

# Tailoring of Phase-Segregation Structures in Two-Soft-Segment Urethane/Urea Polymer Membranes

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**ABSTRACT:** The synthesis of two-soft-segment urethane/urea polymeric membranes with various proportions of the two soft segments, poly(propylene oxide) and polybutadiene, yielded very distinct morphologies depending on the degree of phase segregation. The morphologies were identified with transmission electron microscopy. With a low concentration of polybutadiene, this soft segment segregated into ellipsoidal microdomains dispersed in a poly(propylene oxide) matrix. With an intermediate concentration of polybutadiene, the morphology was characterized by nanoscale phase separation and could be described as a disordered, wormlike domain structure. With a high concentration of polybutadiene, a single phase was observed. This was attrib-

uted to molecular mixing of the two soft segments and was associated with membranes that under the application of a shear stress developed bands that efficiently scattered light. These bands were identified by field emission scanning electron microscopy with a periodicity of approximately 4–5  $\mu\text{m}$ . The change in the membrane morphology from microscale phase segregation to nanoscale phase segregation led to very different membrane gas-permeation properties, that is, a reduction of the  $\text{CO}_2$  permeability from 191 to 90 Barrer. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 315–320, 2007

**Key words:** morphology; structure-property relations; TEM

## INTRODUCTION

The morphology and chemistry of segregated phases determine the physical and chemical properties of many complex polymers, including polyurethanes. A better understanding of the influence of the formulation chemistry as well as the chemistry on the morphology of segregated phases and the correlation of this with the final physical properties of polymers allows the rational development of polyurethane-based materials for a wide range of specific applications.

For thermoplastic polyurethane elastomers, Cooper and Tobolsky<sup>1</sup> first pointed out the importance of phase separation in the definition of structure–property relationships. Later, Bonart<sup>2</sup> and Clough et al.<sup>3</sup> investigated the scale of the microdomain structure resulting from the phase separation of hard and soft segments. Since then, the microheterogeneous nature

of polyurethanes has been the subject of numerous investigations.<sup>4–13</sup>

In the synthesis of polymeric membranes, particularly those based on polyurethanes, the introduction of two soft segments<sup>14</sup> has become an important asset in the creation of different membrane structures due to phase separation because not only hard-segment/soft-segment but also soft-segment/soft-segment interactions can now play an important role. In fact, dynamic mechanical thermal analysis (DMTA) has given evidence that in these membranes, the two soft segments, poly(propylene oxide) and polybutadiene, are mixed or phase-separated according to their relative proportions in the casting solution.<sup>14</sup> Further characterization with attenuated total reflection/Fourier transform infrared spectroscopy has led to the conclusion that hydrogen bonding forms between hard segments and subsequently aggregates of urethane/urea groups form, which are dependent on the relative contents of the two soft segments in the casting solution. The increase in the polybutadiene concentration yields a decrease in the aggregate formation and therefore favors the enhancement of molecular mixing.<sup>15</sup>

In this work, two-soft-segment membranes cast from solutions yielding urethane/urea polymers with two soft segments of poly(propylene oxide) and polybutadiene are investigated with two main objectives:

1. The identification and characterization by transmission electron microscopy (TEM) of the dif-

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ferent structures displayed upon phase segregation at various ratios of the two soft segments.

2. The correlation of the observed structures with the membrane properties, namely, the very specific mechanico-optical properties and the gas-permeation performance.

## EXPERIMENTAL

### Materials

A poly(propylene oxide)-based prepolymer with three isocyanate terminal groups (PU) was supplied by Companhia Petroluimica do Barreiro S. A. (Barreiro, Portugal). The molecular weight was approximately 3500. A polybutadiene diol (PBDO), supplied by Aldrich (Milwaukee, WI), had a number-average molecular weight of 2800 and contained 20–30 wt % vinyl, 10–25 wt % cis-1,4-isomer, and 50–60 wt % trans-1,4-isomer. Dibutyltin dilaurate (DBTDL), supplied by Aldrich, was used as a catalyst. Proanalysis toluene, supplied by Merck (Darmstadt, Germany), was used as a solvent.

### Membrane preparation

The membranes were prepared through the casting of solutions of PU and PBDO into toluene. A catalyst, DBTDL, was added to the solution to promote the crosslinking reactions between the isocyanate groups of PU and the hydroxyl groups of PBDO.<sup>14</sup> The ratio of PU to PBDO was varied to yield crosslinked polymers with different compositions. The polymeric solutions were spread over a glass plate, and the subsequent solvent evaporation was carried out in a first step at 70–80°C for 3.5 h and then in a second step of exposure to atmospheric air for at least 72 h.

