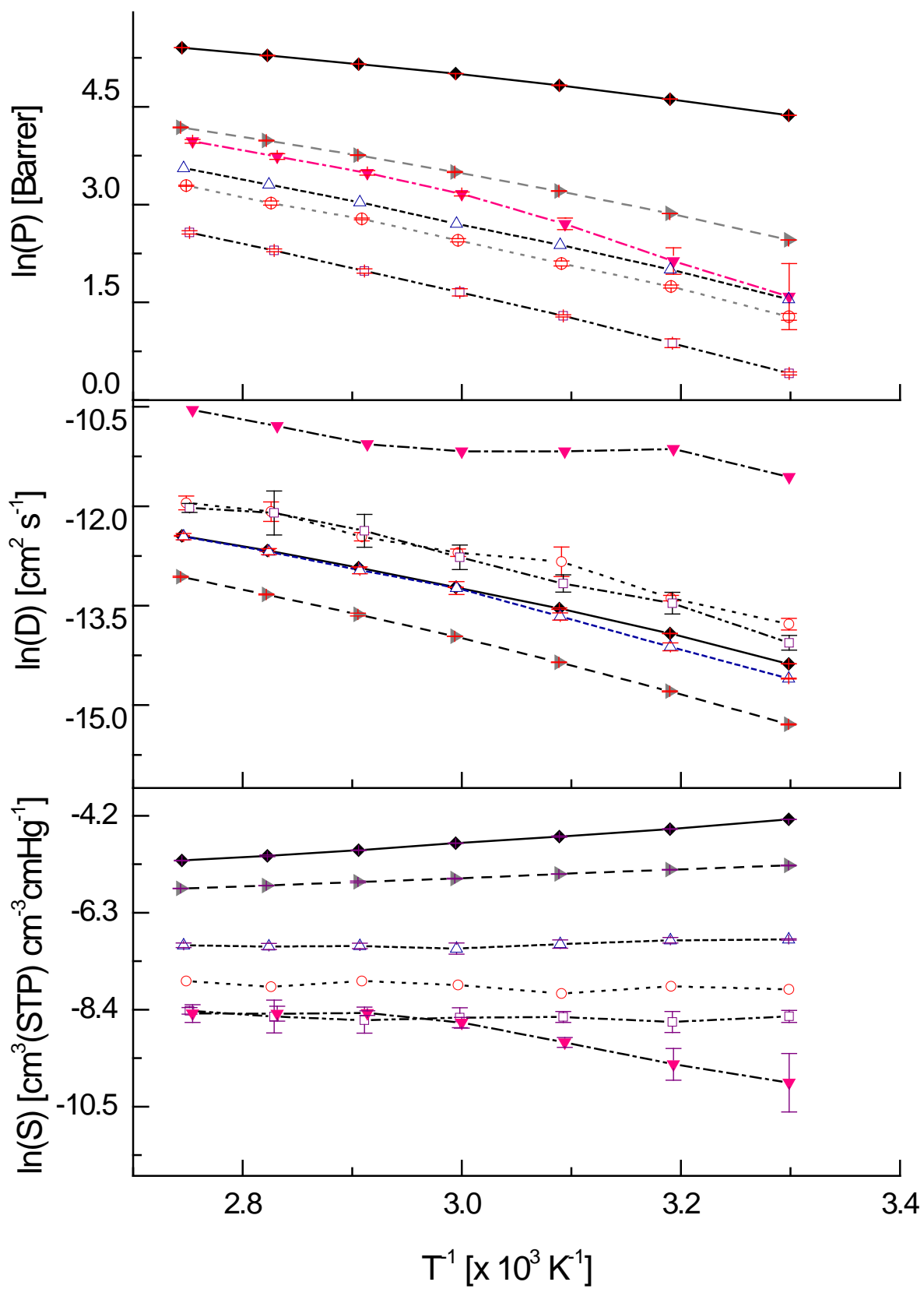


Fig.2

