Modification of polystyrene barrier properties

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This work investigates the possibility of reducing the permeability of polystyrene by adding small amounts of a liquid-crystalline azo compound, 2,3-dimethyl-4-n-butyl-4-(4″-methoxybenzoyloxy)azobenzene (BMA). Addition of BMA to polystyrene can lead to either an increase or a decrease in permeability depending on the effects of BMA concentration and casting conditions on the film morphology. The film morphologies were characterized by polarized light microscopy, wide-angle X-ray diffraction and differential scanning calorimetry; following which the permeability of H_2, N_2, CO_2 and water vapour were measured. Relative to polystyrene, 30–40% decrease in the composite permeability can be achieved with only 2% BMA loading. This decrease is due to the 'antiplasticization' effect of BMA on polystyrene.

(Keywords: polystyrene films; permeability; antiplasticization)

INTRODUCTION

Polystyrene is a commonly used packaging material; however, its barrier properties are limited compared to other more costly polymers. The relatively high permeability of polystyrene to water is a particular problem[1]. While increasing the crystalline content[2] or increased ordering[3] are possible means of reducing permeability, these approaches are not possible with atactic polystyrene. The addition of a discrete, second, impermeable phase has been shown to be an effective method of reducing the permeability of the composite[4]. This method is especially effective with platelet-shaped particles of the second phase[5]. It has also been shown in some cases that addition of a second miscible component can decrease the matrix permeability through 'antiplasticization'[6].

In the present study, we have examined the effect of adding small amounts of an azo compound, 2,3-dimethyl-4-n-butyl-4-(4″-methoxybenzoyloxy)azobenzene (BMA), to polystyrene. The composite films were prepared through solvent casting, as this was an easy method of getting varied film morphologies for study. The BMA/polystyrene can be cast so as to give either homogeneous films in which the BMA is essentially miscible with the polystyrene or films in which there is a significant amount of BMA present as a liquid-crystalline phase dispersed in the polystyrene matrix. The film morphology was studied by various methods such as light microscopy, wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (d.s.c.). The film morphology characteristics were then used to interpret the permeability results.

EXPERIMENTAL

Materials

Films of polystyrene dispersed with BMA were cast from distilled CCl_4, which is a common solvent for both polystyrene and BMA. The polystyrene used was commercially available sheet grade (Polystyron MCG-100, obtained from Polychem Ltd, India). BMA was prepared in our laboratory, according to the procedure published earlier[7]. Three series of films were prepared at three different casting temperatures, i.e. 4, 35 and 55°C. The proportion of BMA in each series at a constant casting temperature was varied from 1, 2, 3, 6 and 10% of the total solids in the casting solution. The polystyrene concentration of the casting solution was kept constant at 5% by weight. The solution containing dissolved polystyrene and BMA was poured on a Petri dish floating on mercury to get a film of uniform thickness ($\approx 70\,\mu$m). The evaporation temperature/casting temperature was controlled to within ± 0.5°C until a solid film was obtained. The film was further dried in a vacuum oven at 50°C for a minimum of 4 days to remove traces of solvent and was stored in a desiccator before being used for permeation studies. Also, thin films (10–15 μm) were specially cast from polystyrene solution of 1% by weight, for light microscopy examination. Infra-red spectroscopy of the finished films gave spectra consistent with the starting BMA/polystyrene ratios.

Morphology characterization

Polarized light microscopy, differential scanning calorimetry and wide-angle X-ray diffraction were used to characterize the film morphologies.

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Polarized light microscopy. A Laborlux 12 Pol S was used to study two types of films: (1) thick films on which permeability measurements were taken; and (2) thin films specially cast giving higher resolution under the microscope.

Differential scanning calorimetry. D.s.c. scans were run on a Perkin–Elmer DSC 7 at a heating rate of 10°C min^{-1}. The temperature range was 50 to 225°C, which encompasses the glass transition temperature T_g of polystyrene and the nematic transition temperature of BMA. The samples were examined from the same films used for the permeability study.

