Porous Elastomeric Beads from Crosslinked Emulsions

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ABSTRACT: The production of porous polymeric particles is attractive for a large number of applications and can be achieved by various techniques. Although numerous production schemes exist for glassy polymers, difficulties arise for soft, rubbery materials that need a chemical crosslinking step, such as elastomers. This is particularly true for poly(dimethylsiloxane) (PDMS), which shows the lowest glass-transition temperature among the polymers. Recent studies suggest *in situ* hydrogen bubble formation or vacuum drying of water droplets dispersed in the polymer matrix in order to generate porous PDMS structures. In this work we report early results based on the chemical crosslinking of water in PDMS emulsion droplets in a mechanically stirred thermostated water vessel. This approach is shown to lead to high porosity PDMS beads (ca. 10^{-3} m particle diameter) with an open structure whose properties (diameter and porosity) are strongly influenced by the starting composition (solvent, surfactant, and polymer types and ratios), as well as the operating parameters (agitation and temperature). The possible uses of these derived beads are discussed. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 967–971, 2002

Key words: porous beads; emulsion; poly(dimethylsiloxane); crosslinking

INTRODUCTION

The elaboration of porous polymeric materials by various processes has been the subject of increased interest in recent years because of their numerous potential applications such as foams, membranes, solid supports, in chromatography, or controlled release media.[1] Pore formation is most often achieved via a phase separation process (temperature or nonsolvent demixing, emulsion, gas bubble formation, etc.) followed by a stabilization step, so the structure does not collapse and shows sufficient mechanical resistance. Stabilization can be achieved for thermoplastics or glassy polymers by simply controlling the solvent removal (e.g., evaporation or spray drying), and the resulting rigid matrix is often resistant

enough for most applications. Interfacial polymerization or coacervation can also be applied to achieve that purpose for specific problems or applications (e.g., microcapsules, core–shell particles, etc.).[2] More recently, the production of high surface polymeric matrices was reported, which were based on bicontinuous polymerized emulsions[3,4]; however, to our knowledge, these processes were limited to thermoplastics [e.g., poly(methyl methacrylate)]. In fact, difficulties in the preparation of porous matrices when soft (i.e., rubbery) polymers are used arise for two major reasons: these are subject to collapse during the solvent evaporation or removal step, and their physical characteristics in the dry state often demand chemical crosslinking stabilization.

Based on the previous considerations, we investigated the possibility of generating poly(dimethysiloxane) (PDMS) porous beads. This exploratory work was motivated by the following series of statements.

Table I   Composition Range of Starting Formulations Screened for Primary Emulsion Preparation

Compound	Water	PDMS	n-Heptane	Span 80
Weight ratio (%)	20 : 34	35 : 45	14 : 30	6 : 10
Volume ratio (%)	18 : 34	30 : 41	20 : 41	4 : 6

The lowest glass-transition temperature among polymers is that of PDMS.[5] Thus, it can be anticipated that the difficulties encountered with porous rubbery polymer production will be theoretically maximized with this compound.

From an applied point of view, PDMS already has numerous applications because of its peculiarities: strong hydrophobicity, high sorption capacity (especially toward apolar compounds), biocompatibility, thermal and electrical stability, optical transparency, film forming ability, and very high permeability toward gases.[6] These properties have promoted a variety of applications such as long-term delivery of drugs,[7] dense membrane processes for volatile organic compound removal,[8] water repellant coatings,[9] electrical insulation, and so forth. For several of these applications, a porous PDMS matrix could be interesting for physical properties tuning, interfacial effects promotion, or mass transfer enhancement.

Studies relevant to the production of porous PDMS matrices are scarce and limited to *in situ* hydrogen bubble generation by a hydrosilylation reaction,[10] vacuum drying of dispersed water droplets from a water in PDMS emulsion,[11] or solvent curing induced demixing.[12] These attempts invariably lead to structures where the polymer constitutes the continuous phase and can hardly be transposed to spherical particle preparation. We show hereafter that porous spherical particles with an open structure (i.e., where PDMS is the dispersed phase) can be generated based on a novel approach combining emulsion production followed by *in situ* chemical crosslinking.

EXPERIMENTAL

A water in oil emulsion was prepared from PDMS (Rhodorsil RTV141-A, Rhône–Poulenc) dissolved in analytical grade n-heptane (Sigma–Aldrich) for the oil phase and distilled water. A silane based catalyst (Rhodorsil RTV141-B, Rhône–Poulenc) was added in another step to induce crosslinking.

Preliminary screening tests showed that a lipophilic surfactant (sorbitan monooleate, Sigma–Aldrich) was suitable for the entire process, providing that a precise concentration range was used.

