

ИССЛЕДОВАНИЕ ФОРМИРОВАНИЯ ПОРИСТЫХ СТРУКТУР НА ОСНОВЕ ПВХ

И.А. Христофорова, А.И. Христофоров

Ирина Александровна Христофорова*, Александр Иванович Христофоров

Кафедра химической технологии. Владимирский государственный университет им. А.Г. и Н.Г. Столетовых, ул. Горького, 87. Владимир, Российская Федерация, 600000

E-mail: khristoforova-i@mail.ru*, khristoforov@mail.ru

В работе представлены результаты экспериментальных исследований фазового равновесия в системах «смесь пластификаторов - порообразователь». В качестве пластификаторов использовались диоктилфталат, бутилбензилфталат, дикрезилфосфат, в качестве порообразователей – простые олигоэфиры (этиленгликоль, диэтиленгликоль, триэтиленгликоль). Был проведен эксперимент и построены тройные фазовые диаграммы состояния данных систем. Выявлено, что пластификатор дифенилкрезилфосфат имеет полную совместимость с диэтиленгликолем и триэтиленгликолем, но не совместим с этиленгликолем. Найдены составы, при которых тройные системы «бутилбензилфталат - дифенилкрезилфосфат – простые олигоэфиры» являются гомогенными. Для систем, содержащих в своем составе триэтиленгликоль, количество должно составлять не менее 20%, а при введении диэтиленгликоля – не менее 30%. При включении в композицию в качестве второго пластификатора диоктилфталата, доля порообразователей должна превышать 70%. Авторами предложена установка для определения фазового равновесия жидких систем. По результатам исследований были разработаны составы и технологический режим получения пористых пленок на основе поливинилхлорида методом термического формования. Выбор метода формования обусловлен рядом преимуществ по сравнению с другими, широко используемыми методами получения пористых пленок и мембран: получение материалов с узким распределением пор по размерам, достаточной прочностью, эластичностью, открытой пористостью. Получены образцы на основе поливинилхлорида эмульсионной марки, бутилбензилфталата, дифенилкрезилфосфата и двух видов порообразователей: триэтиленгликоль и диэтиленгликоль. Температура проведения фазоинверсионного термического процесса - на уровне 180 °С. В ходе экспериментальных исследований получены пористые материалы со следующими свойствами: открытая пористость 38-44%, прочность при разрыве 1,0 – 1,2 МПа, относительное удлинение 43-63%, максимальный размер пор $(2,3 - 2,8) \cdot 10^6$ м, средний размер пор $(0,5 - 1,1) \cdot 10^6$ м.

Ключевые слова: поливинилхлорид, пластификатор, порообразователь, фазоинверсионный термический процесс, пористые материалы, мембраны

RESEARCH FOR FORMING POROUS STRUCTURES BASED ON PVC

I.A. Khristoforova, A.I. Khristoforov

Irina A. Khristoforova*, Alexander I. Khristoforov

Department of Chemical Technologies, Vladimir State University named after A.G. and N.G. Stoletovykh, Gorkiy st., 87. Vladimir, 600000, Russia

E-mail: khristoforova-i@mail.ru*, khristoforov@mail.ru

In this work, we report on phase equilibrium in systems «plasticizer mix - blowing agent». Dioctylphthalate, butylbenzylphthalate and dicresyl phosphate were used as plasticizer, and simple oligoesters (ethylene glycol, diethylene glycol, triethylene glycol) served as a blowing agent. We conducted an experiment and built triple phase diagrams. Diphenylcresylphosphate proved to be fully compatible with diethylene and triethylene glycol, but not to the ethylene one. Triple systems «Butyl benzyl phthalate - Diphenylcresylphosphate - Simple oligoesters» turned out to be homo-

geneous for several created compounds. To achieve this for a triple system, the minimal quantity threshold is either 20% of triethylene glycol or 30% of diethylene. As for the case of dioctyl phthalate for second plasticizer, the minimal threshold for blowing agents is 70%. We constructed a device that allows to detect phase equilibrium for liquid systems. We devised several compounds and a technological process for creating porous PVC-based membranes using thermal molding. We selected such molding due to several advantages when compared to other methods for producing porous membranes, such as: required density, elasticity, open pores, and narrow pore size distribution. We managed to create several samples based on emulsion type PVC, butyl benzyl phthalate, diphenylcresyl phosphate, diethylene and triethylene glycol. During the phase inversion thermal process temperature should be around 180 degrees of celsius. Porous materials have the following properties: open porosity 38-44%, breaking strength 1.0 – 1.2 MPa, relative extension 43-63%, maximal pore size $(2.3 - 2.8) \cdot 10^{-6}$ m, average pore size $(0.5 - 1.1) \cdot 10^{-6}$ m.