Wide-angle X-ray diffraction. A Phillips PW 1730 was used to record spectra in the range of 4–32°, using a Cu Kα source. The amorphous nature of polystyrene and crystalline nature of BMA were studied by these spectra.

Film permeability

Gas permeabilities through the polystyrene/BMA films were measured by the variable-volume method using a permeation apparatus described before[8]. The gases tested were N_2, H_2 and CO_2 at a measurement temperature of 35°C and pressure of $\approx 12.7 \times 10^5$ N m^{-2}. N_2 permeabilities were also measured at temperatures ranging from 35 to 75°C in order to calculate the activation energy for permeation in films cast at 35°C. Water-vapour transmission through polystyrene/BMA films cast at 35°C was measured using the cell shown in *Figure 1.* A known amount of water was added to the cell covered by the test film. The cell was kept at 30°C in a desiccator containing $CaCl_2$. The weight loss, corresponding to the water vapour transported through the film, was measured periodically at time intervals of 24 h. The measurements were continued until consistent weight-loss data were established, typically over a two-week period.

RESULTS

Polarized light microscopy

Two types of films were studied using polarized light microscopy. Thick ($\approx 70\,\mu$m) films used for the permeation studies were examined directly and the results were confirmed by examining thinner films (10–15 μm) cast under the same conditions, i.e. same percentage of BMA and same casting conditions. Both sets of films appear to show essentially similar trends for the film morphologies; however, the resolution is much better with the thin films. The microscopic examination shows two clear trends.

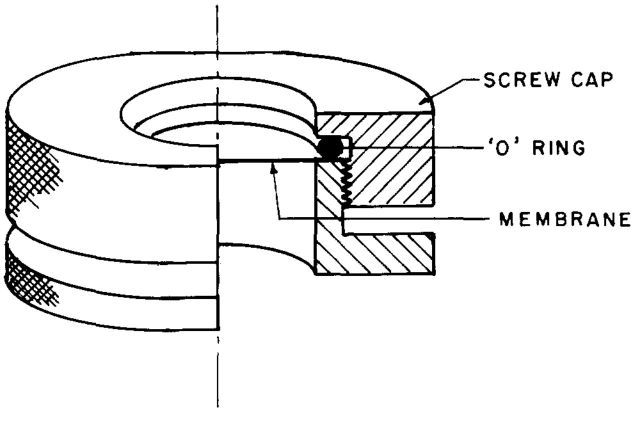

Figure 1 Schematic of cell used for water-vapour transmission measurements. Area of membrane exposed is 19.6 cm^2. Distance from membrane face to water is $\approx$1.5 cm

