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Slowly Odor-evaporating Polyethylene Film Containing Surface-modified Celite Powder

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Abstract: Celite powder surface-modified with cationic surfactant was used to make polyethylene (PE) specialty film that can be contrasted with ordinary film in having high odor storing capacity and long odor lasting period. Mechanical properties of the films were sacrificed as more celite particles were included, whether celite surface was modified or not. The film with CTAB-modified celite showed the best odor storing and lasting properties for five different flavors of odor, three artificial and two natural ones, among the kinds of films developed. Comparisons among the different films are made, together with brief discussion about the reason for differences in odor lasting period and possible application to packaging industry.

Keywords: Odor, Evaporation, Surface-modification, Film, Packaging

Introduction

Celite, a mineral differently called diatomaceous earth, is mainly composed of silica and alumina, and industrially used in filtration of water, beer, wine, and fruit juice or as an additive to agricultural chemical, cosmetic, paint, paper, plastic, and food [1]. Scientifically, celite has been used as chemical reaction catalyst [2,3] and solid support for enzyme [4-6]. The extraordinary high surface area, large pores, and solid structure of celite enjoyed such wide variety of applications. Current inclusion of inexpensive inorganic particles into polymer has been purposed simply as a filler to reduce the cost of polymeric material [7,8]. However, we are intrigued by the fact that the polymeric material can be endowed with special effect such as adsorption of bad smell, storage of volatile molecules, or flame retardation by proper selection of the imbedded inorganic particle, thus resulting in widespread potential application of polymeric material. In order to popularize the use of polymeric material, the general problem, concomitant reduction in mechanical properties of the composite material by introduction of inorganic particle, remains to be overcome to popularize the use of polymeric composite material. Meanwhile, industrial demand for odor-evaporating film is high, because of the potential application in packaging such items as leather stuff, chemicals, fermented foods, toys, cosmetics, and others that convey obnoxious smell to customers. In this paper, our attention is narrowed to slowly odor-evaporating PE film with high storage capacity of odor molecules by taking advantage of the enormous internal pore space of celite. In addition, surface modification of celite is tried to solve the problem of reduced mechanical properties. The reasons for excellent odor-lasting and -storing effect of celite film are discussed together with the possible applications and modification.

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Experimental

Materials and Methods

LDPE and celite powder were obtained from Hanhwa chemical Co. and Celite Korea Co., respectively. Cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DDAB) were from TCI. Twin screw extruder (Bautech BA-19) was used to prepare master batch of PE and celite. PE thin film was made from a single screw blown extruder. Tensile test was performed by universal testing machine (UTM, Lloyd LR 50K) using dumbbell-type specimen prepared according to ASTM D-638 at a crosshead speed of 100 mm/min. Tear strength was measured by Elemndorf tester (Toyo Seiki). Particle size was measured by particle size analyzer (Malvern Mastersizer Micorplus). Elemental analysis was carried out at Korea Basic Science Institute, Pusan, Korea. Three different kinds of odor (banana, strawberry, and apple flavor) concentrate were obtained from Korea-French fragrance Co., and natural odor concentrate (mugwort and pine) was made in our laboratory from herbs obtained from local market. Odor concentration was detected by gas chromatography (HP 9850 series II) equipped with capillary column (HP-1) and FID detector, using nitrogen, air, and hydrogen mixture as carrier gas.

Surface Modification and Characterization

Celite powder (3 kg) in 4 liter of 50 mM CTAB or DDAB solution was stirred for a day and was dried completely after filtration. Loading of CTAB or DDAB was calculated from elemental analysis of nitrogen content of the celite powder.

Comparison of Odor-lasting Period

The celite film (10 cm × 10 cm) that was immersed for two hours in odor solution diluted with methanol by 20 times (v/v) was removed of methanol by nitrogen blowing and the film was contained in a 250 m*l* three neck flask capped with

PE film for two outlets and a septum for gas sampling. An aliquot (100 μl) of odor gas inside the flask was sampled by a gas tight syringe (Hamilton) periodically up to 20 days. The test was repeated five times and the average was plotted for comparison.