Key words: PVC, plasticizer, blowing agent, phase inversion thermal process, porous materials, membranes

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INTRODUCTION

Porous PVC-based membranes can be produced in different ways: either wet or dry molding, sintering, phase inversion thermal process. The latter method is the simplest one from the technological point of view [1]. This process implies required ingredients (PVC, plasticizer, blowing agent) are to be mixed and placed in a metal mold with layer thickness in range $(0.2-0.6) \cdot 10^{-4}$ m. The mold with polymer is placed in heat chamber for heat treatment (with air convection) by temperature range 130-180 °C. After that the mold is retrieved from the chamber and is cooled down together with compound on air. The problem with molding porous membranes this way is that in order to achieve required durability one has to wash blowing agent out of pores. The process takes places at room temperature in the bath with running water. Afterwards the membranes are dried in order to remove moisture. As a result there is air in the pores.

Thermal process has several unique features. For example, the pores with finite structure have spherical shape. Diameter of each cell ranges from 1 to 10 μm . Either holes or pores between those cells have diameter in range from 1 to 10 nm with a narrow distribution of pore size. Only thermal process makes it possible to produce isotropic porous structures of large thickness.

Porous PVC-based materials are used as battery pack separators, sensors for electronic devices [2, 3],

breathable membranes serving for waterproofing of attic space and roofs [4-10], foundations, constructions, bridges and tunnels [11], decoration and sound absorbing materials [12, 13], water purification membranes [14-17]. They are also used as porous carriers for insecticides, perfumes and other substances [18, 19].

In this paper we study phase equilibrium in systems «Plasticizers (mix) – blowing agent» in order to produce open-pore materials.

EXPERIMENTAL TECHNIQUE

Fig. 1 shows the device required for conducting a research of phase equilibrium when dealing with systems «plasticizer (mix) – blowing agent». First one must prepare the device. In order to achieve this, mixer 4 of thermostatic bath 2 is connected to electricity grid via transformer 1 ($U = 220$ V). Heater 3 and bath are heated until the required temperature controlled using thermometer 5. Every temperature requires specific voltage. The original system 13 (either single or two-component) is placed inside cuvette 12.

After that both mixer 14 and heater 3 are turned on, followed by adjusting the temperature of experiment. The speed of mixers 8 and 9 is adjusted by using transformers 6 and 7. After that one more ingredient from burette 10 is added slowly without temperature change using drop counter 11, until content of cuvette 12 becomes persistently turbid by sight.

The composition is calculated and phase equilibrium diagram is built. Another variation of this experiment assumes that the compound remains the same, but the temperature is adjusted slowly in order to find the temperature of system becoming visually turbid. After stabilizing the temperature one can change the composition again and find the point of turbidity for the new composition. Thus it is possible to study diagrams of triple systems.

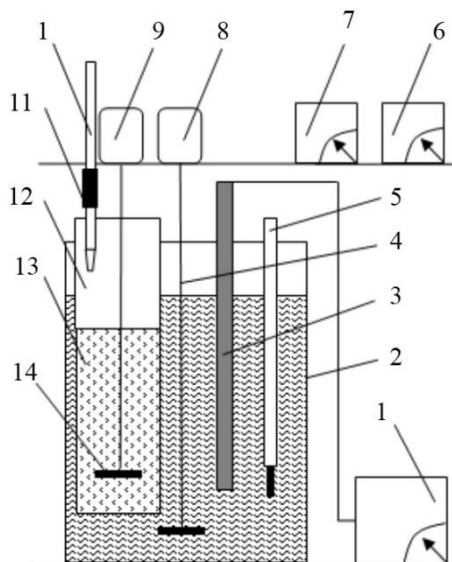


Fig. 1. Device for determining the phase equilibrium in systems «plasticizer — blowing agent»: 1,6,7 — transformers; 2- thermostatic bath; 3 - heater; 4 — mixer; 8,9 — mixers electric motors; 5 — thermometer; 10 — burette; 11 — dropper; 12 — cuvette; 13 - initial solution; 14 — mixer

Рис. 1. Схема установки для определения фазового равновесия в системе «пластификатор – порообразователь»: 1,6,7 - трансформаторы; 2 – термостатирующая баня; 3 – нагреватель; 4 – мешалка; 8,9 – электродвигатели мешалок; 5- термометр; 10 - бюретка; 11 – капельница; 12 - кювета; 13 - исходный раствор; 14 – мешалка

RESULTS AND DISCUSSION

Paper [20] lists research for double and triple phase diagrams in systems «plasticizer – blowing agent – modifying additive». As plasticizers authors used butyl benzyl phthalate (BBP), dioctyl phthalate (DOP), dialkyl phthalate (DAP). Triple (TEG), double (DEG) and single ethylene glycol (EG) served as blowing agent, while butyl cellosolve (BC) served as modifying additive. However, usage of BC in technological process is limited due to its boiling temperature (171.1 C), hence limiting the temperature of producing porous products to 155 °C. Therefore, we decided to research the possibility of using high-temperature boiling liquids. We have chosen diphenylcresyl phosphate (DPCP) – plasticizer for PVC. We used the mix of BBP and DPCP since products

produced by simple DPCP tend to have large shrinkage. This is not acceptable in producing porous materials. Plasticizer mix eliminates this flaw. DPCP is mixed with DEG and TEG. Its high boiling temperature (390 °C) increases varying range of technological modes when making products. We built triple diagrams (plasticizer mix – blowing agents) at temperature 20 °C in order to determine solvent composition and range of homogeneous state, as shown in Fig. 2.

