Polymer Bulletin 52, 267-274 (2004)
DOI 10.1007/s00289-004-0286-9

Polymer Bulletin

Phase separation behavior and morphology development of phenolic resin/PMMA/hexamethylenetetramine blends

Masanori Yamazaki1) (✉) , **Akiko Nishijima**2), **Kazuko Ikeda**2), **Shoji Ichihara**2)

1) Mitsubisi Chemical group Science and Technology Research Center, Inc.
1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan.
3805864@cc.m-kagaku.co.jp, +81-45-963-3196

2) Department of Organic and Polymer Materials Chemistry Faculty of Technology, Tokyo University of Agriculture & Technology.
2-24-16 Naka-cho, Koganei-shi, Tokyo 184-8588, Japan.

Received: 5 April 2004/Revised version: 2 July 2004/ Accepted: 23 July 2004

Summary

In order to obtain materials with nanopores which will be applicable for many fields, the structures of the cured blends of phenolic resin (PhN), poly(methyl methacrylate) (PMMA) and curing agent were studied. After PMMA was extracted from cured blends, the structures of cured phenolic resins were observed with SEM. As a results, it was found that nanosized continuous pore structures were formed in extremely wide composition region if curing temperature was high.

Introduction

The phase separation morphologies of polymer blends and block copolymers have extensively been studied from academic viewpoint or to obtain high performance and functional materials. As a result, various phase separation structures in the shapes and sizes were founded. Among them, microphase separation structures of block copolymers have recently attracted the interest of researchers as a preparation method of nanoporous material with an ordered structure [1-4]. Generally, porous materials with pores in nano-range are thought to be promising materials for catalyst supports, separation mediums, double-layer capacitors and electrodes [5]. In the field of inorganic materials, mesoporous silica and mesoporous carbon have so far been studied and synthesized by so-called the template method [6-8]. The characteristics of mesoporous materials including pore structures have been reported.

However, as synthesis of a special block copolymer is necessary in the block copolymer method, and as removal of template is necessary in the template method, these processes are still laborious and expensive. From these reason, we have proposed a new preparation method using a miscible polymer blend for obtaining a porous carbon with continuous nanopores [9-10]. In our method, the phase separation structures of phenolic resin (PhN) and poly(methyl methacrylate) (PMMA) are changed into porous carbon material with continuous pores. In order to obtain the carbon materials with controlled nanopores using our method, it is very important to investigate the phase separation behavior in curing process and the structure change in carbonization process. It is well known that the structures of phase separation vary with the composition and temperature of the blends. For PhN/PMMA blends, curing condition will also affect the phase separation structures. In this paper, we report preliminary results on the phase separation behavior of PhN/PMMA blends.

Experimental

Preparation of blends

Novolac type phenolic resin (PhN, M_w=936 g/mol, M_w/M_n= 1.4) used was supplied by Gunei Chemical Co. Poly (methyl methacrylate) (PMMA, M_w=73.5 kg/mol, M_w/M_n=1.2) was purchased from Aldrich Chemical Co., and used without farther purification. Typical blend preparation was carried out as follows. 10 g of PhN in a solid form and 1.5 g or 2.0 g of hexamethylenetetramine (HMT) as a curing agent were dissolved in 60 ml of methanol. Then, PMMA and acetone were added to this solution and PMMA was dissolved. The ratio of PMMA against PhN was changed from 9:1 to 0:10. The quantity of acetone was equal to that of methanol in volume. The solution of PhN/PMMA/HMT blends was cast onto Teflon® dish and solvents were evaporated in atmospheric circumstance for several days. Then the sample was put in a vacuum oven at room temperature and was maintained for several days to dry the samples sufficiently. Then the sample was press-molded at various temperatures and times. Besides PhN/PMMA/HMT blends, PhN/PMMA blend samples were prepared in similar procedure and were dried sufficiently at 130°C in a vacuum oven for 24 h. PhN/PMMA blend samples were used in DSC measurements.

