The Potential of Nanocomposite Barrier Technology

Taiichi Sakaya and Nobuhiro Osaki[‡]

Process & production Technology Center, Sumitomo Chemical Co., Ltd.

2-1 Kitasod, Sodegaura-city 299-0295, Japan

[‡]Plastic Technical Center, Sumitomo Chemical Co., Ltd.

2-1 Kitasode, Sodegaura-city 299-0295, Japan

It is needed for flexible transparent substrate to have not only the flexibility but also the ability of the material barrier as same as glass material. We paid attention to the nanocomposite barrier technology as a technique for making both its flexibility and the barrier property that are opposed to each other. This is a technology for appearing the barrier property by bringing the effect of the diffusion delay, so-called "Maze", to the diffusion of the material (gas molecule etc.) that passes by dispersing and combining a small plate of material impermeability filler on the nanometer scale into the resin.

In this study, the possibility of being compatible with flexibility and barrier property is shown by improving the effective aspect ratio using the small plate filler in the nanocomposite barrier technology.

Keywords: nanocomposite, clay, barrier, flexibility

1. Introduction

The material barrier such as tree, stone, glass and metal have been used and developed as food storage package since ancient times. In recent years, the application of these material barrier expands and changed from food packaging to medical and electronic parts packaging, and furthermore, expands as electronic materials, which need material barrier property.

In the electronic material film-formed usage, the material barrier property is required as same performance as that of the glass for applying to the transparent substrate for flexible organic EL panel.

[1]

Item	Target Level
Gas barrier	WVTR < 0.001 g/m ² /day
Transparency	Transmittance > 90%
Linear expansion	Coefficient < 10 ppm/K
Heatproof	Process temp. > 180°C
Flexibility	Curvature radius < 60 mm
Roughness	Ra < 1 nm

Table 1. Required physical properties of film for flexible display substrate. [1]

Currently various techniques for this application have been examined. [1][2][3]

On the other hand, the nanocomposite is widely known. In this technology, it can be realized to harmonize the characteristic of the inorganic material with that of resin by dispersing and combining filler on the nanometer scale into the resin.

This is paid to attention as a technology that can remarkably improve physical properties such as heatproof, a rigidity, a flame resisting, a material barrier property, and low linear expansion, etc. [4]

Heatproof, a material barrier property and a low linear expansion, etc. are indispensable physical properties for a flexible transparent substrate, it can be suggested to apply the nanocomposite to this purpose.

Especially, in the case of nanocomposite barrier technology, the barrier property is appeared by bringing the effect of the diffusion delay, so-called "Maze" to the diffusion of the material (gas molecule etc.) that passes by dispersing and combining a small plate of material impermeability filler on the nanometer

Scale into the resin. [5][6]

In this case, a resin part inferior to the barrier property takes charge of flexibility and a small plate filler part inferior to flexibility takes charge of the barrier property, respectively.

In this article, we would like to discuss how level of compatibility of the flexibility and the material barrier property compared to the glass can be possible by nanocomposite barrier technology.

2. Nanocomposite barrier technology

2.1. Barrier property

Figure 1 shows the model of the effect of the diffusion delay by "Maze". When the aspect ratio of a small plate filler is A , and the volume fraction of a small plate filler is Φ , the relative permeability P/P_0 is shown by Equation 1. [7]

$$P/P_0 = (1 - \Phi) / (1 + 0.5A\Phi) \quad \text{Equation 1}$$

Figure 1. Model of nanocomposite barrier film having plates in resin matrix.[7]

Figure 2[7] shows the relationship between the volume fraction of the small plate filler and the relative permeability P/P_0 at various aspect ratios

of the small plate filler.

Figure 2. Relative permeability vs volume ratio of plate.[7]

In the case of small aspect ratios, the volume fraction of the small plate filler is predominant in the improvement of the barrier property. So, it is necessary to fill most of the volume with the small plate filler to obtain a high barrier performance.

If everything in the layer is made of the small plate filler, a high barrier property is obtained, however, flexibility cannot be given at all.

On the other hand, as the aspect ratio of small plate filler increases, the effect of the barrier property remarkably increases in the area of the small volume fraction.

Barrier property of that of aspect ratio is 1 with 0.99 of volume fraction and the that of aspect ratio is 1000 with 0.2 of volume fraction are almost equal.

Although the higher volume fraction is superior

to the barrier property improvement, actually, there is a limit in the amount of addition of the small plate filler. Because the plate interval narrows as the volume fraction of the small plate filler increases and finally it falls below the width of the size of molecular chain.

When montmorillonite is used as small plate filler, the thickness of each layer is about 1nm. On the other hand, the thickness of one molecule of polyvinyl alcohol is about 0.5nm. Therefore the limit of the volume fraction of the small plate filler is about 0.67 as long as the volume fraction takes the form of Figure 1.

2.2. Flexibility

It can be thought that the flexibility is similar to the elongation of the film. The decrease of the barrier property to the elongation of the nanocomposite barrier film is smaller than that of the barrier film by a metallic deposition as shown in Figure 3. [5]

Figure 3. Crack resistance of nanocomposite barrier film.

The elongation of the convex surface caused by bend becomes a problem in the case of flexible transparent substrate.

When curvature radius R is assumed, growth rate $L(\%)$ of length outside of squarely curved

film is shown by Equation 2 (Figure 4).

$$L(\%) = 100d/R \quad \text{Equation 2}$$

Figure 4. Model of outer surface elongation for film bending.