Results and Discussion

Preparation of Celite Film

Celite was selected over other inorganic powder such as zeolite, silica, and alumina, because of the advantage in internal porosity that could be used for storing odor concentrate: highly porous nature of celite was obvious compared to zeolite as in SEM picture (Figure 1). Average particle size of the celite powder, 3-5 μm, was small enough to be included in 40-50 μm thick PE film. Because celite, mainly composed of silica and alumina, had polar and negatively charged surface area, modification of celite surface with cationic surfactant was necessary to reduce polarity so that nonpolar odor molecules could be captured inside the pores. In addition, surface modification, as mentioned next, might enhance the mechanical properties lowered by the presence of celite particles. The loading of CTAB on celite (0.1 mmol/g) was not small considering the fact that surface modification on inorganic material was generally low [9,10]. Three kinds of celite powder (plain celite, one modified with DDAB, and one modified with CTAB) were used to make 20 wt% PE master batch used for the film preparation. Compounding of PE and celite powder was carried out smoothly by twin screw extruder to produce homogeneous pelletized master batch, and the blowing process for film production, although sometimes malfunctioned due to the aggregation of inorganic particles, was not interrupted by the inclusion of celite. The final films for comparison were PE film, plain celite film, DDAB-modified film, and CTAB-modified film, and the content of celite was 3, 5, 10 wt% for each films, thus resulting in 10 kinds of films (9 celite films plus PE film) for odor-lasting test.

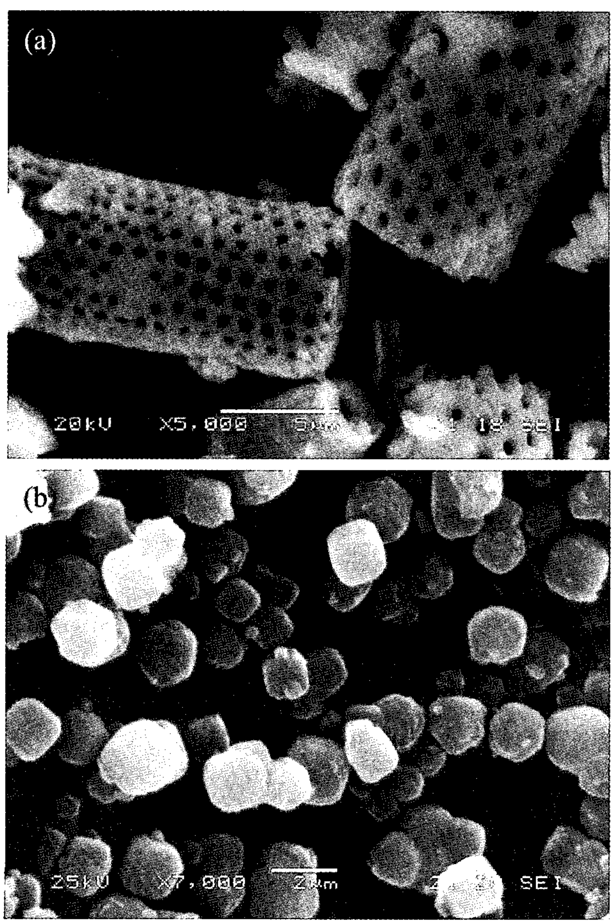

Figure 1. SEM image of (a) celite and (b) zeolite powder.

Mechanical Properties of Celite Film

The mechanical properties of celite-containing film (3, 5, 10 wt% of celite) were compared with PE film. Because we learned from the previous experiments that surface modification of inorganic powder improved the mechanical properties of the thin film, surface modification of celite with cationic surfactant was tried [11]. Maximum stress of celite films was not decreased much, whether the celite surface was modified or not, as more celite was included for both machine direction (MD) and transverse direction (TD) (Figure 2). Actually, the purpose of surface modification of celite with cationic surfactant, CTAB or DDAB, is to reduce the gap in polarity between celite and PE at the contact area by inserting cationic surfactant between them as shown in Figure 3. Strain at break and tear

