

Preparation and Flame Retardancy of 2-EHA/*n*-BA Acrylic PSA Containing Single and Combined Flame Retardants

Eun-Young Park,¹ Ho-Gyum Kim,¹ Jeoung-Cheol Lim,² Dong-Ho Lee,¹ Kyung-Eun Min¹

¹Department of Polymer Science, Kyungpook National University, Daegu, Korea

²Department of Fiber Materials, Yeungnam College of Science and Technology, Daegu, Korea

Received 1 August 2008; accepted 16 January 2010

DOI 10.1002/app.32108

Published online 29 April 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: UV curable acrylic PSAs (pressure-sensitive adhesives) were modified with organic and inorganic flame retardants to improve flame retardancy of PSAs minimize the sacrifice of adhesion properties. The flame retardancy (UL-94 test) of acrylic PSAs were enhanced by the addition of 5–30 wt % of an organic flame retardant such as TCEP (Tris(2-chloroethyl)phosphate), PBPE (pentabromophenyl ether), and TBBPA(3,3',5,5'-tetrabromobisphenol A). Especially, TBBPA is the best flame retardant for acrylic PSAs when it works alone. However, PSAs compounded with aluminum trihydroxide (Al(OH)₃) showed a little reduction

in burning time up to 30 wt %. An apparent synergic effect was observed only for an acrylic PSAs with a combination of TCEP and PBPE flame retardants. The addition of flame retardants brought a no significant effect on curing even in high amount. It was surmised that the miscibility between PSAs and flame retardant was closely related with flame retardancy and adhesion properties of acrylic PSAs. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3092–3097, 2010

Key words: flame retardancy; acrylic; PSA; tack; peel strength; UV

INTRODUCTION

Pressure-sensitive adhesives (PSAs) are characterized by adhesion to solid surface upon application of light contact pressure and short contact time. Commonly used PSAs, based on acrylic copolymers, cover a broad range of label, tape, medical, and electronic products.^{1,2} 2-ethyl hexyl acrylate (2-EHA), *n*-butyl acrylate (*n*-BA), ethyl acrylate (EA), and so on are used as a comonomer and give a good adhesion properties to PSAs.^{3,4}

While the photochemistry of acrylic PSAs has been a subject of numerous studies, little is known about the effect of additives on photolysis and their applications.^{3–7} A growing concern is also raised on flame retardancy of adhesives mainly in the car and aircraft applications, although only a few of them commercially successful.^{8,9} As a thermal pyrolysis of hydrocarbons is showed at 600–800°C, the use of flame retardant inhibits the pyrolysis at the lower temperature.¹⁰

It has been reported that several proposed flame retardants system such as phosphorus, halogens, metal hydroxide, and filler improve the flame retardancy of polymer materials. Further interesting data suggest that the combined flame retardant sys-

tem may lead to the improvement in flame retardancy in comparison with the single flame retardant system. However, this method also has a drawback, e.g., they tend to produce environmental and toxicity issues due to the use of bromine compound.^{10,11}