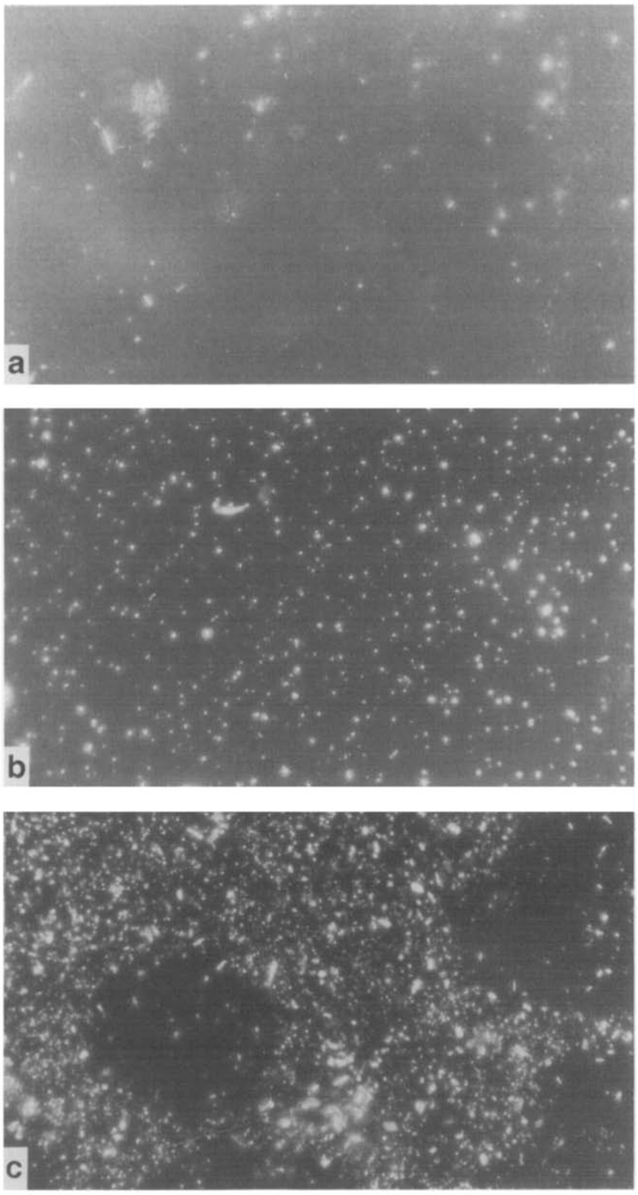

Figure 2 Photographs (taken at 32 ×, polarized light) of 10 μm thick films cast at 4°C with following BMA loadings: (a) 1%, (b) 6%, (c) 10%

As expected, the films show more developed BMA domains as the BMA concentration increases. Films at all three casting temperatures and BMA loading of 1–3% show only a few, randomly scattered, discrete domains of small size. As the BMA loading increases from 1 to 3% these domains become more prominent but are still uniformly distributed in the polymer matrix. At 6 and 10% loading of BMA the domain size further increases, and at 10% loading these BMA domains form interconnected, channel-like structures.

The second trend is that, at higher casting temperature, the degree of phase separation between BMA and polystyrene is less and these films appear more uniform. Films with 6 and 10% BMA loading cast at 55°C show more uniformly distributed domains than do similar films cast at 35°C, while in the case of 4°C well developed assemblies of BMA can be seen for all the films. Typical films are shown in *Figures 2a–c*.

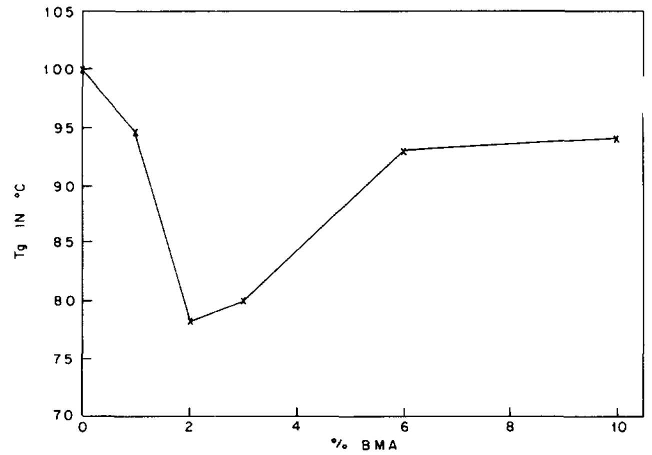

Figure 3 Polystyrene glass transition temperature T_g as a function of BMA loading in films cast at 35°C

Differential scanning calorimetry

D.s.c. data for films with varying BMA loading and all cast at 35°C are summarized in *Figure 3*. As BMA concentration is increased, the polystyrene glass transition temperature T_g, first decreases, passing through a minimum at 2–3% loading, then increases again for 6 and 10% loading. Similar decreases in T_g compared to polystyrene were also observed for films with 3% BMA loading cast at 4 and 55°C. The nematic transition of BMA at 141°C seen when the BMA powder is directly analysed could not be detected in any of the films investigated.