The porous bead production was performed according to the following steps. Distilled water, n-heptane, and vinyl terminated PDMS (RTV141-A) were first introduced at room temperature into a 3-mL flask. The addition of the surfactant and mixing with an ultrasonic probe (600 W, Sonics & Materials) led to a milky white primary emulsion that proved to be stable over a 2-day period at 25°C; no phase separation was observed. In a second step the catalyst (RTV 141-B) was incorporated into the emulsion by means of the same dispersing apparatus. To avoid heterogeneity and localized crosslinking due to the overheating of the probe, a discontinuous use of the ultrasonic emulsifier was advised. A period of 1 or 2 h was applied at this stage to precrosslink the polymer. The mixture was introduced dropwise to a capillary glass tube (1.5-mm internal diameter) in a thermostated stirred vessel containing water at 75°C. Each droplet led to the formation of a bead of approximately 1-mm diameter. Because of their low glass-transition temperatures, the beads had to be cooled *in situ* just after preparation with the intention to maintain their structure and prevent interparticle entanglements. About 10 different formulations (Table I) were used according to the scheme sketched in Figure 1, and these enabled porous bead preparation. The particles were further vacuum dried and put into various solvents without problems. The low surface energy of PDMS prevented particle aggregation problems in either the dry or swollen state.

RESULTS AND DISCUSSION

Conditions Prone to Porous Bead Production

Qualitatively speaking, the successful operation of the production scheme investigated in this work demanded the combination of two opposite
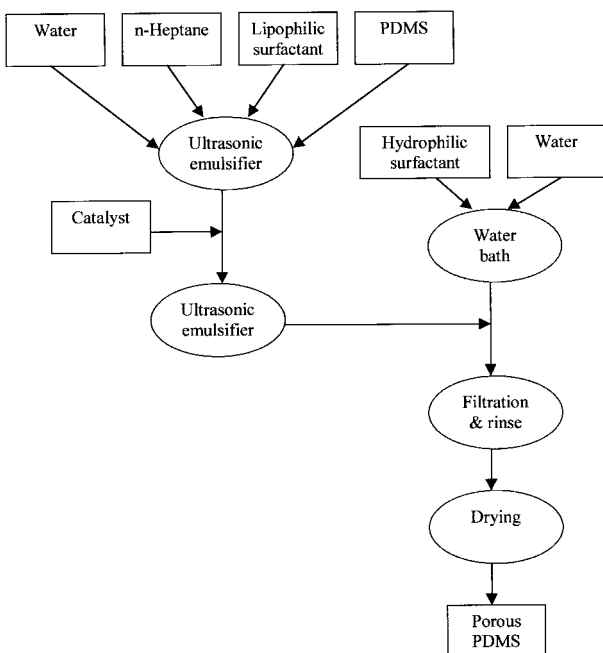
Figure 1 Schematics of the water/PDMS emulsion crosslinking procedure.

phenomena: crosslinking and water income. Crosslinking was necessary to stabilize the emulsion droplet, and it had to be rapid enough (at least at the water–droplet interface) to ensure droplet integrity. The catalyst–polymer weight ratio, PDMS solution viscosity (tuned by the heptane content), as well as water bath temperature were assumed to be the main operating factors for this process. Conversely, water income, which took place as soon as the emulsion droplet was put into contact with the water bath, was desirable in order to promote pore formation, but it could lead to droplet disruption and breakdown. The agitation rate, surfactant type, and water bath temperature are probably the main controlling factors that govern water income.

Thus, there are obviously a large number of parameters from the formulation and processing aspects that play an interdependent role in the porous PDMS particle formation. The quantitative determination of these complex relationships is beyond the scope of this article. Some qualitative observations were collected based on a series of experiments, and they can be summarized as follows:

1. An increase of the polymer proportion in the primary emulsion led to the formation of larger but coarser particles. These could be attributed to the higher viscosity of the droplet continuous phase.

2. An increase in the lipophilic emulsifier content gave smaller particles. This could be due to a larger number of water droplets in the primary emulsion, which could promote the splitting up of the oily globules in the stirred vessel.

3. A temperature of around 75°C and a polymer/catalyst ratio greater than 1:5 were favorable conditions for porous particle production. However, it should be noted that the water bath temperature was limited to a maximum of around 90°C; experiments carried out above this value led to complete destruction of the primary emulsion.

4. Because of their low glass-transition temperature, the polymer beads had to be cooled to ambient temperature *in situ* just after preparation to keep their structure and prevent mutual sticking.

Porous PDMS beads (1–3 mm average diameter) can be obtained with the above recommendations and composition ranges within the concentration windows shown in Table I. About 10 different formulations in agreement with the previous guidelines were successfully tested in terms of porous bead preparation. The stability of these prepared particles was noticeable. In fact, they could be vacuum dried and put into various solvents without any damage, thus showing the efficiency of the crosslinking step. Furthermore, the low adhesion properties of PDMS prevented particle aggregation problems in either the dry or swollen state.

Bead Characterization

Several observation techniques were employed to characterize the bead structures: light microscopy, scanning electron microscopy (SEM), and a stereoscopic apparatus. An ordinary naked-eye examination revealed the foamy appearance of the beads, reflecting their surface heterogeneity and the existence of an outer porosity [Fig. 2(a)].