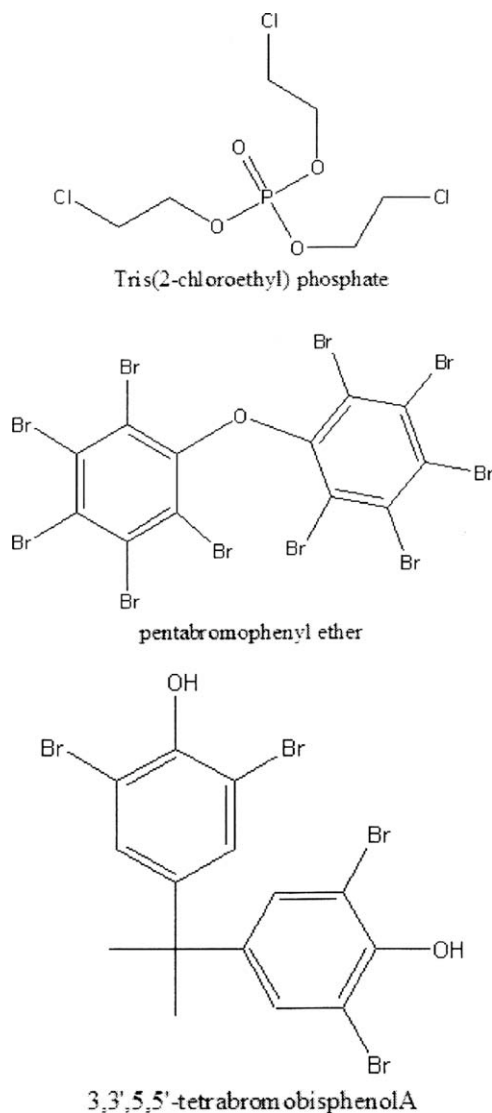
In this work, acrylic PSAs based on 2-EHA/*n*-BA copolymer containing single and combined flame retardant system are prepared by UV irradiation. To reduce the amount of brominated flame retardant, montmorillonite (MMT) is used for synergic effect on flame retardancy of PSAs.¹² The effect of flame retardants concentration on the adhesion properties of PSAs is also examined.

EXPERIMENTAL

Materials

All acrylic monomers, purchased from Aldrich Chemicals, were used as received. Benzil-dimethylketal (BDK) used for photoinitiator was supplied by Ciba Chemicals. Tris-(2-chloroethyl) phosphate (TCEP, chlorine content: 37.3%), pentabromophenylether (PBPE, bromine content: 82.8%), 3,3',5,5'-tetrabromobisphenol A (TBBPA, bromine content: 58%), and Al(OH)₃ were supplied by Aldrich Chemicals. Organically treated montmorillonite (MMT), Cloisite 30B (CEC = 90 meq/100 g) was purchased from Southern Clay Products (TX). Scheme 1 is a chemical structure of flame retardants.

Correspondence to: K.-E. Min (minkyee@knu.ac.kr).



Scheme 1 The chemical structure of flame retardants. (a) TCEP, (b) PBPE, (c) TBBPA.

PSAs preparation

The mixture of 2-EHA (70 mol %) with *n*-BA (30 mol %) was stirred and exposed to a medium pressing mercury lamp (UVA Spot 400/T, Dr. Hönle, Germany) in the presence of 0.1 wt % photoinitiator. The UV intensity of lamp was about 15 mW/cm² and UV chamber was purged with nitrogen to remove air. The PSA sample was obtained by two-step processing. The mixture of components including acrylic monomer, flame retardants, and multifunctional monomer (1,6-hexandiol diacrylate, HDDA, Aldrich Chemical) was prepared simultaneously with varying the mixing ratio. Core-syrup was coated on PET film (25 μm thickness) by using barcoater after photoirradiation of sample for 10 s. The coated PSA film was then photocured for 10 min under nitrogen atmosphere.

TABLE I
Classification of Samples Tested According to UL-94
20-mm Vertical Burning Test Protocol

Rating	t_1^a (s) or t_2^b (s)	$\sum(t_1 + t_2)^c$ (s)	Dripping ^d
V-0	≤10	≤50	No
V-1	≤30	≤250	No
V-2	≤30	≤250	Yes

^a Combustion time after the first application of the flame.

^b Combustion time after the second application of the flame.

^c Sum of t_1 and t_2 values for five specimens.

^d Cotton indicator ignited by flaming particles or drops.

Measurements

The kinetics of the polymerization were examined by the disappearance of the IR absorption of the acrylic double bond at 810 cm⁻¹. The degree of conversion can be calculated from the following equation.

$$\text{Conversion}(\%) = [(A_{810})_0 - (A_{810})_t] / (A_{810})_0 \times 100$$

where $(A_{810})_0$ and $(A_{810})_t$ represent the area of the IR absorption peak at 810 cm⁻¹ of the sample before and after irradiation time t . The viscosity at room temperature of core-syrup was measured by Brookfield viscometer (Model DV-II⁺, spindle number: 2) at 40% torque. Evaluation of flammability was achieved using UL-94 vertical burning test according to the standard ASTM D3801-87. The test protocol is summarised in Table I.