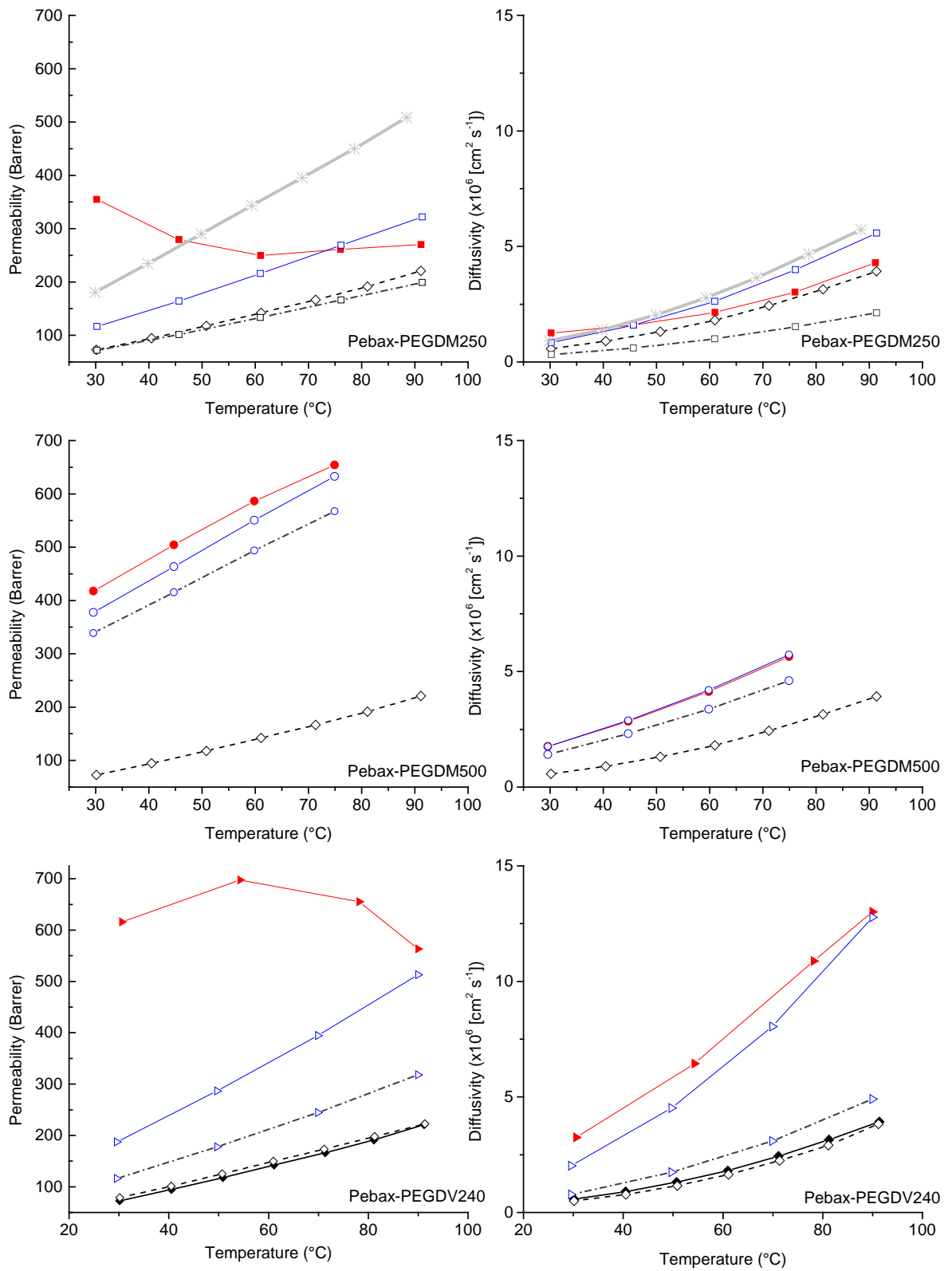


Fig. 3:

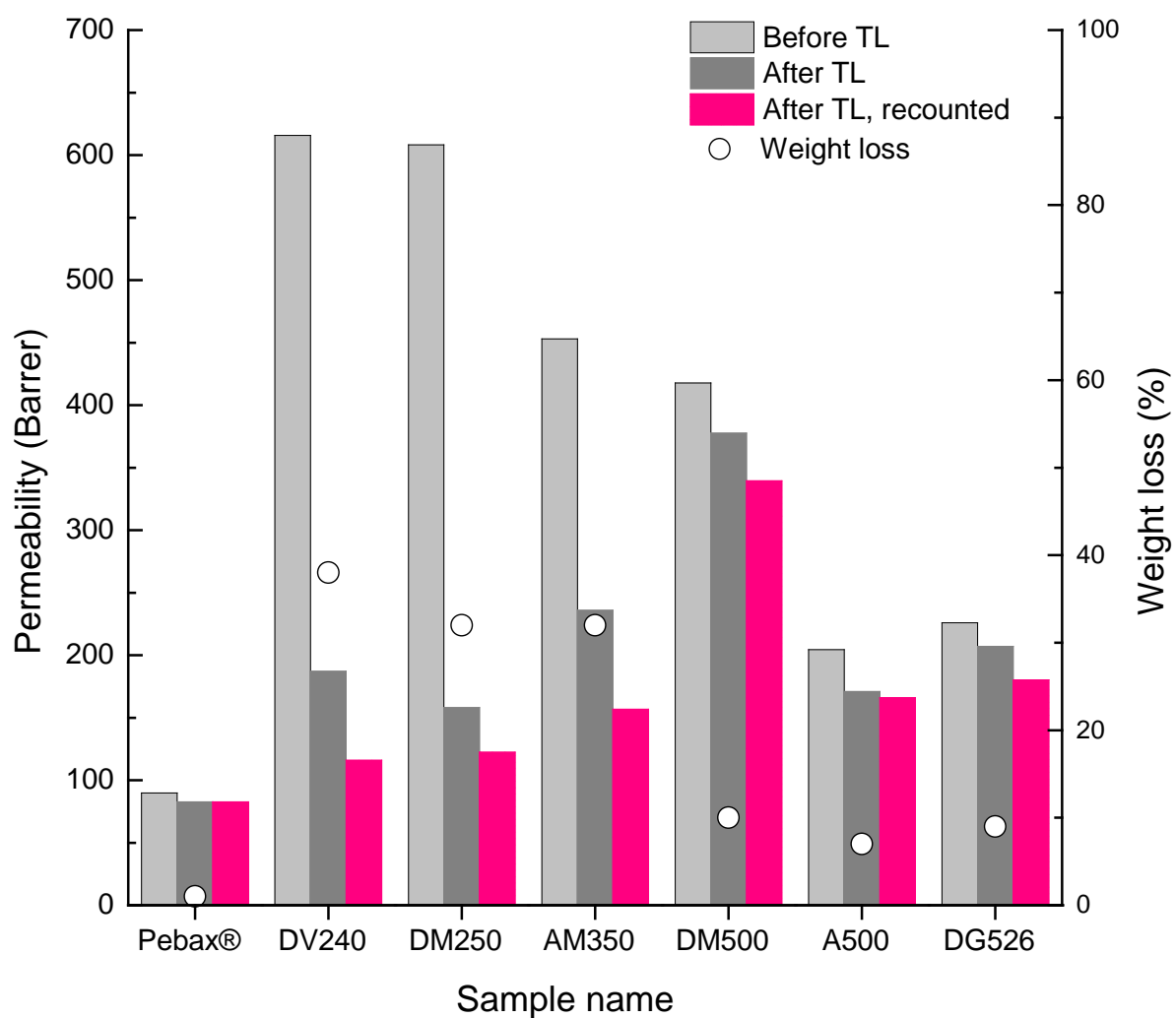


Fig. 4:

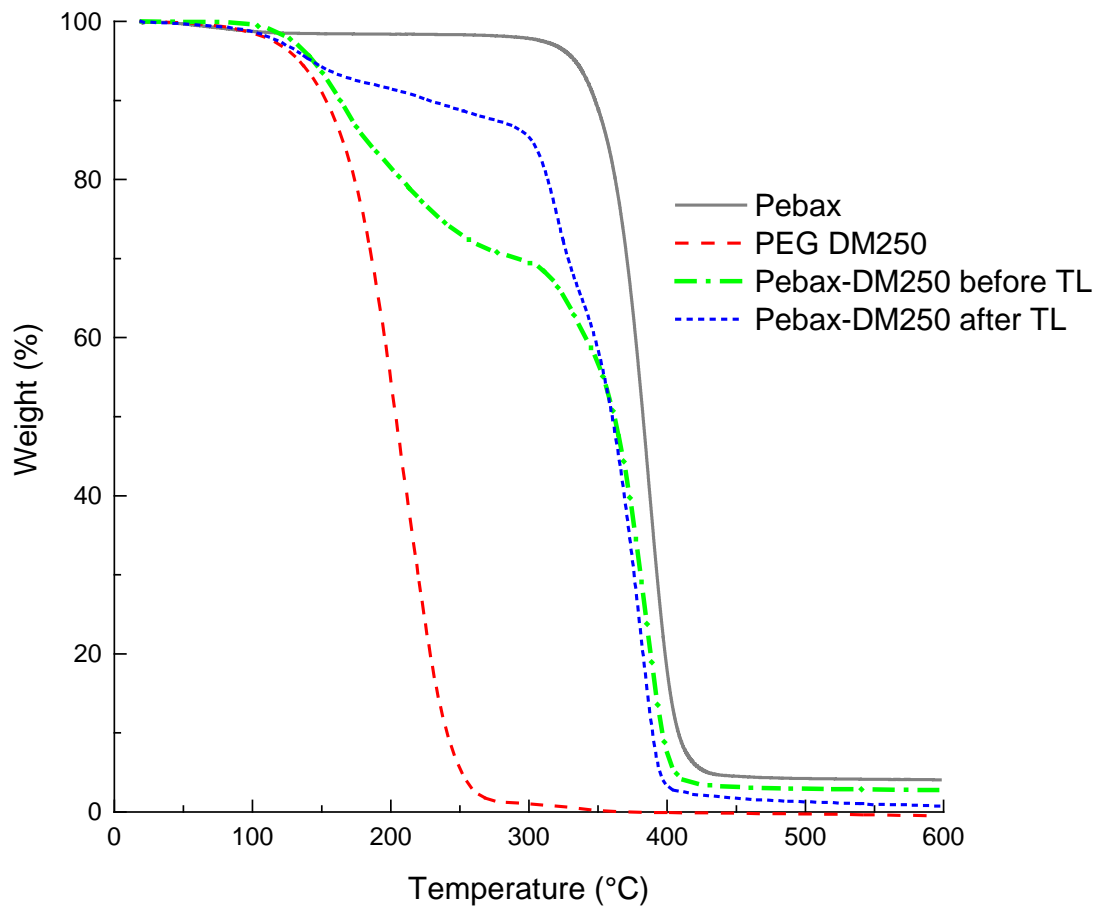


Fig.5.

