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Studies of phenolic resin-based microporous separator materials

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A method is described for the preparation of phenolic resin-based microporous separator materials with improved high-temperature, acid and oxidation resistance.

The effect of the degree of polycondensation of the resin, the quantity of modifying agent, the duration of modification, the ageing time of phenolic resin, the quantity of catalyst, and the pre-curing temperature of the resin upon the properties of the separator material were studied in an effort to improve the separator. The electrical resistance, pore size and volume porosity of separator samples were determined.

1. Introduction

A wide variety of microporous materials are now used as separators in lead–acid batteries. Thermoplastic polymers such as PVC, polyethylene, polypropylene etc. [1–3] are the most common. They all have a low softening temperature which leads to deformation of the separator under service conditions. In addition PVC [4–6] can evolve chlorine into the electrolyte which affects deleteriously the electrodes.

A trend in the production of microporous separators is the use of thermosetting resins [7–9]. Their main advantage is the high thermal stability and the excellent oxidation resistance.

The function of a separator in a lead–acid cell is complex and many of the requirements are conflicting. The separator is intended to keep the plates of opposite polarity apart, so that the electrolyte forms the sole internal conducting path between them. This means the separator must be a microporous material with high volume porosity and with small pore size.

The separator must be able to resist the strong oxidation in acidic media at 45–55° C, prevent antimony transfer and inhibit the growth of dendritic lead. In addition it must have low electric resistance up to 0.3 ohm cm^2 (although some manufacturers extend the limit up to 0.45 ohm cm^2 [10]).

The properties of a microporous separator material are critically dependent upon a large number of experimental variables.

This paper is aimed at the investigation of the effect exerted by the synthesis and modification conditions of the alkali condensed phenol-formaldehyde resin as well as separator manufacturing techniques upon the properties of the separator.

2. Experimental

2.1. *Materials*

Phenol 98%, formalin 37%, sodium hydroxide, silica, phenol–sulphonic acid 75% and polyester felt 38.4 g m^{-2} were used.

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2.2. *Synthesis, modification and filling of the phenol–formaldehyde resin*

Phenol and formalin in molar ratio 1.5 : 1.0 and 1 wt % sodium hydroxide (with respect to the phenol) were mixed in the reaction vessel. The condensation polymerization was carried out at 60–65° C for 4–6 h.

To 200 g phenol–formaldehyde resin with low molecular weight at 25–30° C, 60 g water, 10–40 g resorcinol and 30 g formalin were added. With respect to the entire mass in the reaction vessel, 30 wt % silica were also added.

Modification was carried out at 50–55° C for 0–60 min according to Table 2.

2.3. *Manufacture of microporous separator samples*

An aqueous solution of phenol–sulphonic acid (2.5–15 wt %) was added to the modified resin immediately before the formation of the microporous separator sample.

This mixture was poured into a mould, which consists of two heated plates. The temperature of the mould varied between 70° C and 100° C depending on the experimental programme. The polyester felt was placed on the lower plate.

Pre-curing was carried out during 1–4 min at constant temperature.

The separator sample was then washed with water, dried and subjected to additional thermal treatment at 180° C for final curing and evaporation of water, which acts as a pore forming agent.

2.4. *Tests*

The degree of polycondensation of the phenolic resin was determined by the solubility of the resin in water.

The ability of the resin to cure by including water was determined visually, observing the curing of the mixture resin–catalyst in a test tube at 70° C.

The electrical resistance was measured in a special test cell in which the separator, pre-soaked for 4 h in sulphuric acid (s.g. 1.28) using a 'Betatest Ω 9' milliohmmeter. The instrument is based on the four wire measurement technique, where a galvanostatic a.c. current is passed through the cell, using a high precision active rectifier, indicator and compensation circuitry. The zero of the system is set in the absence of a separator and a direct reading of the resistance value is obtained by simply inserting the separator together with its leak-proof frame.

Pore size and distribution of the pores in a separator were determined by a Mercury Porosimeter Model 1500, (Carlo Erba, Italy).

