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Effect of specific interactions on film casting of high temperature polymers

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Summary

Cast films were prepared from polybenzimidazole and a polyimide as well as from their blends over the whole composition range. The solvent was N,N'-dimethyl acetamide (DMAc), which was removed by washing with water and drying. The amount of solvent retained by the films depended on sample preparation conditions and significantly influenced the stability of the polymer. Vapour absorption and FTIR studies have shown that solvents enter into strong interaction with the polymers, especially with the polybenzimidazole component. The thorough removal of solvents is an essential condition for the utilization of films prepared from these polymers.

Introduction

Interest in polymers with superior electric and mechanical properties has increased significantly all over the world in the last few decades. Usually excellent thermal and chemical stability are also expected from such materials. Poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (PBI) meets these requirements, but its high glass transition temperature makes its processing almost impossible with traditional techniques. In order to improve processability, this polymer is often blended with polyimides (PI) having similarly good dielectric and mechanical properties, as well as chemical resistance. Blends of PBI with various polyimides have been widely studied and considerable attention is now paid to these materials (1-10).

Preparation of PBI blends is usually carried out by film casting, precipitation from solution or fiber spinning. Very few solvents are able to dissolve PBI, one of them is N,N'-dimethyl acetamide, thus blends are prepared from this solvent. Polar groups in PBI enter into strong interaction with solvent molecules, which makes removal of the last traces of solvent difficult as a result. One of the most frequently used techniques for solvent removal is washing the film in hot water and subsequently drying it in an oven. Table 1 lists some of the preparation techniques published to date. It is clear from the table that numerous and sometimes very different techniques are used for the preparation and purification of PBI/PI blends. A systematic study of the most important factors influencing film properties, i.e. duration of washing with water, length and temperature of drying, has not been carried out yet. The thermal analysis of PBI/PI blends has shown that 1 - 5 wt% solvent remained in the prepared blends even after the tedious purification procedure used. All results indicated that solvent retention is due to the interaction of the solvent with the PBI component of the blend (2,8,10). Liang et al (2) claimed that apparent compatibility, i.e. parameters characterizing compatibility, of PI and PBI can be significantly influenced by the presence of a solvent strongly interacting with one of the components. We assume

Table 1 Film casting techniques for PBI/PI blends

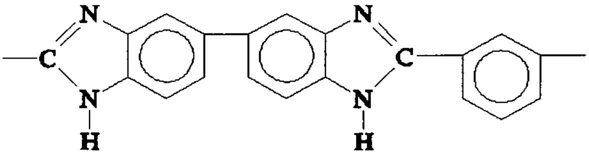
Ref.	Solvent evaporation in N_2		Washing with water		Vacuum drying	
	T (°C)	t (h)	T (°C)	t (day)	T (°C)	t (h)
1	80	24	50	1	200	72
2	80	24	60-70	7	?	?
3	80	24	70	7	200	72
4	80	24	50	1	80	?
5	80	48	50	7	180	>336
6	125	24	50	several	125-150	12
7	125	24	50 or 80	several	200	3
8	80	24	70-80	3	200-220	168
9	50-250	72	-	-	300	72

that the ternary solution of PI, PBI and DMAc is homogeneous at all the concentrations used. After the evaporation of the solvent a homogeneous blend is obtained, the phase separation of the components is kinetically hindered because of the low segmental mobility in the glassy state. However, above the glass transition temperature phase separation occurs, which is strongly influenced by the presence of any small molecular weight contaminations (e.g. solvent, water). As a consequence the conditions of sample preparation (solvent removal, drying) strongly influence the properties of the resulting films.