DSC measurements

Glass transition temperatures (T_g) of blend samples were determined with DSC model 8120 manufactured by Rigaku. Temperature scale of the DSC was calibrated using melting temperature of indium and zinc with the heating rate of 10°C/min. DSC curves of press-molded PhN/PMMA/HMT samples were measured with 10°C/min from –20°C to 200°C. The samples were held at 200°C for 10 min in DSC and cooled to –20°C with the rate of 20°C/min. Then, the samples were heated again from –20°C to 200°C with the rate of 10°C/min, and DSC curves of the second run were measured. T_g of PhN/PMMA blend samples were also measured in the same condition.

Morphology observations

PMMA was extracted from the press-molded samples with acetone. Then the samples of PhN rich phases thus obtained were broken to make cross-sections for observation. The morphological features of the cross-section were observed with scanning electron microscopy (SEM), JSM-6300F manufactured by JEOL, operating at 1.5 kV. When curing was insufficient, the sample collapsed in the extraction process. In such case, cross-section was made before extraction, and then, the surface was washed with acetone instead of full extraction of PMMA.

Results and discussion

Thermal behaviors of PhN/PMMA and PhN/PMMA/HMT blends

To examine the miscibility of PhN and PMMA, T_g of the blends were measured with DSC. Fig. 1 shows the composition dependence of T_g of PhN/PMMA blends. Only one T_g was observed on the first and the second run of DSC. This means that PhN and PMMA are miscible with each other and phase separation does not occur without a cross-linking agent.

Figs. 2(a) and (b) show DSC curves for the first and the second run of PhN/PMMA/HMT blends. The ratio of PhN, PMMA and HMT was 50/50/7.5. As shown in fig. 2(a), all DSC curves exhibited an exothermic drift just above each curing temperature that was indicated in the figure. Generally, a curing reaction almost stops when the glass transition temperature of the system becomes equal to the sample temperature. Therefore, it is thought that the observed exothermic drift is due to the re-curing reaction of PhN component, and T_g of cured PhN rich phase in first run is just below of the exothermic drift observed. The inflection observed near to 100 °C corresponds to T_g of PMMA rich phase.

As shown in fig. 2(b), after the sample was held at 200 °C for 10 min the exothermic drift disappeared. This means that the curing reaction of PhN finished after the sample was kept at 200 °C for 10 min. The composition dependence of T_g of the cured PhN/PMMA/HMT blends determined from the second run is summarized in fig. 3. In fig. 3, T_g of PMMA rich phase is slightly higher than that of PMMA. When curing temperature is high, the curing reaction rapidly proceeds and the cured PhN phase remained in the PMMA rich phase. The difference of T_g between PMMA and PMMA rich phase in the blend will be due to the cured PhN remained in PMMA rich phase.

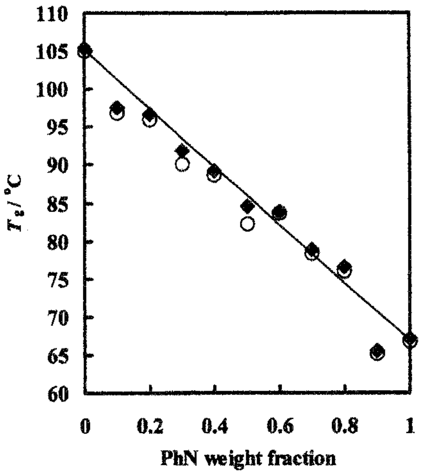

Fig. 1 Composition dependence of T_g of PhN/PMMA blends.

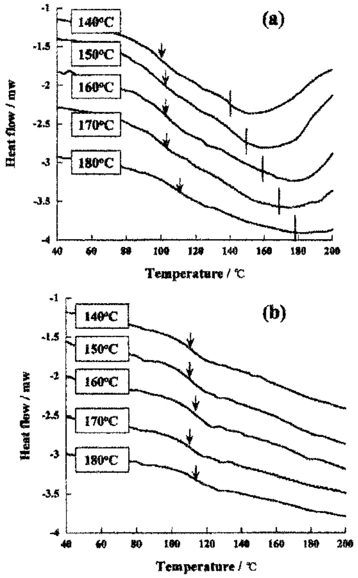

Fig. 2 Typical DSC curves obtained from first run for PhN/PMMA/HMT=50/50/7.5 blends cured at various temperatures.