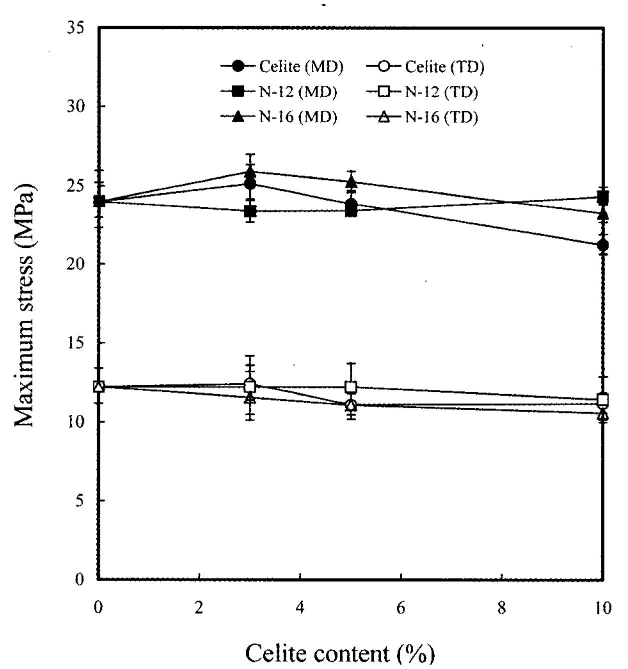

Figure 2. Max. stress vs. celite content profile of various celite films.

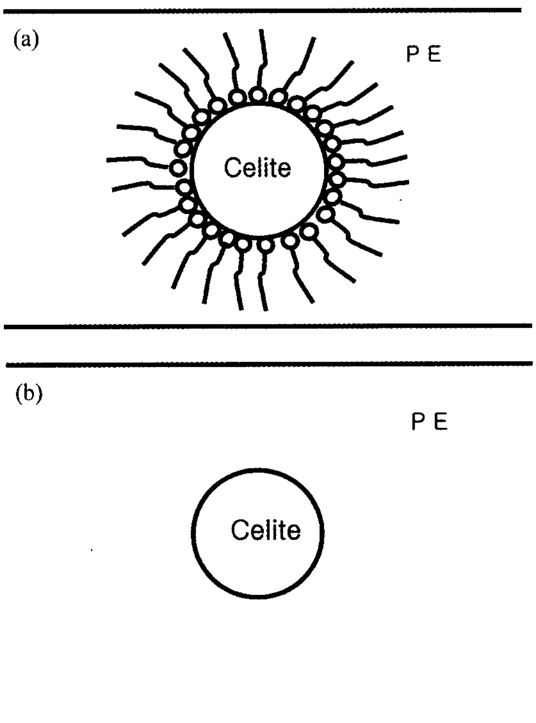

Figure 3. Schematic of (a) surface-modified and (b) plain celite film.

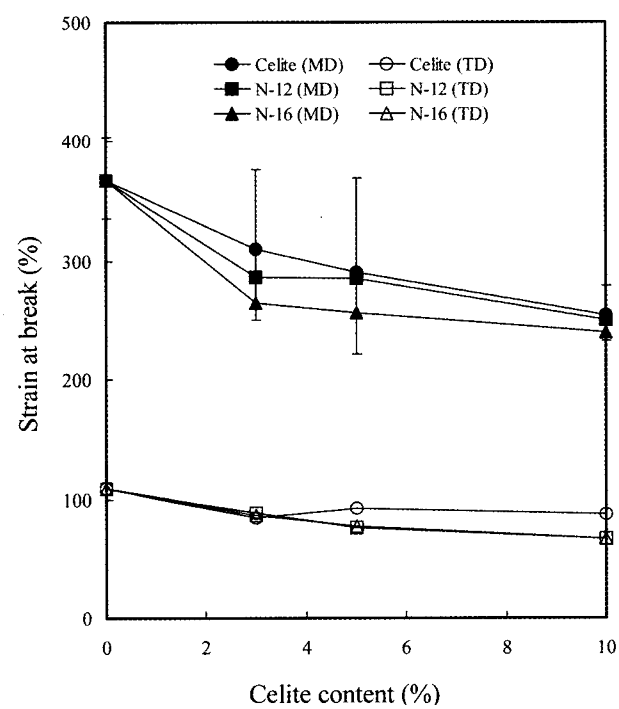

Figure 4. Strain at break vs. celite content profile of various celite films.