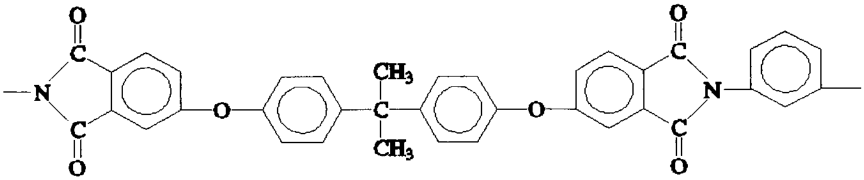
Preliminary experiments indicated that solvent content significantly influences the thermal stability of neat polybenzimidazole. The temperature related to the initiation of thermal degradation of PBI became approximately 20 °C higher after the solvent content of the film was decreased from 7 to 2 wt% by washing with water. In the present study attention was focused on the determination of the effect of the interaction between the solvent (N,N'-dimethyl acetamide) or water and the polymers (PBI, PI) on the preparation of films and the influence of the sample preparation protocols on their stability.

Experimental

The polybenzimidazole (PBI) used in the experiments was the poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] product of Hoechst Celanese Corp.



The polyimide [poly([2,2'-bis(3,4-dicarboxyphenoxy)phenyl]-propane-m-phenylene-diimine] was produced by General Electric Co. under the trade name of Ultem 1000.



PBI was dissolved in the N,N'-dimethyl acetamide in a stainless steel reactor at 260 °C and 3-4 bars pressure for 2 hours. The solution was diluted to 2 w%. N,N'-dimethyl acetamide solution of the same concentration was prepared also with the polyimide under ambient conditions.

Films were cast from the two polymers and a series of blends were also prepared for further studies. 50 ml of the solutions were poured into Petri dishes of 100 mm diameter. The majority of the solvent was evaporated in a ventilated oven at 80 °C in about 60 hours. The films were washed with water at 60 °C in order to remove further solvent. Duration of washing with water was varied between 0 and 7 days. Traces of moisture were removed by drying in an oven at 170, 190 or 210 °C. The films were dried for various lengths of time between 0 and 1500 hours and they were stored in a desiccator containing silica gel until further use. Thickness and size of the films were varied by changing the volume used for casting, or the diameter of the Petri dish, respectively.

Thermal stability of the films was determined by TGA measurements on a Mettler TA 3000 thermal analyzer. The measurements were carried out on 5-10 mg samples in the temperature range of 35 and 800 °C at a heating rate of 20 °C/min. All measurements were made in nitrogen atmosphere.

In order to determine the interaction of the solvent and water with the polymers, films were stored in desiccators containing either the DMAc or water. Shifts in the peak frequency of various characteristic groups of the polymers were followed by FTIR spectroscopy on a Mattson Galaxy 3020 single beam apparatus. The measurements were carried out as a function of storage time.

Results and Discussion

Weight loss of PBI/PI blends occurred in 4 steps of various intensities in the temperature interval of 40 and 800 °C. Assignment of the decomposition stages could be done by the analysis of the thermograms