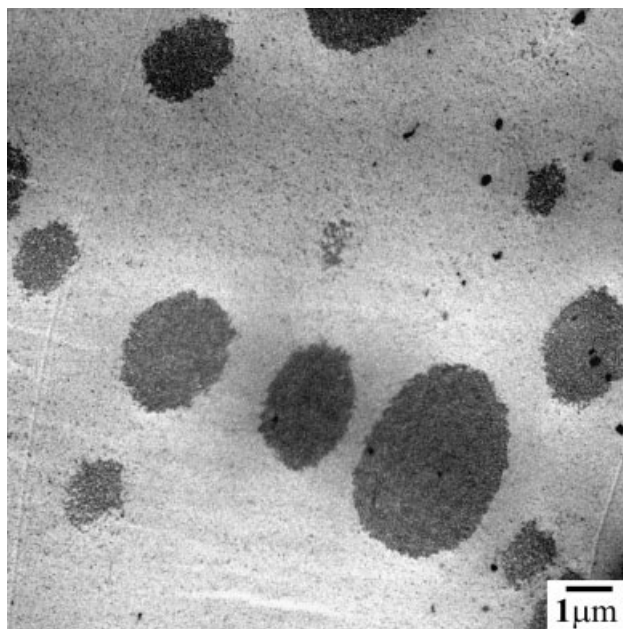
### Characterization

The membranes prepared from casting solutions with different relative contents of the two soft segments were analyzed with TEM for phase-morphology investigations. For that, osmium tetroxide was used to selectively stain chemically unsaturated moieties and to provide contrast between the two soft segments. TEM images were taken with a Carl Zeiss CEM 902 transmission electron microscope operated at an accelerating voltage of 80 kV. Before the imaging, the films were ultramicrotomed into 60-nm-thick sections and stained in osmium tetroxide vapor for 24 h.

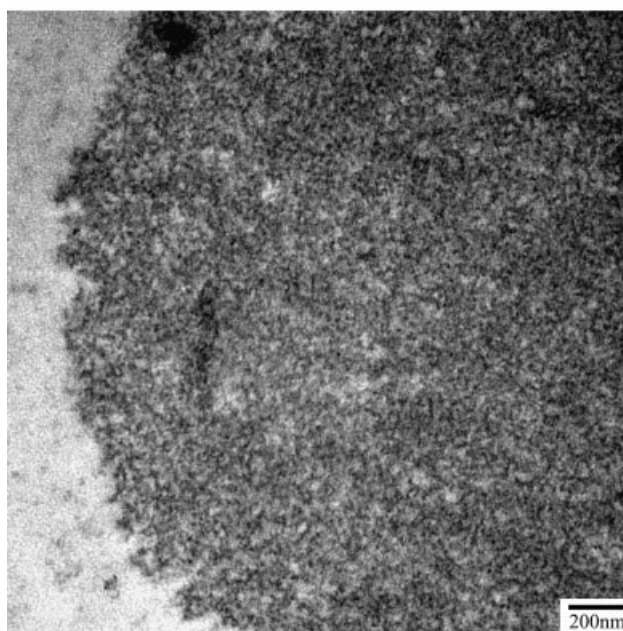
Field emission scanning electron microscopy (FESEM) was carried out with a JEOL JSM-6340F microscope with a field emission source, which was operated with a voltage of 3 kV. The surface of the membrane film was gold-coated with a Bal-Tec MD 020 instrument before the imaging.

## RESULTS AND DISCUSSION

Figures 1 and 2 show a series of TEM micrographs of the bulk morphology of the two-soft-segment urethane/urea polymers with different ratios of PU to PBDO. Osmium tetroxide preferentially stained the unsaturated carbon linkages of the PBDO soft segments, and thus the dark regions in the TEM micrographs correspond to PBDO domains.