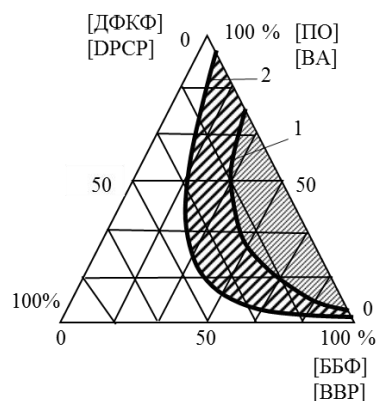


Fig. 2. Triple phase diagram for BBP — DPCP — blowing agent system state (BA): 1- TEG; 2 — DEG (20 °C)
Рис. 2. Тройная фазовая диаграмма состояния системы ББФ - ДФКФ - порообразователь (ПО): 1 - ТЭГ; 2 - ДЭГ при 20 °C

As one can see, to make BBP-TEG system homogeneous at 20 °C, DPCP concentration should be at least 20 %, and for BBP-DEG this number is at least 30 %. It turned out impossible to get the boundary for disintegration into phases in case of BBP-EG-DPCP due to full incompatibility of EG with DPCP.

Similar research was conducted for DOP plasticizer. According to result diagram heterogeneous state covers almost all the diagram, and the area of open-porous structure genesis is very small (Fig. 3).

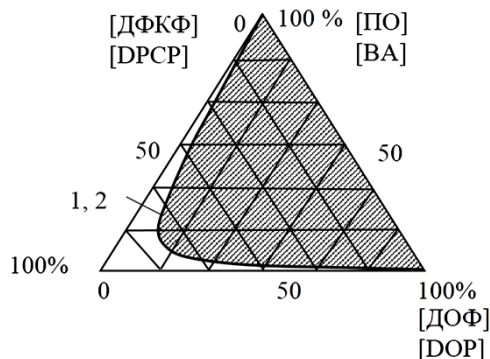


Fig. 3. Triple phase diagram for DOP — DPCP — blowing agent system state (BA): 1- TEG; 2 — DEG (20 °C)
Рис.3. Тройная фазовая диаграмма системы ДОФ - ДФКФ - порообразователь (ПО) при 20 °C: 1 - ТЭГ; 2 – ДЭГ

In order to make system homogenous, DPCP concentration should be at least 70 % using either TEG or DEG. Boundary curves disintegration into phases are practically identical. Therefore, blowing agent does not influence system state.

BBP based systems have the smallest area of heterogeneous state (Fig. 2). Therefore, further research was conducted using multi-component solvent. BBP and DPCP mix was used for plasticizer, and either TEG or DEG was used as a blowing agent.

Based on the conducted research porous materials were produced at temperature 180 °C with 15 min duration.

For TEG the best properties had materials produced with composition [PVC] = 40%, [BBP: DPCP:TEG] = 0.8:0.2:2.0 = 60%.

Material properties are: open porosity W – 44%, breaking strength σ_p – 1.0 MPa, relative extension ε – 63%, maximal pore size d_{\max} – $2.8 \cdot 10^{-6}$ m, average pore size d_{cp} – $1.1 \cdot 10^{-6}$ m, vapor permeability – 410 g/(m²·day), sound absorption coefficient – 0.74 (1000 Hz), apparent density – 660 kg/m³, operating temperature range -15...+60 °C.

For DEG the best properties had materials produced with composition [PVC] = 40%, [BBP: DPCP:DEG] = 0.43:0.57:2.0 = 60%. Material properties: W = 38%, σ_p = 1.0 MPa, ε = 43 %, d_{\max} = $2.3 \cdot 10^{-6}$ m, d_{cp} = $0.5 \cdot 10^{-6}$ m.

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CONCLUSION

Experiment data shows that the usage of plasticizer mix (DPCP+BBP (DOP)) is efficient enough for lowering the critical temperature of disintegration when dealing with systems «plasticizer – blowing agents». Research indicates that DPCP is unlimited when mixing with either TEG or DEG, but is incompatible with EG. The BBP-TEG system is homogenous at 20 °C for 20 % concentration of DPCP and 30 % for DEG. As for DOP-TEG and DOP-DEG mix, concentration of DPCP should be at least 70 %. Usage of pure DPCP in mix with either TEG or DEG, as shown in preliminary researches, is unacceptable due to high shrinkage of product – more than 8 %.

Usage of triple solvent butyl benzyl phthalate – diphenylcresyl phosphate – glycols at 20 °C in homogenous state allows to produce open-pore materials both for TEG and DEG serving as blowing agent.

In case of using DEG as blowing agent one needs higher dose of second plasticizer diphenylcresyl phosphate (at least 30 percent) to achieve homogenous state, compared to usage of TEG (at least 20 %).

The best material produced using DEG has properties in summary inferior to material produced using TEG.

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