Wide-angle X-ray diffraction

Typical WAXD spectra for the polystyrene/BMA films are shown in *Figure 4*. Polystyrene by itself shows only a broad peak with a maximum at 19.4°, while BMA in powder form gives several sharp peaks. The spectra for the polystyrene/BMA films are highly dependent on loading and casting temperature. At higher casting temperatures (35 and 55°C) and low BMA loadings (1–3%), the spectra resemble that of pure polystyrene without any detectable BMA phase. At these temperatures the presence of a distinct BMA phase can be detected only at higher loadings (6–10%). In contrast all films cast at 4°C exhibit some characteristic BMA peaks.

Gas permeation

Permeation data for films cast at 35 and 55°C as a function of BMA loading are shown for N_2 in *Figure 5* and for H_2 in *Figure 6*. These films show a sharp decrease of 25–38% in the N_2 permeability and 20–25% in the H_2 permeability. The activation energy for N_2 permeation (*Table 1*) is ≈100% higher for the BMA-containing samples than for pure polystyrene. The decrease in permeability is most marked at low BMA loadings of 1–3%. The decrease in permeability is also more marked in the case of N_2 than for H_2, thus resulting in an increase in the H_2/N_2 selectivity with increased BMA loading. The decrease in permeability is related to the size of the penetrant gas, as CO_2 shows a similar 30% decline as N_2.

Films cast at 4°C showed irregular and non-reproducible data for N_2 permeation; hence these data are not presented. Surprisingly, though the N_2 permeability varied by several times, the H_2 permeability for the films cast at 4°C was relatively unchanged. By contrast the permeability data for the films cast at 35 and 55°C are

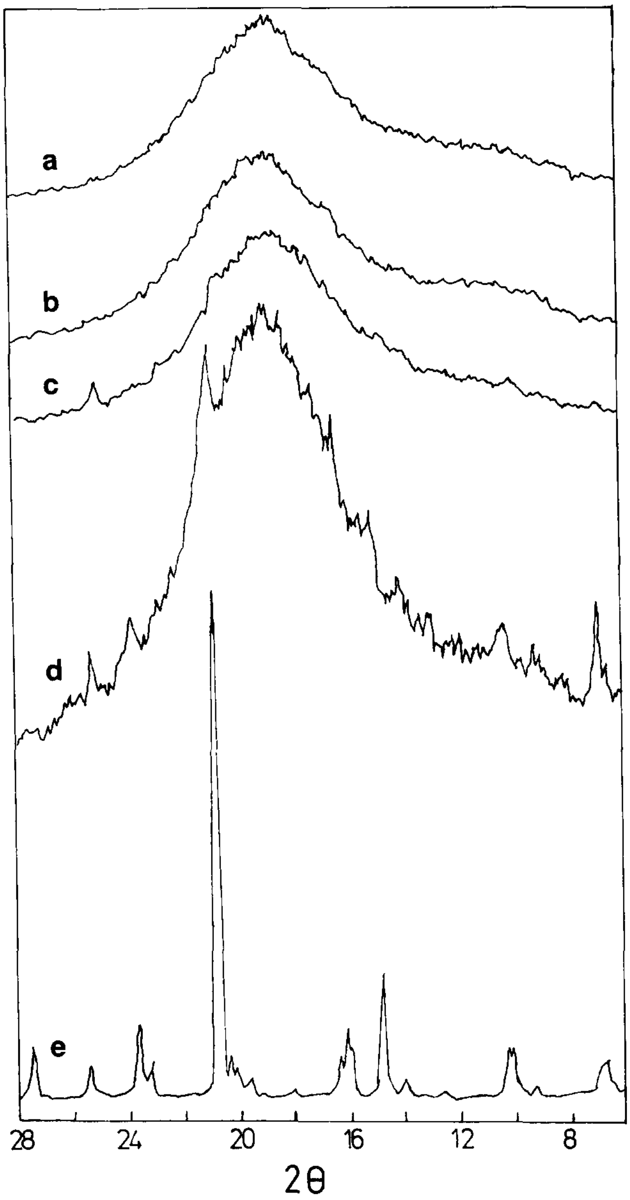

Figure 4 Wide-angle X-ray diffraction spectra for following films: (a) polystyrene cast at 35°C; (b) 2% BMA loading, cast at 35°C; (c) 10% BMA loading, cast at 35°C; (d) 10% BMA loading, cast at 4°C; (e) BMA in original powder form