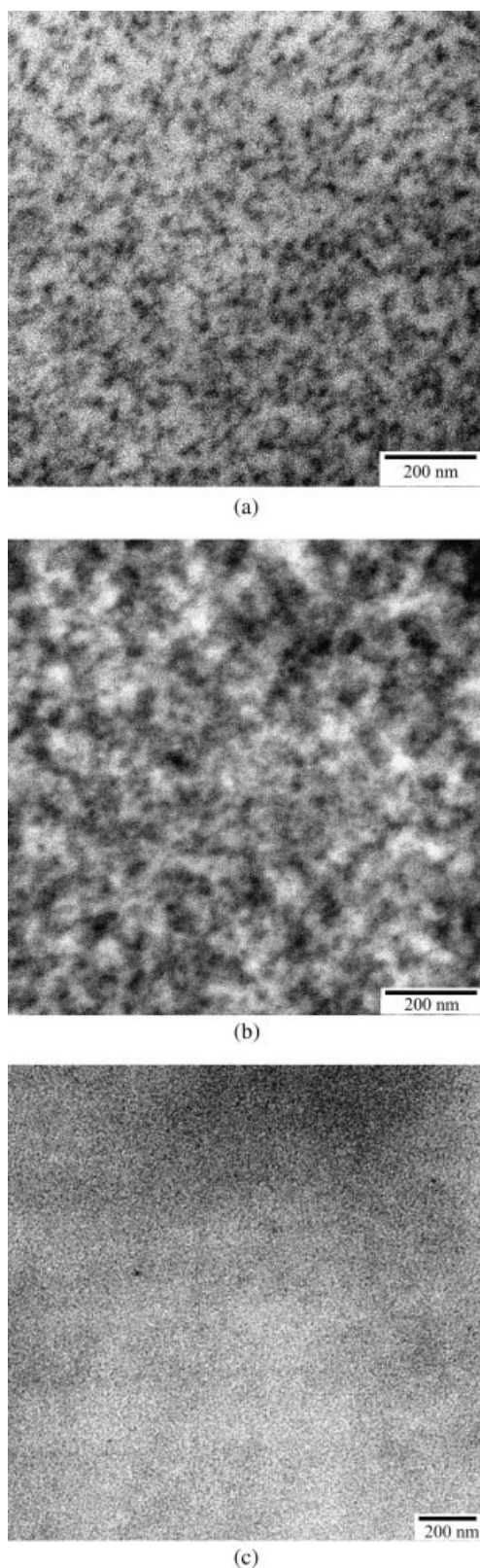


(a)



(b)

**Figure 1** TEM micrographs of a PU/PBDO urethane/urea membrane containing 10 wt % PBDO at (a) lower and (b) higher magnifications.



**Figure 2** TEM micrographs of PU/PBDO urethane/urea membranes containing (a) 25, (b) 50, and (c) 60 wt % PBDO.

The membranes with PBDO concentrations lower than 60 wt % showed two-phase morphologies characteristic of phase separation. In Figure 1, the micrographs of the membrane with 10 wt % PBDO reveal microphase separation consisting of large domains richer in polybutadiene and scattered in a matrix richer in poly(propylene oxide). The PBDO richer domains have an ellipsoidal shape with dimensions of approximately 1–4  $\mu\text{m}$ . In Figure 1(b), a higher magnification of the domains shows that they do not consist of pure PBDO, but a kind of disordered structure seems to be present.

In Figure 2(a), with respect to a micrograph of a membrane in which the PBDO concentration was increased to 25 wt %, a pronounced change in the morphology can be observed. The phase separation occurs now at the nanoscale, and the phase domains corresponding to this very fine morphology can be described as a disordered, wormlike domain structure. In Figure 2(b), for the membrane with a PBDO concentration up to 50 wt %, the same kind of morphology of nanoscale domains can be observed.

In contrast to these observations, the membranes with PBDO concentrations equal to or higher than 60 wt % showed no microstructure. Figure 2(c) presents a micrograph of a membrane with 60 wt % PBDO characterized by a single-phase morphology. The TEM observations are in accordance with the reference made previously to DMTA data,<sup>14</sup> which reported a unique glass-transition temperature for membranes with a PBDO concentration of 60 wt % or higher. Moreover, the idea that in this range of PBDO concentrations there is molecular mixing of the two soft segments is now confirmed by TEM.

On the other end, for the range of lower PBDO concentrations, the DMTA data yielded two glass-transition temperatures attributable to the segregation of the soft segments, poly(propylene oxide) and polybutadiene.<sup>14</sup> In fact, the TEM observations confirm that in this range of PBDO concentrations, there is phase segregation, and more importantly, they give direct evidence of morphological changes occurring upon the variation of the PBDO content. These morphological patterns can be characterized in terms of the size and shape of the phase domains. In this work, two types of phase-separation morphologies were identified: (1) a morphology characterized by microscale domains and (2) a morphology characterized by nanoscale domains.

Overall, we can say that an increase in the PBDO concentration leads to an increase in the mixing of the two soft segments, and this occurs through an evolution of the phase-separation morphology from a morphology composed of microscale domains to a morphology of nanoscale domains and finally to a single-phase morphology in which the two soft segments are molecularly mixed.