All tack measurements were performed using a TE-6001 probe tack tester (Sangyo, Japan). The sample was placed on probe tip for 10 s, and then testing occurred at peel rate of 10 cm/s. The tack value was recorded as the average of 10 times of test results. The effect of adding flame retardants on

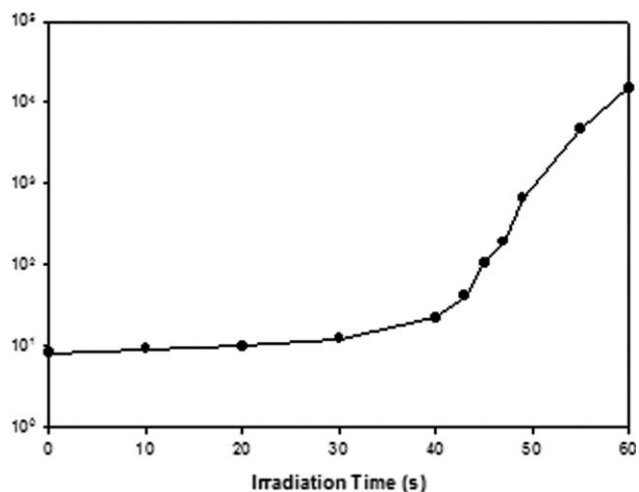


Figure 1 Relation between core-syrup viscosity and UV irradiation time.

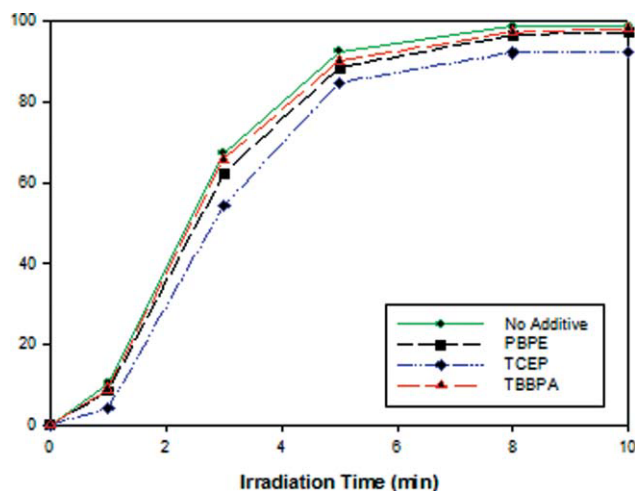


Figure 2 Conversion of PSA as a function of UV irradiation time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

surface energy of PSAs was monitored by Phoenix 300 contact angle meter (AH TECH). To evaluate the thermal degradation temperature with increasing flame retardants content, thermogravimetric analysis (TGA) was carried out using Setaram TA 4000 (Shimadzu, Japan) equipment. The measurements were performed from 25 to 600°C using a heating rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Characterization

Figure 1 shows the influence of UV exposure time on core-syrup viscosity of 2-EHA (70 mol %)/*n*-BA (30 mol %) system. The viscosity is abruptly increased after 40 s of exposure time. %Conversion obtained for UV irradiation of acrylic formulation is shown in Figure 2. In the presence of bromine flame retardants, the conversion reaches 90% under 5 min of irradiation. In case of halogenated phosphate flame retardant, TCEP gives a small decrease in conversion. This behavior may be attributed to both the miscibility between core-syrup and flame retardant and the activation energy in curing process.

