Physical Properties of Garnet-Filled Polyurethane Foam Composite

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ABSTRACT: Garnet-filled polyurethane foam composite was prepared by solvent-free reaction. Density, hardness, and compression strength were measured to study its basic physical properties. Percent volume loss and arithmetical mean surface roughness were investigated as an abrasion property to determine its potentiality as an abrasive and establish a relationship between basic properties and abrasion properties. These properties were measured as functions of blowing agent content, and garnet was used as filler. The particle size of the garnet and the polyol mixing ratio were also changed to investigate the dependence of properties on formulation. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1336–1343, 2001

Key words: garnet; polyurethane; composite; foam; abrasive

INTRODUCTION

Polymer composites, common in almost all of polymers, are usually prepared to reinforce their physical properties, or give certain functions. In case of polyurethane, fillers are also used to reduce its cost, improve physical properties, and impart functions. Inorganic fillers like glass fiber, glass flake, calcium carbonate, mica, and talc are used to increase hardness of foam, absorption of energy applying it, increase elasic modulus and thermal resistance, and to impart flame resistance.[1–5]

Polyurethanes are usually produced by the reaction of a polyisocyanate with a polyol or other reactants containing groups reactive with isocyanate. The hydroxyl-containing component is usually used as a reactive material with polyisocyanate, and it covers a wide range of molecular weights, functionality, and types (ether,ester). The polyisocyanate also can be a variable in its

structure; aromatic, aliphatic, polycyclic, etc. The physical properties of polyurethanes are dependent on selection of polyols and isocyanates. As their physical properties are varied, the end-products derived from polyurethanes can be used for wide range of applications such as plastics, fibers, elastomers, films, and surface coatings.[1–8]

In this study, garnet was used as a filler to give abrading property to polyurethane foam composite. Garnet is an inorganic material having a quite high degree of hardness, which can make it applicable as an abrasive and jewel. In a practical application, it is used as an abrasive for display panel (cathode-ray tube, liquid crystalline display, plasma display panel, etc.) in the powder state.[9,10] The garnet-filled polyurethane composite, having abrading property, can be expected to be applied as an abrasive, not in a powder state. When it is employed in a practical abrasion process, it can make the process simpler and less costly due to the reduction of the amount of abrasive used. It can also prevent environmental problems because of diminishing use of garnet powder scattered during the process.

Table I   Summary of Polyols That Were Used in This Study

Materials	HD 401	GP 1000	GL 3000	FA 702
Hydroxyl value	400	168	56	35
Average molecular weight	400	100	3000	6500
Functionality	3	3	3	4

To study basic physical properties of garnet-filled polyurethane composites, density, hardness, and compression strength were measured as functions of blowing agent content and filler and polyol formulation. Percent volume loss and arithmetical mean roughness were also measured to investigate abrasion properties and the relationship between basic properties and abrasion properties.

EXPERIMENTAL

Materials

An industrial grade polyisocyanate of 28% NCO content and four types of polyols having different hydroxyl values used in this study were obtained from Korea, the Polyol Co., Ltd. Both tetraethyl-diamine used as a catalyst, and polyether silox-ane used as surfactant, were also obtained from the same company. As a blowing agent, water, a common blowing agent for polyurethane, is only used. Garnets whose average particle sizes were 9, 16, 30, and 80 μm were prepared as fillers. Table I shows properties of four types polyols used in experiments.

Mixing and Foaming Procedure

All mixings and foaming reactions of this study were based on a solvent-free reaction. First, a proper amount of polyol was mixed for 1 min at a speed of 2000 rpm by high-shear mixer. Additives except filler; catalyst, surfactant, and water were added to the polyol blend, and mixed for 1 min at a the speed of 3000 rpm. On equimolar amount of polyisocyanate was next added and mixed for 10 s at 4000 rpm mixer speed. After finishing the mixing procedure, the filler was added and mixed for 1 min at a speed of 6000 rpm by high-shear mixer. The mixed compound was then poured and clamped in the mold. The foaming reaction took place at 60°C for 6 h.