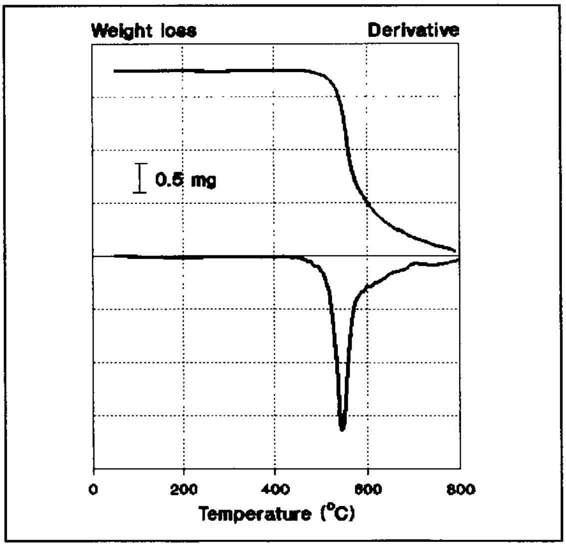


Figure 1 *TGA analysis of a PI film; sample: 7.7 mg*

of the PBI and PI components. Samples with and without washing were measured and their thermograms compared under equal conditions. Weight loss of PI is presented in Fig. 1. A single weight loss step was detected on the thermogram of both the washed and unwashed samples. This indicated about 45 w% weight decrease between 440 and 800 °C and was assigned to the thermal decomposition of PI. 2 or 3 steps were detected on the thermogram of the PBI sample depending on its preparation, i.e. whether it was washed with water, or not. Thermogram of a PBI film washed with water is presented in Fig. 2. The sample was subjected to a minimum drying necessary for the handling of the sample. Analysis and comparison of the thermograms lead to the assignment of the steps. The first weight loss stage between 40 and 300 °C belongs to the evaporation of water, the second, between 350 and 550 °C, to the loss of DMAc, while the third step was the result of the thermal degradation of the polymer.

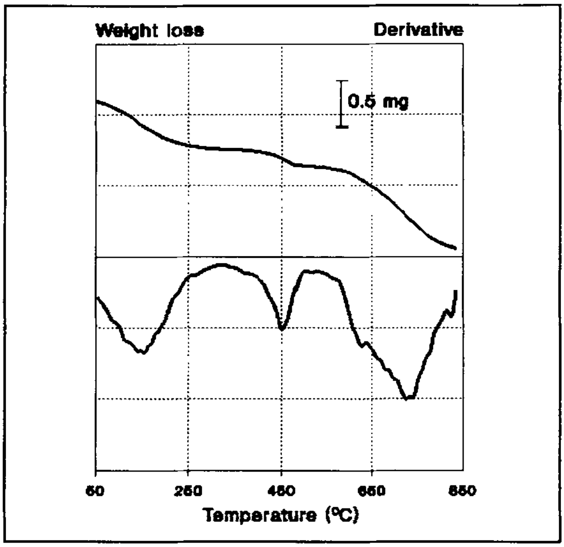


Figure 2 *Three characteristic weight loss steps on the TGA trace of PBI; sample weight: 9.6 mg*

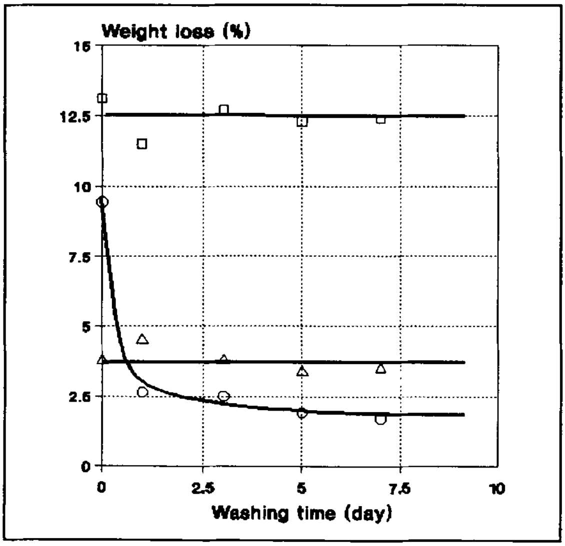


Figure 3 *Dependence of the weight loss of PBI on the time water washing. Symbols:* (Δ) *Peak 1*, (○) *Peak 2*, (□) *Peak 3*

The fact that weight loss associated with water or solvent (N,N'-dimethyl acetamide) removal could not be detected on the thermogram of PI indicates that this polymer enters only into weak interaction with them. PBI, on the other hand, forms strong secondary bonds with both substances, thus conditions of sample preparation, i.e. temperature and duration of washing or drying, are important for the quality and properties of the final film.