TABLE II
UL-94 Test Results of PSA with PBPE Flame Retardant System

Composition (wt %) PSA/PBPE	t_1 (s)	t_2 (s)	$\sum(t_1 + t_2)$ (s)	Dripping	Rating
100 : 0	56	58	569	Yes	Fail
95 : 5	42	48	453	No	Fail
90 : 10	38	42	400	No	Fail
85 : 15	36	38	386	No	Fail
80 : 20	7	13	99	No	V-1
75 : 25	5	8	61	No	V-1
70 : 30	1	1	13	No	V-0

TABLE III
UL-94 Test Results of PSA with TBBPA Flame Retardant System

Composition (wt %) PSA/TBBPA	t_1 (s)	t_2 (s)	$\sum(t_1 + t_2)$ (s)	Dripping	Rating
100 : 0	56	58	569	Yes	Fail
95 : 5	37	42	391	No	Fail
90 : 10	4	10	610	No	V-1
85 : 15	1	2	17	No	V-1
80 : 20	1	1	12	No	V-1
75 : 25	1	1	10	No	V-0
70 : 30	1	1	5	No	V-0

TABLE IV
UL-94 Test Results of PSA with TCEP Flame Retardant System

Composition (wt %) PSA/TCEP	t_1 (s)	t_2 (s)	$\sum(t_1 + t_2)$ (s)	Dripping	Rating
100 : 0	56	58	569	Yes	Fail
95 : 5	41	43	426	No	Fail
90 : 10	13	15	141	No	V-1
85 : 15	6	8	66	No	V-1
80 : 20	3	4	35	No	V-0
75 : 25	2	3	34	No	V-0
170 : 30	2	3	31	No	V-0

TABLE V
Bromine Contents in Flame Retardants

Flame retardant contents (wt %)	PBPE	TBBPA
5	4.1	2.9
10	8.3	5.8
15	12.4	8.7
20	16.6	11.6
25	20.7	14.5
30	24.8	17.4

TABLE VI
UL-94 Test Results of PSA with Combined Flame Retardant System (PBPE/ATH)

Composition (wt %) PBPE/ATH	t_1 (s)	t_2 (s)	$\sum(t_1 + t_2)$ (s)	Dripping	Rating
0 : 0	56	58	569	Yes	Fail
2.5 : 2.5	53	54	536	No	Fail
5 : 5	47	47	473	No	Fail
7.5 : 7.5	47	47	471	No	Fail
10 : 10	14	15	152	No	V-1
12.5 : 12.5	11	12	115	No	V-1
15 : 15	9	10	95	No	V-1

TABLE VII
UL-94 Test Results of PSA with Combined Flame Retardant System (TCEP/ATH)

Composition (wt %)	t_1 (s)	t_2 (s)	$\sum(t_1 + t_2)$ (s)	Dripping	Rating
TCEP/ATH					
0 : 0	56	58	569	Yes	Fail
2.5 : 2.5	52	52	522	No	Fail
5 : 5	39	44	414	No	Fail
7.5 : 7.5	30	35	331	No	Fail
10 : 10	12	13	125	No	V-1
12.5 : 12.5	4	4	40	No	V-0
15 : 15	1	1	7	No	V-0

H. G. Kim reported that the use of halogen-contained phosphorus flame retardant like 2,2,2'-tris(chloroethyl)dichloro phosphate leads to the decrease of final conversion of epoxy acrylate under UV irradiation.¹³

Flame retardancy

Single flame retardant system

The effect of flame retardant on the UL-94 test is summarized from Table II to IV. Neat material is highly combustible and classified as "fail" of UL-94 test. The best ranking reaches V-0 in UL-94 test is achieved with 30 wt % of PBPE and 15 wt % of TBBPA in each PSAs. On the other hand, when the addition level is up to 10 wt % of TCEP flame retardant, the rank reaches V-1 and V-0 in UL-94 test of PSA with 20 wt % of TCEP. These results show that the halogenated phosphate flame retardant is more effective for acrylic PSA above 20 wt % of flame retardant.

The addition of $\text{Al}(\text{OH})_3$ does not enhance flame retardancy of PSAs when it used alone. This result is not remarkable in comparison to PSA/MMT system. The bromine content in each flame retardants is listed in Table V. From the data, the better flame retardant effect than others could be explained by the fact that the miscibility between core-syrup and flame retardant more clearly affect the flame retardancy of PSAs than bromine content of flame retardant.