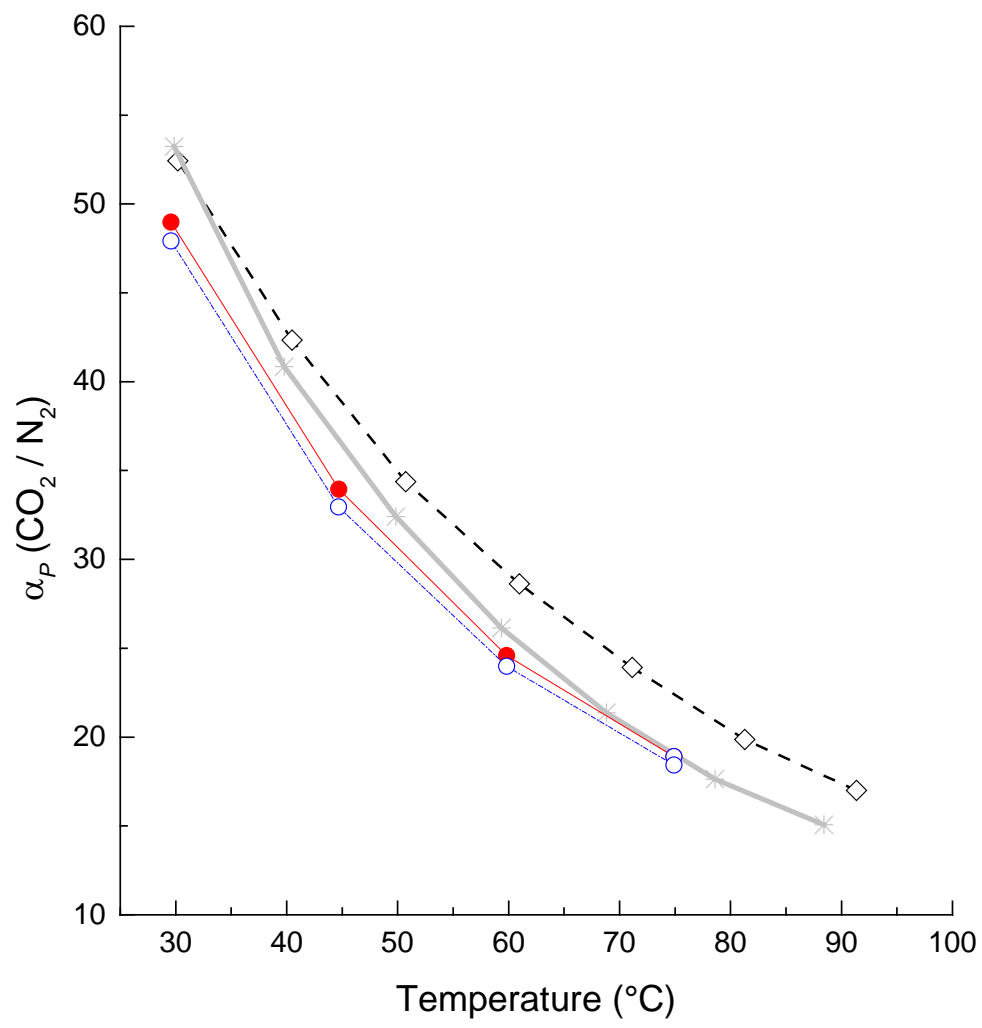


Table 1. Permeability, diffusion and solubility coefficients of various gases at 30°C and activation energies of permeability E_p , diffusion E_d , and enthalpy of sorption ΔH_s for Pebax[®] 1657 and Polyactive[™] 1500 and Pebax[®] based blends