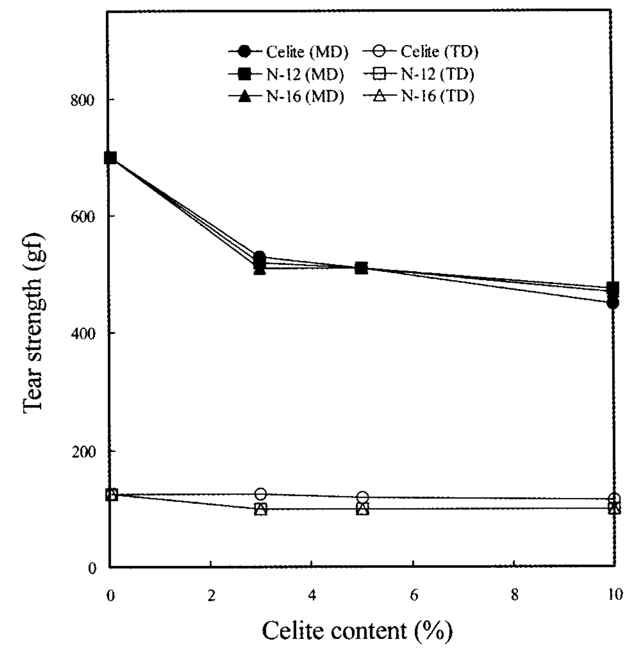

Figure 5. Tear strength vs. celite content profile of various celite films.

strength data did not show any differences as compared to unmodified celite film (Figure 4 and 5). Mechanical property of thin film containing inorganic powder generally decreased as more inorganic powder was included, a reasonable result occurring from the disruption of PE structure by heterogeneous inorganic particles. Similar trend was observed for the celite containing films and the surface modification did not improve the mechanical properties of the films.

Evaluation of Odor Capture and Lasting Period

Three different flavors of artificial odor (banana, strawberry and apple) were used for odor release test. Celite films were immersed in methanolic odor solution for soaking the odor molecules into the pores, and the films were placed in a three-neck flask where evaporated odor could be escaped through the covered PE films. Because a custom-made PE bag used for the odor release test in the beginning could not differentiate odor evaporation rate depending on the type of celite films due to the highly porous nature of PE bag, a three-neck flask replacing the PE bag resolved the problem (Figure 6). Odor concentration inside the flask was checked by gas chromatography at 2-5 days interval up to 20 days. As seen in Figure 7, CTAB-modified film (N-16) contained 27 times more banana flavor odor than PE film, and 10 times higher odor concentration, even after 20 days, was observed for N-16 film as compared to PE film. DDAB-modified film (N-12), one that was modified with shorter hydrocarbon chain, showed only 2.6 times higher odor concentration at the start and 2.3 times higher one after 20 days compared to PE film. The film with plain celite did not differentiate itself from PE film, showing almost similar odor storage and release properties to those of PE film. As for strawberry flavor, N-

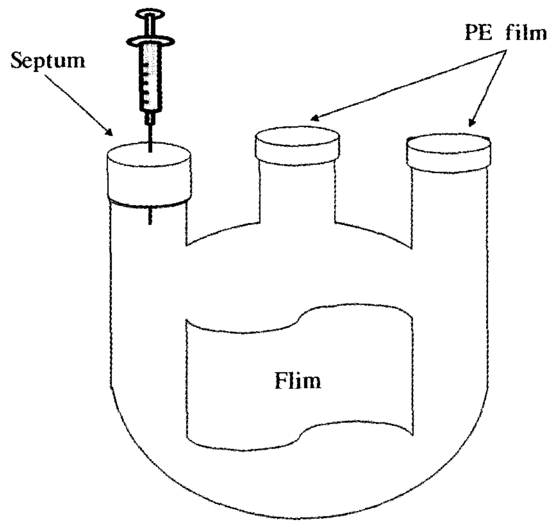

Figure 6. Schematic of odor-test glassware.