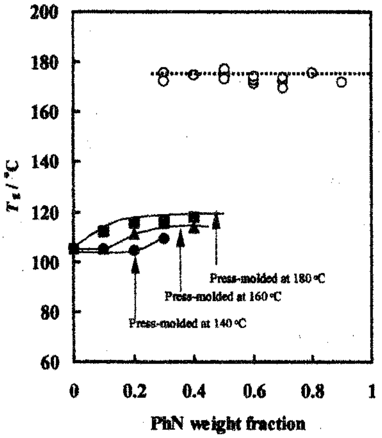

Fig. 3 Composition dependence of T_g of PhN/PMMA/HMT blends obtained from second run of DSC.

Phase separation structures based on SEM observation

When PhN rich phases obtained by extraction of PMMA from PhN/PMMA/HMT blends are converted into carbon material, the morphology of the blend affects on the pore structures in the carbon. Therefore, to know what structure can be formed is very important. Fig. 4 shows the typical results of SEM observations. The composition of the samples shown in fig. 4 is PhN/PMMA/HMT=40/60/6 and the curing conditions are shown in the caption. As PMMA component was extracted before SEM observation, the photographs shown in fig. 4 reflect the structures of PhN phases. The structures of the samples cured at 140 °C are ambiguous. However, as seen from fig. 4, both the structures of pores and PhN of the samples cured above 160 °C are continuous. Namely, the phase separation structures of the blend cured above 160 °C are co-continuous at this composition. As shown in fig. 4, the sizes of co-continuous structures became large when curing temperature was high. However, the size itself of phase separation of the sample cured at 200 °C was much smaller than that usually observed in the polymer blends of linear polymers. In many cases, the size of phase separation is micron order [11-13]. The effect of curing time on the phase separation size was smaller than that of the curing temperature.

Fig. 5 shows the temperature-composition diagram of the phase separation structures of cured PhN/PMMA/HMT blends. After curing, all samples examined became turbid because of the phase separation. Open triangles in the figure represent that the cured samples collapsed during long time extraction by acetone. The area covered by open triangles is low PhN concentration region. Therefore, it is thought that PhN in this region became dispersed phase and/or curing was insufficient.