Volume porosity was determined by checking the actual and apparent density of the separator material using a helium picnometer, Micrometrics Instrument Corporation [10].

3. Results and discussion

As is known the solubility of low-molecular weight phenol–formaldehyde resin in water depends on the degree of polycondensation. At constant ratio of the initial components, it depends on the temperature and pH of the medium and on the reaction time.

We investigated the influence of the degree of polycondensation of a resin modified with 5–20% resorcinol on its capability to cure in one phase.

From the data in Table 1 is seen that the modified phenolic resins cure, releasing water from the system at 5% resorcinol content. In spite of the strong hydrophilic nature of resorcinol in this case, its quantity is insufficient to promote retention of water in the gelling process. A homogeneous porous mass with a strong hydrophilic nature was obtained using resin with water solubility of 20 vol %, which was modified by the addition of more than 10% resorcinol.

Phenol–formaldehyde low-molecular weight

Table 1. Ability of modified phenol–formaldehyde resin (MPhR) to cure in one phase (+) and in two phases (–) depending on the degree of polycondensation of phenol–formaldehyde resin (PhR) and the quantity of resorcinol

Quantity of resorcinol (wt %)	*Solubility of PhR in water* (vol %)			
	30	20	15	10
5	–	–	+	+
10	–	+	+	+
15	–	+	+	+
20	–	+	+	+

Table 2. Characteristics of separator samples as a function of the modification time of the resin at 55° C. All samples were prepared using 7% catalyst

Modification time (min)	*Electrical resistance* (ohm cm²)	*Volume porosity* (%)	*Volume of pores with diameter up to 1 μm* (%)	*Life-time, of the mixture* (min)
0	2.16	43.0	35	7
15	0.22	54.4	82	5
30	0.16	55.5	92	3
45	0.46	48.3	85	1
60	–	–	–	–

resins with higher solubility (30 vol %) and resorcinol content above 10% do not release water during curing, but the samples obtained are inhomogeneous in structure and have large visible pores. This is probably, due to the presence of a substantial quantity of unreacted monomers, in particular formaldehyde, which is released spontaneously.

The experiments were continued using resin with 20 vol % water solubility modified by 15% resorcinol.

During the modification process it was established that modification time affects the porosity of the separator material with other conditions constant.

A series of microporous separator samples were prepared varying the duration of modification. Data obtained in this experimental are given in Table 2.

It can be seen that the time of modification at temperature 50–55° C should not exceed 45–50 min. The resin sample No. 4, obtained during a 45 min modification time, gelled in less than a minute after adding the catalyst. This leads to shortcomings in the formation of the separator sample. On the other hand, the comparatively low volume porosity and high electrical resistance of the material indicate the presence of closed pores, i.e., in the process of pre-curing the resin reaches a higher stage of crosslinking than that necessary prior to the final heat treatment.

Sample No. 1 is obtained by heating the reacting mass up to 50° C and quick cooling to 20° C.

Fine drops of water are observed on the surface of the separator samples after pre-curing, which indicates that the pore forming agent is ejected. This fact explains the high electrical resistance and the low volume porosity. The optimum modification time is considered to be 30 min when all the requirements for a good microporous material are met.

It was established that the ageing time of the resin at 20 ± 5° C exerts a major effect on the properties of the porous material.

Table 3 shows that the best results were obtained using phenol–formaldehyde resin during the second hour after its synthesis. Probably processes of additional internal tightening (crosslinking) of the resin which occur after 24 hours following synthesis, lead to a degrading of the properties of the separator samples.

The amount of catalyst used is of crucial importance for the porosity and size of the pores. The latter was varied from 2.5–15.0 wt % with respect to the resin. The increase of the quantity of catalyst above 10–10.5% reduced the life-time of the system resin-catalyst below 1 min, which makes the mixture unsuitable for forming. Using 15 % catalyst, the resin gells almost immediately.