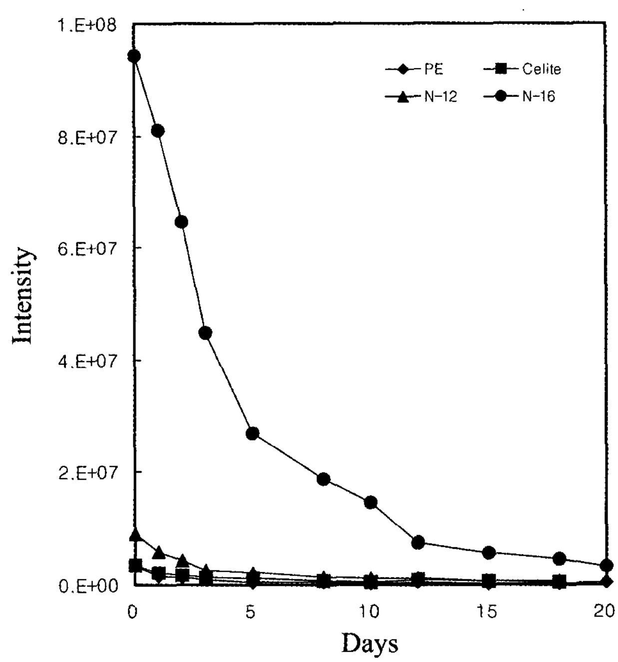

Figure 7. Banana flavor odor release profile of various films.

16 film had 23 times at the start and 18 times after 20 days higher odor concentration than PE film. N-12 and plain celite films had mere superiority over PE film (Figure 8). Apparent differences were observed in the case of apple flavor, too: 32 times at the start and 37 times after 20days higher odor concentration of N-16 film than those of PE film was found; N-12 film showed 6.3 times at the start and 2.2 times after 20 days higher ones; celite film also showed 6.7 times and 2.9 times higher ones (Figure 9). From the above results, N-16 film was superior to other films in keeping higher odor concentration and having longer odor lasting period,

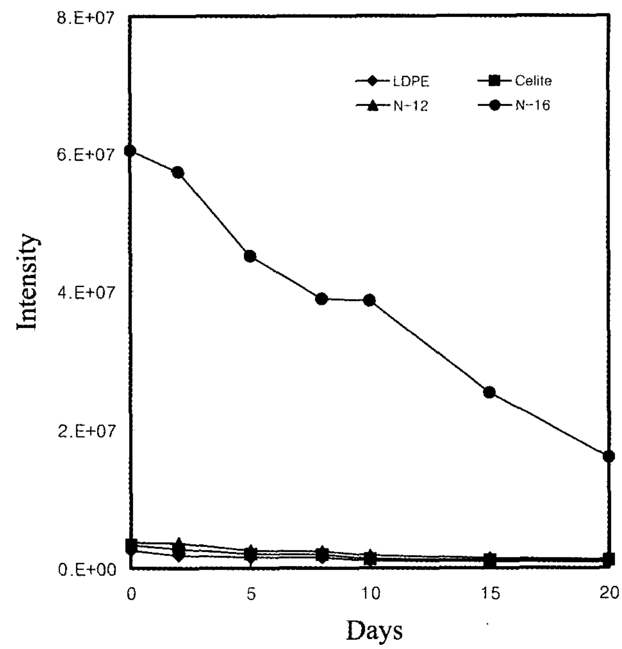

Figure 8. Strawberry flavor odor release profile of various films.