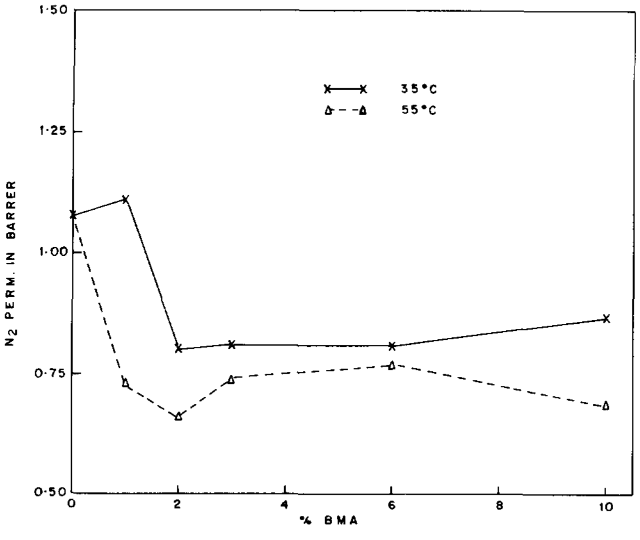

Figure 5 N_2 permeability at 35°C and 12.7×10^5 N m^{-2} as a function of BMA loading in films cast at 35°C (——) and 55°C (– – – –)

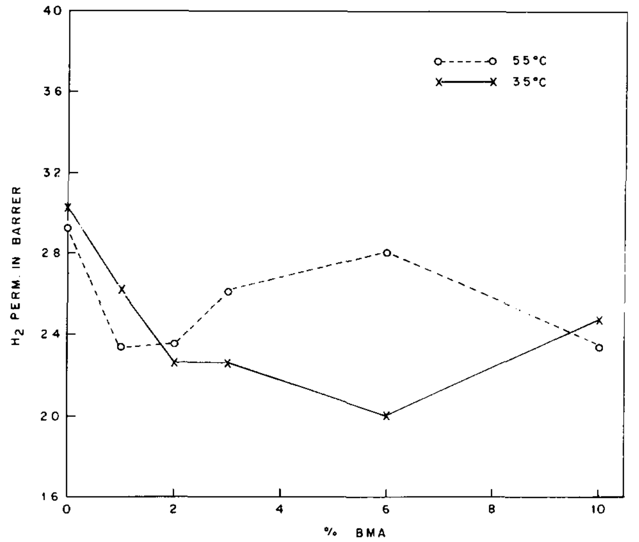

Figure 6 H_2 permeability at 35°C and 12.7×10^5 N m^{-2} as a function of BMA loading in films cast at 35°C (——) and 55°C (– – – –)

Table 1 Activation energy for N_2 permeation (ΔE) and intercept (P_0) calculated from an Arrhenius plot of log(permeability) *versus* $1/T$ (K^{-1}) for films cast at 35°C

BMA (%)	$-\Delta E$ (kcal mol^{-1})	$P_0(10^{-4})$ (cm^3(STP) cm/cm^2 s cmHg)
0	5.2	0.02
1	9.1	3.3
2	10.3	15.9
3	10.1	12.7
6	11.1	65.4
10	10.9	41.4

Table 2 Water-vapour permeability (P) for films cast at 35°C and varying BMA loadings

BMA (%)	$P(10^{-11})$ (mol cm/cm^2 s)
0	1.55
1	1.34
3	1.07
10	1.11

much more reproducible. The replicability of the permeability measurements was checked in two ways: (i) repeated measurements on the same film and (ii) measurements on film samples prepared at different times under the same conditions. The standard deviation calculated by both methods is similar and corresponds to $\approx 3\%$ of the permeability values for the films cast at 35 and 55°C.