TABLE VIII
UL-94 Test Results of PSA with Combined Flame Retardant System (TCEP/PBPE)

Composition (wt %)	t_1 (s)	t_2 (s)	$\sum(t_1 + t_2)$ (s)	Dripping	Rating
TCEP/PBPE					
0 : 0	56	58	569	Yes	Fail
2.5 : 2.5	18	20	192	No	V-1
5 : 5	4	4	42	No	V-0
7.5 : 7.5	3	3	29	No	V-0
10 : 10	2	2	23	No	V-0
12.5 : 12.5	1	1	16	No	V-0
15 : 15	1	1	10	No	V-0

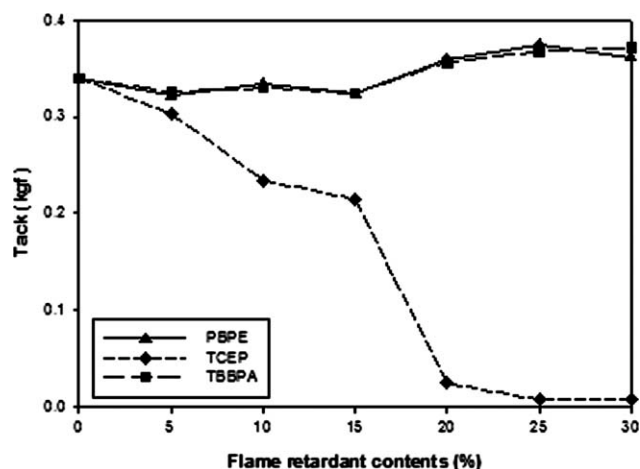


Figure 3 Tack of PSA/single flame retardants system.

Combined flame retardant system

It has been reported that the flame retardancy of polymers can be improved by incorporating combined flame retardant.^{12,14-17} UL-94 test results of acrylic PSA with combined flame retardant are collected from Table VI to VIII. M. A. Khattab suggested that the use of combined flame retardant consist of PBPE and $\text{Al}(\text{OH})_3$ lead to the decrease of flame retardancy of rubber materials.¹⁸ He also reported that this combined system appears as a high performance for cellulose and other thermoplastic polymer.¹⁸ In our study, the synergic effect of combined flame retardant is observed in formulation up to 10 wt % of each flame retardant. In case of TBBPA/TCEP combined system, it was not able to prepare the PSA sample because of its rapid viscosity rising in mixing stage. Instead of high-toxic bromine flame retardant system, it is thought that the use of combination TCEP- $\text{Al}(\text{OH})_3$ as a synergist may be a substitutes for acrylic PSAs.

As shown in Table VIII, the more significant synergic effect is achieved by the use of TCEP-PBPE

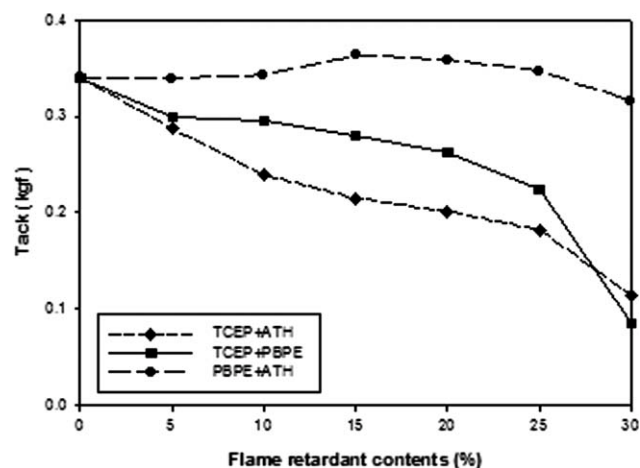


Figure 4 Tack of PSA/combined flame retardant system.