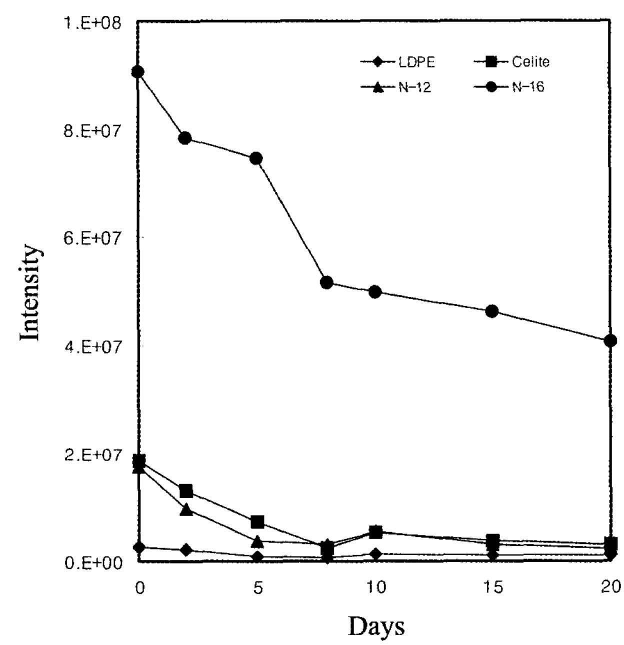

Figure 9. Apple flavor odor release profile of various films.

suggesting that surface modification with long hydrocarbon chains reduced the surface polarity of celite and, therefore, attracted more odor molecules into the pores by intermolecular interactions such as van der Waals force (Figure 10). The disappointing results of N-12 film emphasize the importance of hydrocarbon chain length on inorganic particles as in reverse phase HPLC column [12].

In addition to artificial flavors, natural herb extracts were

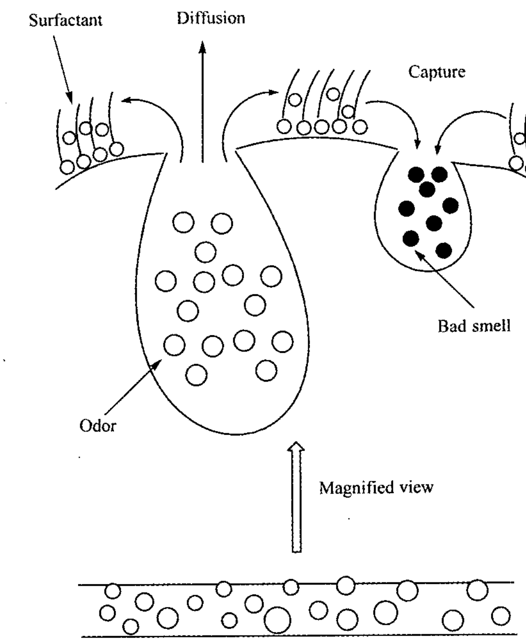

Figure 10. Schematic of odor storage and release profile.

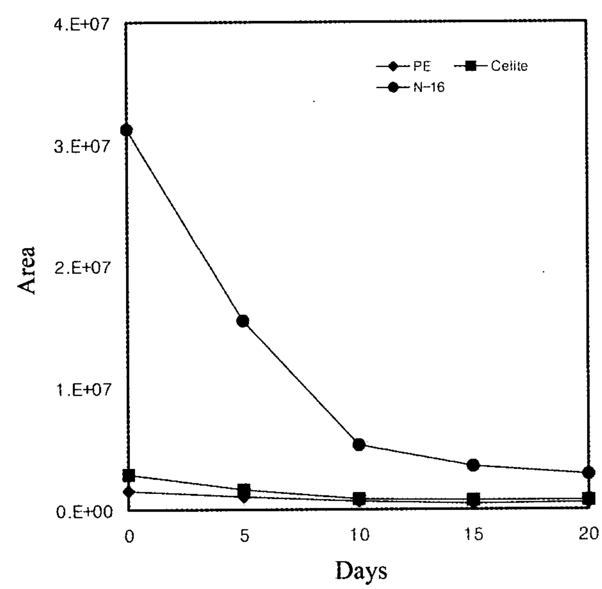

Figure 11. Mugwort odor release profile of various films.