Washing time

Duration of washing of the films in water at 60 °C was varied between 0 and 7 days. All samples were dried at 190 °C for 48 hours. Thermogravimetric analysis of the samples yielded three weight loss steps, which were designated Peak

1 (loss of water, 40-300 °C), Peak 2 (loss of solvent, 350-550 °C) and Peak 3 (degradation, 550-800 °C) on the derivative curve of the thermogram. Weight losses for the three processes are plotted against the time of washing in Fig. 3. The figure clearly shows that weight losses due to the 1st and 3rd processes remain constant, while the one associated with the second peak decreases with time. This result proves that the second step involves the evaporation of the solvent, on the one hand, while it also indicates that washing with water decreases the solvent content of the polymer. Solvent content of the film continuously decreases with increasing time of washing leading to an improvement in the stability of the polymer. Although the largest part of the solvent is removed in the first 24 hours, some decrease in DMAc content is observed even after 7 days. The solvent remaining in the polymer is less than 2 w% of the total sample weight, which assures sufficient stability according to the results of thermal analysis showing an increase in the initiation temperature of degradation on solvent removal. Similar results were obtained on PBI/PI blends indicating that the PI content does not take part in the absorption of the solvent. Based on these results washing time was held constant at 7 days in further experiments.

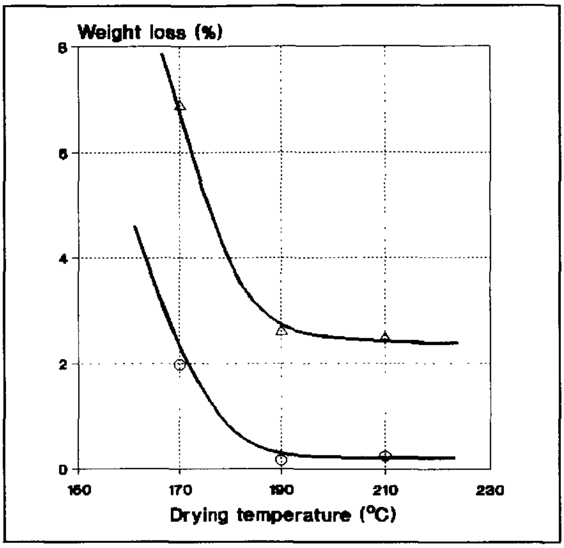


Figure 4 *Effect of drying temperature on the weight loss of PBI films between 40 and 500 °C.* (○) *washed,* (Δ) *without washing*

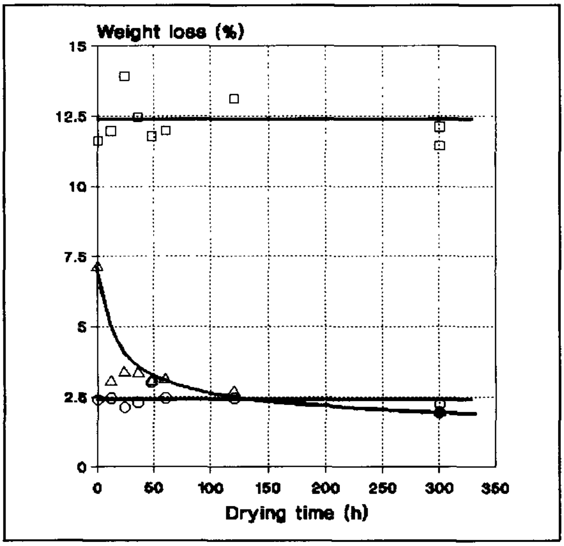


Figure 5 *Dependence of the weight loss of PBI films on the duration of drying. Symbols are the same as in Fig. 4.*

Temperature and time of drying

Samples washed for 7 days were dried at 170, 190 and 210 °C between 0 and 1500 hours. Samples were regularly weighed during the drying period to follow weight loss. The changes in the weight of the samples were very small at 170 °C indicating limited evaporation of water. The amount of water removed increased with temperature, but at 210 °C discolouration of PBI was observed, the sample degraded. Thus 190 °C proved to be the optimum temperature for drying, which was supported also by the thermal analysis of the samples. Weight loss of the samples between 40 and 500 °C was determined for the samples dried for 1500 hours. This temperature interval provides for the removal of both water and solvent. The determined weight losses are plotted against the temperature of drying in Fig. 4 for the washed and unwashed samples. The figure unambiguously proves that the temperature of drying plays a role in solvent removal, and indirectly shows that stability of the prepared samples is the best at 190 °C.