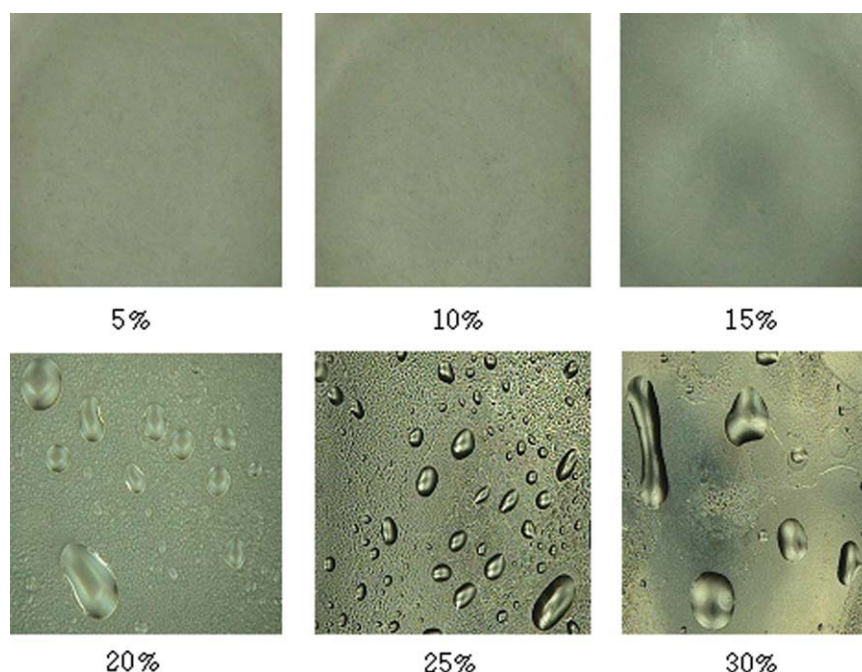


Figure 5 Optical microscopic surface image of PSA/TCEP flame retardant system. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

combination even in formulation 5 wt %, respectively. Recent study supports that the combined flame retardant 2,2,2'-trichloroethyl dichlorophosphate and decabromodiphenyl oxide improves the flame retardancy of epoxy acrylate with small loading without loss of adhesion property.¹³

In previous related studies, it is observed that polypropylene(PP)-MMT nanocomposite has better flame retardancy compared with conventional PP-halogen flame retardant system.¹² Also the presence of fillers such as zeolite, talc, and calcium carbonate offer superior flame retardancy compared with polymer-brominated materials system.¹⁵ It is assumed that this improvement of flame retardancy is attrib-

uted to well-dispersed MMT layers as a barrier intercepting oxygen and heat transfer.¹⁰ In our study, however, it is found that synergic effect of MMT loading on flame retardancy of acrylic PSAs is not observed in all combined system.

Adhesion properties

Tack

As Figures 3 and 4 shows, the effect of flame retardant content on tack property of acrylic PSA/brominated flame retardant system is insignificant. In the case of acrylic PSA/TCEP system, tack is decreased with the amount of flame retardant. The similar tendency is observed in PSA/combined flame retardant system, the considerable decrease of tack is observed in PSA/TCEP/ $\text{Al}(\text{OH})_3$ system. The decrease of tack of acrylic PSA in the presence of TCEP may be owing to the immiscibility between them, which is also observed in decrease of %conversion as a function of flame retardant amount. In earlier study, a slight decrease in miscibility between phosphate flame retardant and polymer matrix may be accompanied with the decline of thermal stability of polymer at high temperature.¹⁹ Poor dispersion of halogen-containing phosphorus flame retardant, TCEP, can be observed by the optical microscopy, some agglomerates present as shown in Figure 5.

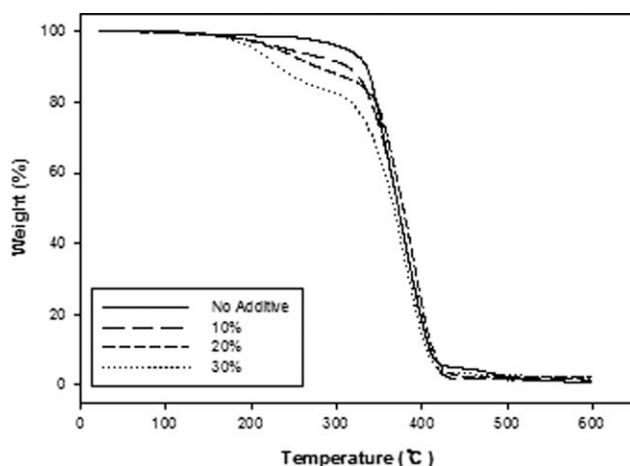


Figure 6 TGA curves of PSA with TCEP/PBPE combined flame retardant system.