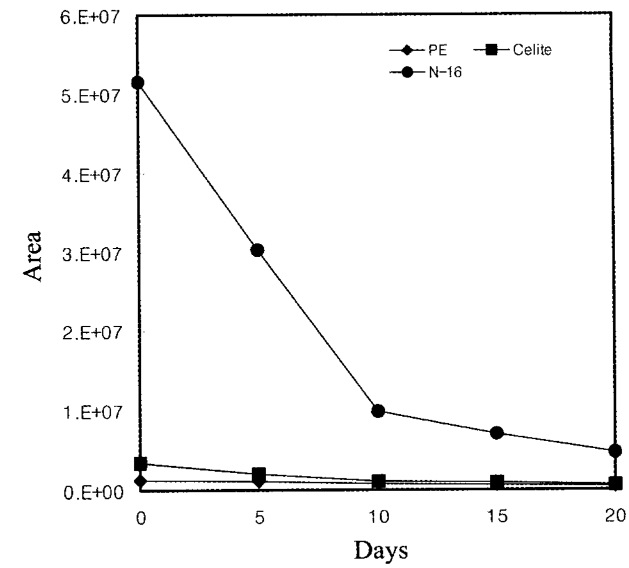

Figure 12. Pine odor release profile of various films.

also tried for the above films. Methanolic concentrate from mugwort known as herb medicine was used for the artificial flavors and same test method was applied. As in Figure 11, N-16 film showed excellent odor storing and lasting properties compared to other films: 20 times at the start and 5.5 times after 20 days higher odor concentration was observed. We omitted N-12 film for natural herb due to the poor performance observed before, and plain celite film, as expected, was not effective at all. Another natural flavor, pine extract, was tested by the same method. Once again, superior performance of N-16 film was shown: 42 times at the start and 9.6 times after 20 days higher odor concentration was observed. Plain celite film was not effective, either (Figure 12). The above results are summarized in Table 1.

Over all, odor storing capacity and odor lasting period could be substantially improved, although the expected enhanced mechanical properties were not observed, by adopting surface-modified celite film, especially N-16 film, on the condition that the hydrocarbon chain length should be long enough to adsorb odor molecules. So far, any kind of odor lasting packaging film was not reported within our knowledge; the combination

Table 1. Comparison of relative odor intensities of various celite films with PE film

Film type	Banana		Strawberry		Apple		Mugwort		Pine	
	S[a]	F[b]	S	F	S	F	S	F	S	F
PE film	1	1	1	1	1	1	1	1	1	1
Celite[c]	1	1	1.3	1.3	6.7	2.9	1.9	1.4	2.8	1.2
N-12[d]	2.6	2.3	1.4	1.4	6.3	2.2	-[f]	-	-	-
N-16[e]	27	10	23	18	32	37	20	5.5	42	9.6

[a]S means the relative odor intensity at the start and [b]F does the relative intensity after 20 days. [c]Celite film has plain celite; [d]N-12 film does celite modified with dodecyltrimethylammonium bromide; [e]N-16 film contains celite modified with cetyltrimethylammonium bromide. [f]Test was not applied.

of porous celite and PE film together with surface modification with surfactant is a breakthrough in the point that huge odor storage and controlled release are realized. The slightly reduced mechanical properties are still acceptable in packaging application [13,14]. The surface modification technology can be applied to other specialty films such as anti-rust film, antiseptic film, photo-gray film, and etc. Continuous efforts are being made in our laboratory to develop related specialty films.

Conclusion

Celite was selected among other inorganic particles due to the high porosity used for the capture of odor molecules inside. Understanding of the celite pore structure, surface polarity, nature of odor molecules, film manufacturing process and problems of current odor-evaporating film leaded us to surface modification method, and the method proved to be working successfully as compared to PE film. The chain length of hydrocarbon attached on celite surface was also a very important factor in determining sufficient adsorption of odor molecules to celite surface. The celite-based technology can be applied to other specialty films or composite materials by replacing the odor molecules with other volatile chemicals such as anti-rust or antiseptic agent.

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