The bead cross sections were observed with SEM, and a coarse inner porosity surrounded by a finer structure was found [Fig. 2(b)]. The latter constituted PDMS excrescences, which explained the rough aspect of these objects. The hypothesis of a high open porosity structure, which was suggested by microscopic examination, was checked
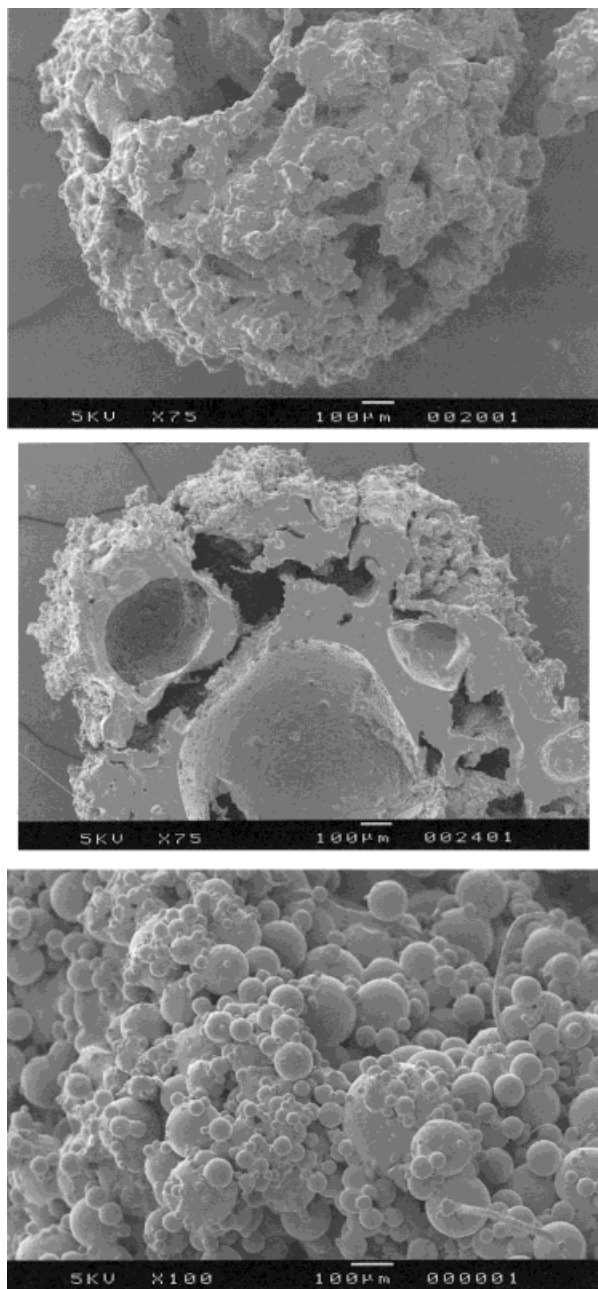
Figure 2 The SEM examination of porous PDMS beads: (a) overview, (b) cross section, and (c) surface.

in a second step by systematic density determination with a helium pycnometer. The fact that a pore-free PDMS density was obtained by this technique confirmed the fact that all free volume in the bead was accessible to helium. Based on the two previous observations, an open bead structure could be postulated, which is of value for applications based on high direct interfacial area and low pressure drop properties.

The attainment of the open porous structure was striking. In fact, when crosslinking a water/PDMS/water emulsion one would preumptively expect a particle structure where the polymer remains the continuous phase while water droplets dispersed during the primary emulsion step form closed pores. The SEM observation clearly revealed that the polymer particles formed a dispersed phase but remained embedded together by mechanical bridging, which probably resulted from mutual crosslinking [Fig. 2(c)]. Thus, a phase inversion phenomenon, which was attributable to either a temperature change or composition modification when the droplets were put in contact with the water bath, could be postulated.

CONCLUSION

This work reported early attempts to generate porous PDMS particles, which were based on a combination of emulsion production and chemical crosslinking. It was shown that particles with a diameter in the millimeter range, an open structure consisting of dense PDMS spheres (ca. 10-μm diameter), and chemically stuck together with sufficient mechanical resistance could be produced based on this process. Several potential applications of the particles were considered that essentially dealt with the interfacial area enhancement that should promote mass transfer kinetics. For instance, the use of a bead of porous PDMS particles could be of value for the removal of trace volatile organic compounds from either aqueous or gaseous fluxes according to the selective sorption properties of PDMS toward these compounds.[13] Aerosol treatment such as oil droplet removal could also be considered based on similar arguments. Another aspect was the incorporation of guest molecules within the particles for controlled release applications. Flavors or active compounds initially dissolved in the oily primary emulsion phase could be interesting candidates. The possibility to regenerate the particles after use and recycle them, given their good chemical and thermal resistance, is another attractive feature. Potential applications could also be based on the use of PDMS beads as precursors of porous inorganic materials as already attempted on dense PDMS matrices via partial pyrolysis[14] or silica shell covering.[15]

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