The versatility of the morphologies displayed by the two-soft-segment polymer membranes may be an important asset in the design of new applications. In the case of a current application of polyurethane membranes for gas permeation, this feature of phase-separation tailoring may bring insight into the transport mechanisms and the optimization of membrane performance in terms of the permeation fluxes. In this line, membranes with different PBDO concentrations were tested for gas permeation, and the one with 10 wt % presented the highest value of 191 Barrer for CO<sub>2</sub> permeability.<sup>16</sup> An increase of the PBDO concentration to 25 wt % caused an accentuated reduction of the gas permeability to 90 Barrer. This value practically did not change with further increases in the PBDO concentration.

In a previous work,<sup>16</sup> we characterized membranes with positron annihilation lifetime spectroscopy (PALS). We compared the CO<sub>2</sub> permeability to the hole size and overall free volume in these two-soft-segment membranes and found that they were correlated. However, the changes observed in those free volume parameters were of much lower magnitude than the changes found in the permeability, and we concluded that the hole size and overall free volume could not by themselves describe these changes. As gas permeation requires the physical passage of molecules across a polymer membrane, we assume that interconnectivity, which is not mirrored by the overall amount of the effective free volume seen by PALS, must play a determining role in the outcome of the permeation features.

In this work, Figures 1 and 2 correspond to TEM micrographs of membranes with very different permeabilities, and this can directly be attributed to the changes in the solid-state morphology of the membranes. The highest values of the permeability correspond to membranes characterized by a morphology of large domains richer in PBDO dispersed in a matrix richer in PU. When the morphology changes to a fine phase separation of wormlike domains in which the phases are more connected, the permeabilities decrease significantly from 191 to 90 Barrer.

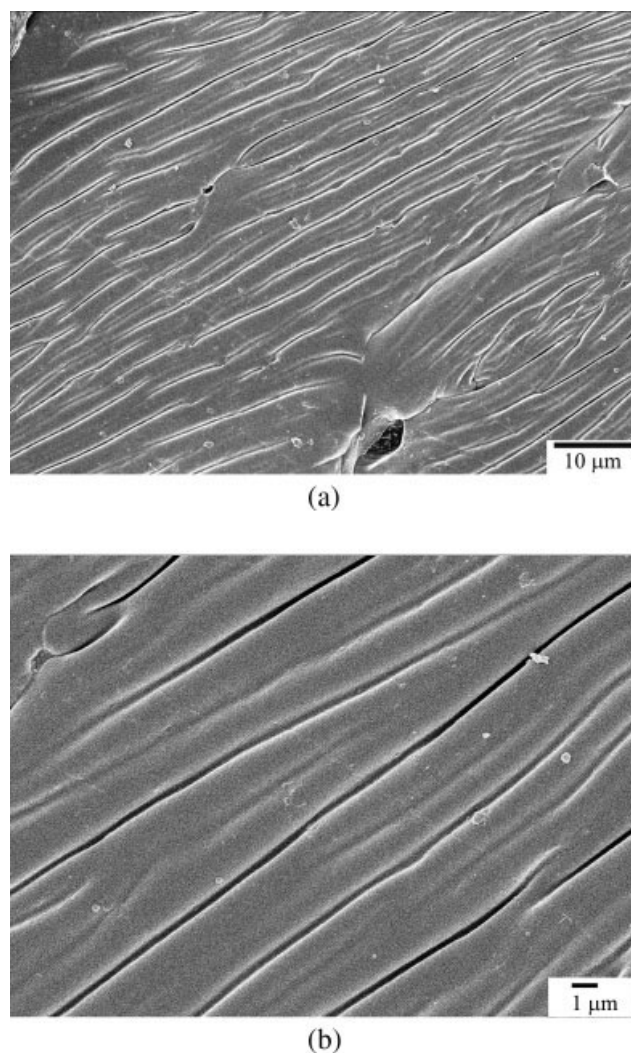
The aforementioned observations are in accordance with the studies of Kim et al.,<sup>17</sup> who showed the relation between the gas-permeation properties and morphology for blends of polycarbonate and poly(methyl methacrylate). The authors found that the permeability for miscible blends was lower than that for immiscible blends. Furthermore, immiscible blends having a domain–matrix structure showed higher permeability than immiscible blends having an interconnected structure. This higher permeability was justified by the higher diffusion coefficient.