Water-vapour permeation data through films cast at 35°C are presented in *Table 2*. These data are consistent with the gas permeation with increasing BMA loading. The film with 1% BMA loading shows a 13% decrease compared to pure polystyrene, while films with 3 and 10% BMA loading show a decrease of $\sim 30\%$.

DISCUSSION

The results indicate the following general trends: (i) At low BMA loadings ($\lesssim 3\%$) and higher casting temperatures (35 and 55°C), the BMA/polystyrene films are mostly homogeneous. These films show lower permeabilities than do pure polystyrene films. (ii) At higher BMA loading and/or at 4°C casting temperature, a second discrete BMA phase can be seen in the polystyrene matrix. The higher amount of BMA does not decrease the flux further, and in several cases leads to non-reproducible, higher permeability values.

The existence of a discrete BMA phase can be detected from both WAXD and light microscopy data (*Figures 2* and *4*). The characteristic BMA peaks at 15° and 21° in the WAXD spectra are apparent only for films cast at 4°C or from films containing 6–10% BMA loading. For the other films, light microscopy does show some ordering in spots (see *Figures 2a–c*); however, these areas are relatively few and unconnected. D.s.c. was not able to detect either the nematic or the crystalline transition of BMA in any of the films. This may indicate that the liquid-crystalline domain sizes that exist are too small to be detected by d.s.c.

The film morphology is affected both by the miscibility of BMA in the polystyrene matrix and also by the kinetics of the casting process. Visual observations indicate that, at lower casting temperatures, BMA reaches its solubility limit faster than the polystyrene, thus leading to a well developed BMA phase before complete solidification of the polystyrene. At higher casting temperatures, the two processes take place at similar speeds, giving a more homogeneous film.

Literature indicates at least two possible mechanisms for explaining the reduced permeability in the BMA/polystyrene system: (i) antiplasticization and/or (ii) increased tortuosity of the diffusion path because of the second impermeable phase. At low additive concentrations, the BMA can function as an antiplasticizer; by occupying the space between polymer chains it reduces the free volume available for solute transport, thus decreasing the permeability[6]. As with conventional plasticizers, there is a decrease in the T_g (see *Figure 3*). However, with conventional plasticizers, there would also be an increase in the polystyrene interchain spacing d_{sp} (location of the amorphous peak maximum in the WAXD spectra)[9] and also an increase in permeability. Here, by contrast, we see no change in the d_{sp} value and a decrease in permeability. The higher activation energy for permeation as shown in *Table 1* indicates a decrease in free volume[10] for the BMA/polystyrene films compared to polystyrene. Interestingly, increasing BMA loadings beyond 2–3% does not further reduce the permeability nor does it increase the activation energy significantly. This indicates that the BMA is not miscible in polystyrene beyond this value.

While it has been shown that addition of a crystalline or impermeable phase will decrease the permeability through the composite[4], this mechanism does not appear applicable in the present case. As already pointed out, the decrease in permeability in the BMA/polystyrene case is not monotonic with loading as would be expected from models describing an impermeable phase dispersed in a matrix[11]. Also, under conditions where the BMA liquid-crystalline phase is significantly enhanced, the permeability is not reduced but is in many cases even greater than that in polystyrene. This may be due to molecular-sized defects arising in the composite matrix or surface adsorption of the permeating species on the BMA liquid-crystalline phase. As an example, the data for films cast at 4°C, where the discrete BMA phase is most pronounced, shows that, while the H_2 permeability is reasonably constant with increased loading, the N_2 permeability values are highly scattered but on the whole increased.

CONCLUSIONS

On addition of as little as 2–3% BMA to the polystyrene matrix, the permeability of N_2, CO_2 or H_2O can be decreased by $\approx$30–40%. Further increase in BMA loading does not decrease the permeability further. Low loadings of BMA and casting at higher temperatures give more homogeneous BMA/polystyrene films (reduced incidence of a discrete BMA liquid-crystalline phase). Characterization of the film properties and study of the permeability decrease is consistent with antiplasticization of the polystyrene matrix by the azo compound.

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