Thermal stability

TGA curves and residue (wt % at 550°C) reveals declined thermal stability of our PSA/flame

retardant system as shown in Figure 6. It is assumed that those results mean PSA/combined flame retardant system has a poor miscibility, which can also negatively affect the thermal stability of PSA.

CONCLUSIONS

Various acrylic PSAs formulation containing different type and ratio of flame retardant is prepared. An apparent influence of flame retardant TBBPA, brominated flame retardant is achieved for the formulation above 15 wt %. It is also observed that combined system consist of brominated and halogenated phosphate flame retardant increase flame retardancy of PSAs more significantly. On the other hand, it is found that existing fillers such as Al(OH)₃ and MMT does not affect the flame retardancy of PSAs as a synergist. The addition of flame retardant in acrylic PSAs has a negative effect on adhesion properties in case of halogenated phosphate flame retardant. The different behavior in adhesion properties is also observed in brominated flame retardant system. This may be attributed to low surface energy of PSAs affected by miscibility between PSAs and flame retardant. It is expected that the enhanced flame retardancy of acrylic PSAs by adding combined system will extend the versatile applications in electric and electronic industries.

References

1. Satas, D. Handbook of pressure-sensitive Adhesives Technology, 2nd ed.; Van Nostrand Reinhold: New York, 1989.
2. Istvan, B. Pressure-Sensitive Adhesives and Applications, 2nd ed.; Marcel Dekker: New York, 2004.
3. Pizzi, A.; Mittal, K. L. Adhesive Technology and Application; Marcel Dekker, New York, 2003.
4. Kinloch, A. J. Adhesion and Adhesives, Science and Technology; Kingston, 1986.
5. Czech, Z. J Appl Polym Sci 2001, 81, 3212.
6. Hong, J. H. UV Radiation Coating; Chosun University Press, 2002.
7. Lees, W. A.; Moulds, R. J. Int J Adhes Adhesives 1995, 15, 95.
8. Park, S. J.; Song, S. W.; Lee, J. R.; Min, B. G.; Shin, J. S. J Korean Ind Eng Chem 2005, 15, 41.
9. Hwang, T. S.; Lee, B. J.; Yang, Y. K.; Choi, J. H.; Kim, H. J. Prospect Ind Chem 2005, 8, 36.
10. Lee, M. S.; Kim, J. H. Prospect Ind Chem 2005, 8, 21.
11. Park, S. J.; Song, S. W.; Lee, J. R.; Min, B. R.; Shin, J. S. J Korea Ind Eng Chem 2004, 15, 41.
12. Lee, J. H.; Nam, J. H.; Lee, D. H.; Kim, M. D.; Kong, J. H.; Lee, Y. K.; Nam, J. D. Polymer (Korea) 2003, 27, 569.
13. Kim, H. G.; Lee, D. H.; Min, K. E. Polymer (Korea) 2007, 31, 55.
14. Shim, I. W.; Jo, H. J.; Park, H. S.; Kim, S. K.; Kim, Y. G. Polymer (Korea) 2006, 30, 238.
15. Kwak, S. B.; Hwang, S. D.; Nam, J. D.; Ko, J. S.; Choi, H. K.; Kong, J. H. Polymer (Korea) 2002, 26, 260.
16. Choi, S. S.; Im, W. B.; Kim, J. H.; Hwang, Y. A.; Woo, J. W. Elastomer 2002, 37, 224.
17. Howell, B. A.; Cho, Y. J. J Therm Anal Calorim 2006, 85, 73.
18. Khattab, M. A. J Appl Polym Sci 2000, 78, 2134.
19. Baek, K. H.; Lee, J. Y.; Hong, S. H.; Kim, J. H. Polymer (Korea) 2004, 28, 404.