The permeation of gases in nonporous, homogeneous polymer membranes is assumed to occur by a solution–diffusion mechanism, and in the steady-state,

the permeation fluxes are quantified by the integrated form of Fick's first law, in which the permeability coefficient is the product of the diffusion coefficient and solubility coefficient.<sup>18</sup> In homogeneous polyurethane membranes prepared from a poly(propylene oxide)-based prepolymer, the measured value of the permeability coefficient for CO<sub>2</sub> is 50 Barrer.<sup>16</sup>

In this work, the introduction of a second soft segment, polybutadiene, led to the synthesis of heterogeneous membranes with different structures depending on the relative amounts of the two soft segments and with enhanced gas-permeation properties. Although the solution–diffusion mechanism can still be applied to heterogeneous membranes, it is very difficult to relate the diffusion and solubility coefficients of the heterogeneous membranes with the corresponding coefficients for the single-phase membranes. In our system, the polybutadiene soft segment of the membranes had higher chain mobility than the PU soft segment; this was evidenced by its lower glass-transition temperature, which was associated with the higher CO<sub>2</sub> diffusion coefficients of the PBDO soft segments. In the literature, a value of  $10.5 \times 10^{-7}$  cm<sup>2</sup>/s has been reported for the diffusion coefficient of CO<sub>2</sub> in polybutadiene,<sup>19</sup> and a value of  $0.63 \times 10^{-7}$  cm<sup>2</sup>/s has been reported for this diffusion coefficient in a poly(propylene oxide) polyurethane.<sup>20</sup> With respect to the solubility coefficient, one would expect CO<sub>2</sub> to have higher solubility in PU than in PBDO. The PU segments have polar and flexible ether linkages that would favor CO<sub>2</sub> solubility. It is well established in the literature that the presence of polar groups in the polymer main chain favors CO<sub>2</sub> solubility.<sup>21–25</sup> The polar groups of the polymer are assumed to have dipolar interactions with the polarizable carbon dioxide molecules.

According to this discussion and to the strong evidence that the very different permeabilities of the PU/PBDO membranes can be correlated to the different phase-separation morphologies, we propose to assess the overall gas-permeation performance through an effective permeability coefficient,  $P_e = P\beta/\Theta$ , where  $P$  is the permeability coefficient,  $\Theta$  is a tortuosity factor accounting for the geometrical modification of the transport path, and  $\beta$  is a factor taking into account the permeation enhancement due to structural parameters. In the more phase-separated membranes prepared with 10 wt % PBDO, the permeability to CO<sub>2</sub> was 191 Barrer, a much higher value than the value of 50 Barrer<sup>16</sup> for single-phase PU membranes and higher than the value of 127 Barrer<sup>19</sup> reported in the literature for single-phase polybutadiene membranes. As already stated, for the membranes with 25 wt % PBDO, there was a strong reduction of the CO<sub>2</sub> permeability to 90 Barrer, and that could be attributed to the very tortuous path of the membranes with phase separation at the nanoscale [Fig. 2(a)]. The



**Figure 3** FESEM micrographs of a PU/PBDO membrane with 60 wt % PBDO submitted to a shear stress at (a) lower and (b) higher magnifications.

increase in the PBDO concentration leading to molecular mixing of the two soft segments did not significantly change the permeabilities.

The TEM data give clear evidence that the increase in the PBDO concentration promoted the enhancement of the mixing of the two soft segments. More important is the fact that the membranes with PBDO concentrations of 60 wt % or higher had very specific mechanico-optical properties.<sup>25,26</sup> It is now confirmed that in this range of PBDO concentrations, the membranes upon the application of a shear stress display very interesting patterns of light scattering, and with the support of optical microscopy observations, Godinho et al.<sup>26</sup> attributed these light scattering patterns to the development of bands approximately 4  $\mu\text{m}$  thick. The membrane with 60 wt % PBDO was submitted to shear stress and then analyzed with FESEM. The corresponding micrographs are in Figure 3,

showing evidence of bands approximately 4–5  $\mu\text{m}$  thick.

## CONCLUSIONS

We observed through TEM that two-soft-segment urethane/urea membranes with poly(propylene oxide) and polybutadiene presented three different types of morphologies: a single-phase morphology and two different phase-separated morphologies. In membranes with 10 or 20 wt % PBDO, large domains rich in PBDO were dispersed in a matrix that was predominantly PU. In the polymers with compositions ranging from 25 to 50 wt % PBDO, the morphology was characterized by a disordered, wormlike nanostructure. For the membranes with PBDO concentrations higher than 60 wt %, the morphology was formed by a single phase. It was confirmed that the morphology of the PU/PBDO polymers played an important role in the polymer membrane properties, namely, the gas-permeation and mechanico-optical properties. The first ones strongly depended on the morphology of the phase segregation in micro/nanostructures. With respect to the mechanico-optical properties, the development of bands 4–5  $\mu\text{m}$  thick upon the application of shear stress was characterized with FESEM in single-phase-morphology membranes.

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