Gas	P [Barrer]	E_p [kJ mol ⁻¹]	D [x10 ⁻⁶ cm ² s ⁻¹]	E_d [kJ mol ⁻¹]	S [x10 ³ cm ³ (STP) cm ⁻³ cmHg]	ΔH_s [kJ mol ⁻¹]
Pebax[®] 1657						
H ₂	4.9	36.7	9.54	12.5	0.05	24.2
CH ₄	4.7	30.1	0.46	32.4	1.02	-2.3
N ₂	1.5	32.8	0.78	31.5	0.19	1.2
O ₂	3.6	30.2	1.04	27.6	0.35	2.6
CO ₂	79	15.5	0.57	28.8	13.9	-13.4
Polyactive[™] 1500						
H ₂	17.6	29.7	7.04	20.5	0.25	9.2
CH ₄	10.5	31.1	0.27	29.7	3.89	1.4
N ₂	3.4	36.6	1.55	26.9	0.22	9.7
O ₂	8.7	31.3	1.43	27.7	0.61	3.6
CO ₂	181	15.9	0.91	28.6	19.9	-12.7
Pebax[®] DM500						
H ₂	28.4	24.9	9.55	18.6	0.30	6.3
CH ₄	26.5	24.2	1.56	24.2	1.70	-0.1
N ₂	7.9	28.6	2.36	22.7	0.33	5.9
O ₂	17.7	25.3	2.6	21.9	0.68	3.4
CO ₂	378	10	1.76	22.8	21.5	-12.8
Pebax[®] A500						
H ₂	15	28.7	9.4	18	0.16	10.7
CH ₄	11.3	29.2	0.92	29.4	1.24	-0.1
N ₂	3.3	32.1	1.29	32.7	0.26	-0.6
O ₂	8.1	29.0	1.73	26.1	0.47	2.9
CO ₂	171	14.8	1.06	27.2	16.1	-12.4

Table 2. Ideal permeability, diffusion and solubility selectivities for some gas pairs at 30°C and corresponding activation energies (kJ mol⁻¹) for stable pure and blend materials.

Gas	$\alpha(P)$	$\alpha(D)$	$\alpha(S)$	$E(\alpha_P)$ [kJ mol ⁻¹]	$E(\alpha_D)$ [kJ mol ⁻¹]	$E(\alpha_S)$ [kJ mol ⁻¹]
Pebax[®] 1657						
CO ₂ /N ₂	53	0.73	72	-17	-2.7	-15
CO ₂ /H ₂	16	0.06	270	-21	16	-38
O ₂ /N ₂	2.4	1.3	1.8	-2.5	-3.9	1.4
Polyactive[™] 1500						
CO ₂ /N ₂	53	0.59	91	-19	0.10	-19
CO ₂ /H ₂	10	0.13	80	-15	4.2	-19
O ₂ /N ₂	2.6	0.92	2.8	-3.3	-0.80	-2.5
Pebax[®] DM500						
CO ₂ /N ₂	48	0.75	64	-17	-5.5	-12
CO ₂ /H ₂	13	0.18	72	-14	9.2	-23
O ₂ /N ₂	2.2	1.1	2.0	-3.1	-6.6	3.5
Pebax[®] A500						
CO ₂ /N ₂	52	0.82	63	-21	1.7	-22
CO ₂ /H ₂	11	0.11	101	-14	8.1	-22
O ₂ /N ₂	2.5	1.3	1.8	-5.3	0.80	-6.1

Table 3. Thermal properties of PEBAX blended with LMWPEGs

Material	T_g^{PEG}	T_c^{PEG}	T_m^{PEG}	T_c^{PA}	T_m^{PA}
Pebax	-	-18	16	160	205
DM250	-	-48	-38		
DM500	-	-1	13		
Pebax - DM250 before TL	-	-30	10	-	205
Pebax - DM250 after TL	-	-20	17	-	205
Pebax - DM500 before TL	-52	-2	22	-	200
Pebax - DM500 after TL	-52	-4	23	-	201

T_g^{PEG} : Glass transition temperature of the polyethylene glycol block, °C

T_c^{PEG} : Crystallization temperature of the polyethylene glycol block, °C

T_m^{PEG} : Melting temperature of the polyethylene glycol block, °C

T_c^{PA} : Crystallization temperature of the polyethylene glycol block, °C

T_m^{PA} : Melting temperature of the polyethylene glycol block, °C