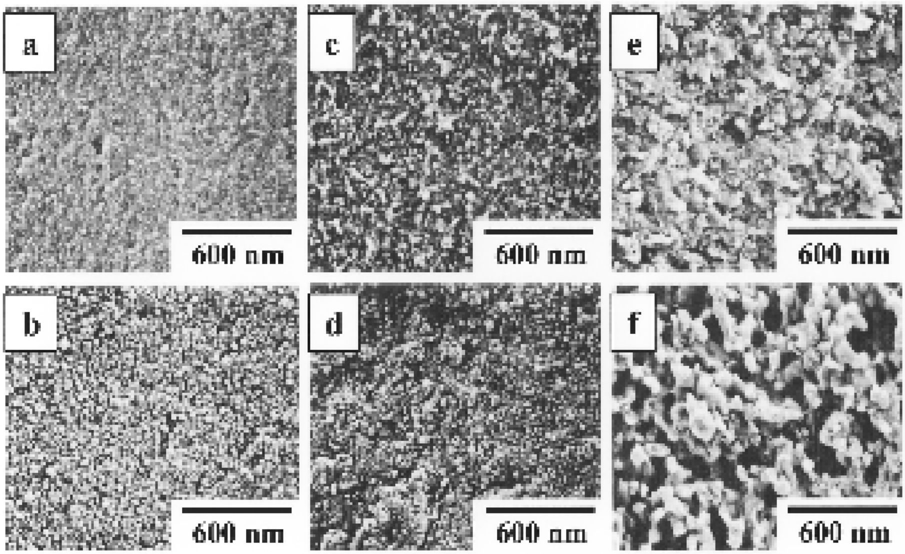

Fig. 4 SEM photographs of PhN/PMMA/HMT=40/60/6 blend. (a) press-molded at 140 °C for 8 min, (b) press-molded at 140 °C for 30 min, (c) press-molded at 160 °C for 8 min, (d) press-molded at 160 °C for 30 min, (e) press-molded at 180°C for 8 min, (f) press-molded at 180 °C for 30 min. PMMA component in each sample was extracted with acetone for several hours before SEM observation.

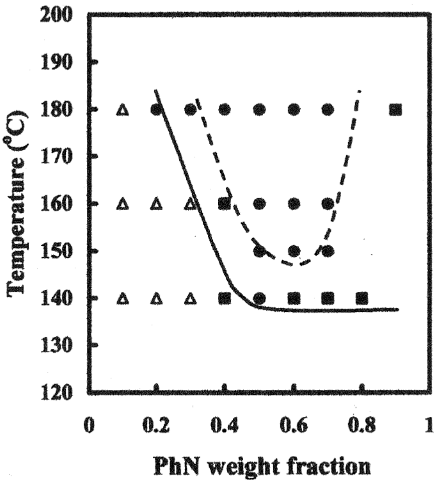

Fig. 5 Morphology diagram of PhN/PMMA/HMT blends cured for 30 min. (●); the region where co-continuous structure was observed, (■); the region where the structure formed did not collapse by extraction process though co-continuous structure was not observed, (△); the region where phase separation structure formed was collapsed during long tern extraction.

Filled squares in the figure represent that the cured samples did not collapse but the structures were seemed not to be co-continuous from SEM observations. The point that PhN is 90% and cured at 180 °C has a dispersed phase structure and the dispersed phase was PMMA rich phase. The phase structures of the samples cured at 140 °C and presented by filled square also seemed to be a dispersed structure. At this temperature, PhN in the samples was not sufficiently cured because T_g of PhN rich phase became equal to the curing temperature. The phase separation of PhN/PMMA/HMT blends was induced by the curing of PhN, that is, the increase of molecular weight of PhN. Therefore, at this temperature, phase separation is also stopped at relatively early stage. If the phase separation proceeds with nucleation and growth mechanism, this will be a reason that very smaller phase separation structure was observed in the sample cured at low temperature (fig. 4(a, b)).

The phase separation structure of the samples presented by the filled circles in fig. 5 is co-continuous structure. When PhN/PMMA/HMT blends was cured at 180 °C, the region of the composition, which gives the co-continuous structure, became very wide.

When PhN/PMMA/HMT blends are cured at low temperature and if T_g becomes equal to the curing temperature, not only the curing of PhN but also phase separation are stopped. If the curing reaction is stopped at relatively early stage, phase separation of PhN/PMMA/HMT blends should also be stopped at relatively early stage, because it is caused by the increase of molecular weight of PhN. If rigid network is not formed at that temperature, both the curing reaction and the phase separation will continue when the sample is brought to higher temperature.

The results of this experiment are shown in fig. 6. The structure of the sample cured at 140 °C for 1h was the smallest as shown previously. When the sample was kept at 200 °C for 10 min after it was cured at 140 °C for 1h, the pahse separation structure drastically grew up (fig. 6(b)). The size of the phase separation structure of the post-cured sample is similar to that cured at 180 °C for 30 min (fig. 4(f)). This result means that rigid network is not formed when the blend sample is cured at 140 °C and the observed structures of the samples cured at low temperatures are on the way of phase separation. Fig. 6(c) shows the effect of the quantity of curing agent. Except the amount of curing agent, HMT, the other conditions were same to those of fig. 6(b). The size of phase separation became small by the increase of HMT amount. Fig. 6(d) shows the structure obtained for different PhN/PMMA ratio under the same condition. In this case, the structure with relatively uniform periodicity was obtained. However, it was an exceptional example in this work and typical structure was like fig. 6(a-c).