When film thickness d is assumed to be $300\mu\text{m}$ and curvature radius 30mm , L becomes 1%.

On the other hand, pattern diagrams of the extension transformation of the nanocomposite (It is assumed that only the resin expands without small plate filler expanding.) are shown in Figure 5.

Figure 5. Model of nanocomposite barrier film elongation.

It is possible to expand to the value in which resin ratio $(1-\Phi)$ is multiplied by growth rate of resin L_p when it is ideal because the resin of H shape(VH) in the shaded portion can contribute to the extension (Equation 3).

For the resin of about $L_p=10$, even $\Phi=0.9$ is possible to fill $L=1$.

$$L(\%) = L_p(1-\Phi) \quad \text{Equation 3}$$

3. Attempt of flexibility and barrier property's coexisting

3.1. Model

In such a nanocomposite structure, the flexibility appears by the H shape resin, and the barrier property appears by the aspect ratio and volume fraction of the small plate filler.

As previously described, if the limitation of the volume fraction of the small plate filler is about 0.67, it is necessary to increase the aspect ratio for further improvement of barrier property. The clay mineral such as montmorillonite is known as a small plate filler of high aspect ratio. [8]

The aspect ratio of small plate filler that can be commercially available is from 100 to up to 1000, though there is a report of the synthesis of monocrystalline montmorillonite of particle diameter $10\mu\text{m}$ (its aspect ratio is about 10000) under the condition of ultra high temperature and ultra high pressure. [9][10]

Therefore the method of condensing small plate filler [11] or the method of coating resin solution on the layer that consists of small plate filler [12] are designed as a method of improving the effective aspect ratio.

Figure 6 shows the form of the nanocomposite that drastically improves the effective aspect ratio of small plate filler with keeping the resin of H shape.

Normal aspect ratio

Enhanced effective aspect ratio

Figure 6. Model of nanocomposite barrier film having plates enhanced effective aspect ratio using plates only layers.

This conformation can be formed by placing the both sides with the resin layers or the usual nanocomposite layers, after forming the thin layer that consists almost only of small plate filler.

In addition, a remarkable increase of the effective aspect ratio by overlapping small plate fillers can be expected in this form.

3.2. The model's proof

To verify this model, the accumulating body of five-layered composition was formed. In this experimentation, montmorillonite as small plate filler and polyvinyl alcohol as resin were used, and the layer of the montmorillonite 100% is pinched with the layer of the montmorillonite 30%.

Scheme 1 shows the process.

Scheme 1. The process of nanocomposite barrier film having plates enhanced effective aspect ratio by using montmorillonite layers.

According to the section transmission electron microscope photography, the usual nanocomposite layer and the layer only of small plate filler were observed, and it was revealed that model structure were formed. (Figure 7).

Figure 7. Transmission electron micrograph (cross section) of nanocomposite barrier film having plates enhanced effective aspect ratio.

Results of model film and reference film were shown in Table 2.

	model	reference
Base film (15 μ m)	o-nylon	o-nylon
Thickness of L1 (μ m)	0.007	0.12
Thickness of L2 (μ m)	0.010	none
Total thickness of coating layers (μ m)	0.042	0.12
Oxygen transport ratio (ml/m ² · d · MPa)	16	53
Oxygen permeability (ml · μ m/m ² · d · MPa)	0.67	6.36
L 2 layer's Oxygen permeability (ml · μ m/m ² · d · MPa) ^{*2}	0.32	none

Table 2. Gas barrier property of nanocomposite barrier film having plates enhanced effective aspect ratio by using montmorillonite layers.

*1: measured by ox-tran 10/50A (modern control Co.Ltd) under 23°C-90%RH.

Relative permeability of L 2 layer was calculated and shown in Table 3, as aspect ratio of montmorillonite was 460 by [6].

Layer	Φ	A	P/P ₀	P
L1	0.3	460	0.01	6.36
L2 ^{*1}	0.9	460	0.0005	0.32
L2 ^{*2}	0.3	10000	0.0005	0.32

Table 3. Calculated relative permeability of L 2 layer using results in Table 1.

*1: Calculated volume ratio of plates under aspect ratio constant.

*2: Calculated effective aspect ratio under volume ratio of plates constant.

The value of the relative permeability level in Table 3 was re-plotted in Figure 8.

Figure 8. Relative permeability vs volume ratio of plate. Table 3 (●) was re-plotted.

The volume fraction of the layer consists of small plate filler corresponds to 90% when the aspect ratio is assumed to be 460.

The effective aspect ratio reaches 10000 when assuming the volume fraction to be 30%, though there is no method of obtaining the effective aspect ratio.

Both of model film and reference film were very flexible, so any damages of coating layer were not observed in watching under various conditions, such as coating, winding and rewinding.

It was revealed that the barrier ability of relative permeability 1/10000 level was able to be achieved by this model.

Further we are going to examine the decrease of the barrier ability under various winding and elonging conditions.

4. Conclusions

It can be suggested that both the flexibility and the barrier property are able to improve by increasing the effective aspect ratio of small plate filler in the nanocomposite barrier technology.

If the aspect ratio of small plate filler or the effective aspect ratio of the set of the filler can be increased more remarkably, theoretically, the barrier ability can be improved still more.

Though it did not touch in this article, of course the choice of the species of resin greatly influences the performance.

The film consists of high barrier resin shows high barrier ability. Furthermore, there is room for the performance improvement by building a new form of the nanocomposite.

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