Table 3. Characteristics of separator samples as a function of the ageing time of modified phenol–formaldehyde resin

Ageing time (min)	*Electrical resistance* (ohm cm²)	*Volume porosity* (%)	*Volume of pores with diameter up to 1 μm* (%)
60	0.41	58.8	36
90	0.32	56.2	48
120	0.21	56.3	90
180	0.19	59.4	95
240	0.21	58.0	94
300	0.20	56.6	96
1440	0.38	51.7	82

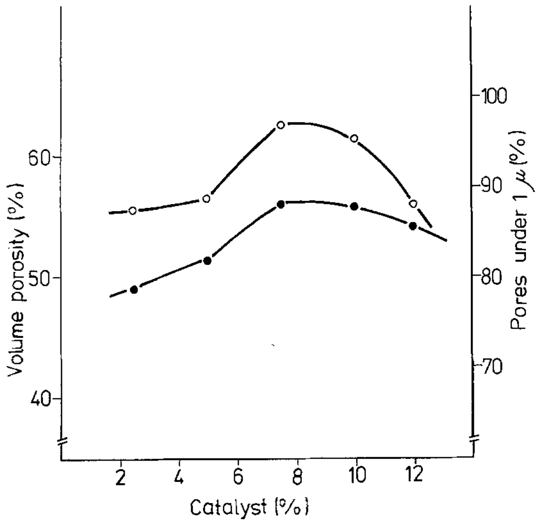

Fig. 1. Effect of the quantity of catalyst on the volume porosity (●) and the pore size (○) of the separator samples.

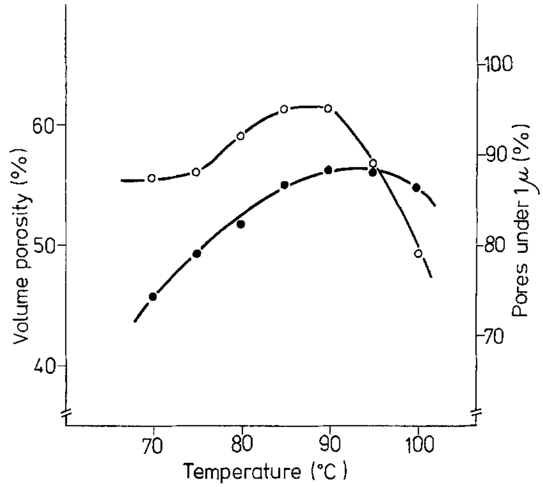

Fig. 2. Effect of the pre-curing temperature of modified phenol-formaldehyde resin on the volume porosity (●) and the pore size (○) of separator samples.

Figure 1 shows that with the increase of the quantity of the catalyst from 2.5 to 7.5% the porosity of the material increases and from 7.5 to 10.5% the porosity remains almost constant. The dependence of the size of the pores on the quantity of catalyst is similar. The optimum quantity of the catalyst was found to be 7–10 wt % with respect to the resin.

The optimal temperature of pre-curing of the resin was determined using 8% catalyst (Fig. 2). At 70–80° C the reaction of crosslinking proceeds with an unsatisfactory rate, with partial phase separation and rejection of water, as seen in Fig. 2. An appropriate temperature of pre-curing is 90 ± 3° C.

At temperatures above 93° C, the quantity of pores smaller than 1 μm is reduced (Fig. 2).

The time of pre-curing was also investigated. It was established that the electrical resistance of the separator sample is influenced substantially by the duration of thermal treatment at 90° C and at 8% catalyst content. It was found that when pre-curing duration in the mould is 1.5–2.5 minutes, the electrical resistance of the obtained samples is 0.16–0.35 ohm cm. Durations less than 1 min are insufficient for pre-curing and the separator sample deforms when retracted from the mould. At a pre-curing time of 3–4 min the resin reaches a greater extent of crosslinking which interfers with the pore formation process. As a result a separator sample with closed pores is obtained, volume porosity decreases below 50% and the electrical resistance is higher than 0.6 ohm cm^2.

4. Conclusion

The conditions for the modifying of water soluble phenol–formaldehyde resin with resorcinol and the method for the preparation of microporous separators for lead–acid batteries were optimized and with relatively simple techniques a microporous separator with low electrical resistance combined with high volume porosity and small pores was manufactured.

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