In the fig. 6, the observed structures are the cured PhN phases. From these photographs, not only PhN phases but also PMMA phases in the cured blends seem to be continuous, that is, the phase separation structures are co-continuous. If the concentrations of PMMA and HMT, and the curing conditions are well selected, it will possible to obtain porous materials with controlled phase separation size and shape in nano-range.

It is well known that spinodal decomposition gives a co-continuous structure [14]. There is also a possibility that co-continuous structures are obtained even in the binodal region when the relaxation times of two phases are largely different [15]. As the studies of phase separation process were not carried out in details in this work, we cannot discuss the reason that co-continuous phase separation structures are obtained. However, as very small structures obtained at 140 or 160 °C are thought to be the structures at relatively early stage of curing and phase separation, it will be reasonable to think that the structures obtained at 180 °C also grow through small structures. It is known that, when a cross-linkable monomer/solvent system is polymerized, resultant structure is microgel connected with relatively low cross-liking density parts [16]. In the case of PhN/PMMA/HMT blends, phase separation occurs in the process of gelation. From this viewpoint, it is thought that the grains observed in fig. 4 and fig. 6 are derived from microgels, and thin rods that connect grains are derived from relatively low cross-liking density parts. In any case, the details of the phase separation process are still unclear. However, it was found that we could obtain the porous material with very fine continuous pores in wide composition range from PhN/PMMA/HMT blends.

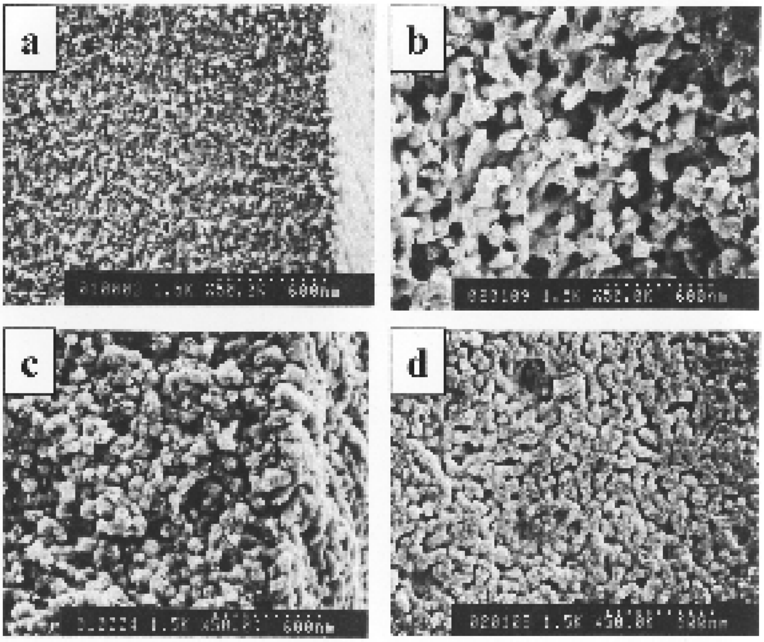

Fig. 6 SEM photographs of PhN/PMMA/HMT blends. Compositions and curing conditions are (a) PhN/PMMA/HMT=50/50/7.5, press-molded at 140°C for 1 hr, (b) PhN/PMMA/HMT=50/50/7.5, press-molded at 140°C for 1 hr, then annealed at 200°C for 10 min, (c) PhN/PMMA/HMT=50/50/10, press-molded at 140°C for 1 hr, then annealed at 200°C for 10 min, (d) PhN/PMMA/HMT=70/30/10.5, press-molded at 140°C for 1 hr, then annealed at 200°C for 10 min.

Acknowledgements.

We would like to express a special thanks to Ms. N. Kataoka and Dr. M. Takashima in Analytical division of Mitsubishi Chemical group Science and Technology Research Center for help with the SEM observations.

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