The effect of drying time was studied by thermogravimetric analysis on samples washed for 7 days and dried at 190 °C. Weight losses characterizing the three processes described earlier (Peaks 1 to 3) are plotted against the duration of drying in Fig. 5. In contrast to Fig. 3, weight losses related to the 2nd and 3rd processes are constant, only the amount of removed water changes. The figure indicates that the loss of solvent and the degradation of PBI is independent of the length of drying, but water removal is not. Although the largest part of the water is removed in the first 24 hours, weight loss is significant even after 300 hours.

Interaction

Thermal analysis of PBI/PI blends, as well as that of the polymer components have us already provided indirect proof concerning the interaction of water and the solvent used with PBI. The results clearly showed that the polyimide does not bind water or N,N'-dimethyl acetamide, whereas PBI enters into strong interactions with water or DMAc. Absorption of solvent vapour and subsequent FTIR analyses supplied further proof of these interactions. Films of PBI and PI were placed in a desiccator containing the DMAc or water and spectra were recorded at regular intervals. In agreement with previous results the spectrum of PI did not change as a function of time. Frequency of the NH vibration of PBI (3408 cm^{-1}), however, decreased significantly as an effect of water absorption, which is to be expected in view of the strong H-bonding character of water and the nitrogen atoms of the imidazole ring at the same time. Frequency of the NH vibration was plotted against the logarithm of absorption time in Fig. 6. The results show that absorption of water results in a nearly 30 cm^{-1} shift in the frequency of NH vibration. Absorption of N,N'-dimethyl-acetamide leads only to a negligible shift in any of the characteristics peaks of PBI, including that associated with the NH bond, and even this small shift appears only after such a long time that a part of the film already dissolves.

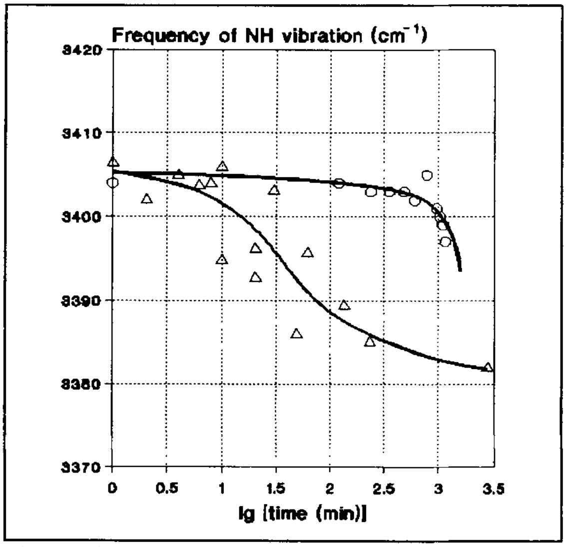


Figure 6 *Shift in the frequency of the NH vibration in PBI as an effect of solvent vapour absorption.* (○) *N,N'-dimethyl-acetamide,* (△) *water*

According to the spectra recorded during solvent absorption, N,N'-dimethyl acetamide does not enter into interaction with the imidazole ring, but it may form charge transfer complexes with the benzene ring of PBI.

Conclusions

The study of the sample preparation conditions of PBI/PI blends and that of the component polymers have shown that the solvents remaining in the prepared films significantly influence their stability. The time of washing, as well as the time and temperature of drying are important factors in the preparation technique. Complete removal of the solvent or water is difficult because they enter into strong interaction with PBI. Water forms H-bonds with the imidazole ring, while N,N'-dimethyl acetamide forms charge transfer complexes with the benzene rings of PBI. The polyimide used does not interact either with solvent or water very strongly. Use of a standard protocol is thus necessary both in theoretical study and practical utilization of PBI and its blends.

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