Testing of Physical Properties

Density was determined by the ASTM 3489 method using a $20 \times 20 \times 25$-mm specimen. Hardness was measured using a durometer type A (Asker. Co. Ltd., Japan) by the ASTM 2240 method, and the thickness of the specimen were 10 mm. The procedure for the compression strength was an ASTM 695 method. The universal testing machine (UTM) for the test was an Instron 4465, and the size of the sample for the compression strength test was $12.5 \times 12.5 \times 25$ mm. In this condition, 25, 40, and 65% compression stress were measured, and the crosshead speed for compression was 8 mm/min. A rotating drum abrader was used for measuring abrasion properties. The procedure used for abrasion properties was a non-ASTM procedure, but was designed to reflect surface abrasion. Arithmetical mean roughness (Ra) and percent volume loss were measured after abrading on the surface of a cathode ray-tube panel, of which the Ra value was 0.303 μm at a speed of 200 rpm for certain times—5 and 20 min. Arithmetical mean roughness (Ra) was measured by a surface tester 301 (Mitutoyo. Co. Ltd., Japan), after abrasion. Arithmetical mean roughness (Ra) can be defined as in eq. (1) and Scheme 1.

$$Ra = 1/N \sum_{I=1}^{N} Yi \qquad (1)$$

RESULTS AND DISCUSSION

The Effect of Blowing Agent

Table II is the formulation for studying the blowing agent effect on the physical properties of the polyurethane foam composite. The physical properties of the polyurethane foam composites were measured using different water contents.

Figure 1 shows the results of density changes as a function of water content. As the water content was increased, the density of the polyurethane foam composite was decreased. Because the amount of gas released was directly proportional to the amount of water used, the density of the system was decreased linearly, depending on the amount of water used. The hardness of the poly-
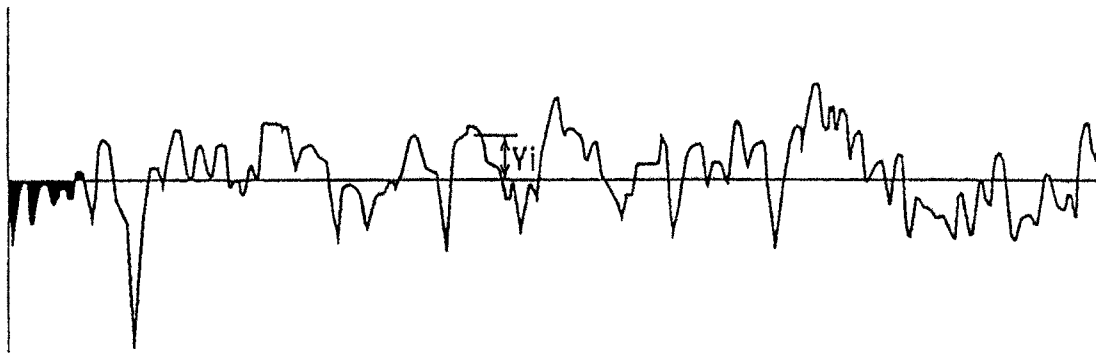
Scheme 1. Example scheme for defining RA

urethane foam composite with various water contents is shown in Figure 2.

The hardness declined with growing water content. The change of compression strength of the polyurethane composite by different water content is shown in Figure 3. Figure 3 indicates compression strength at 25, 40, and 65% compression.

The compression strength of the polyurethane foam composite decreased with increasing water content at all compression rates. This can be explained by reduction of hardness due to the increase in density.[1–5] Figure 4 shows the percent volume loss, a kind of abrasion property of polyurethane foam composite, with respect to water content after 5 min of abrading.

The percent volume loss is important because it is possible to estimate the lifetime of the product when applied as an abrasive. The results of Figure 4 indicate that the percent volume loss decreased with increasing water content. The increase in the foaming rate by more blowing agent can be suspected as the reason for a decrease of the abrasion resistance as well as basic physical
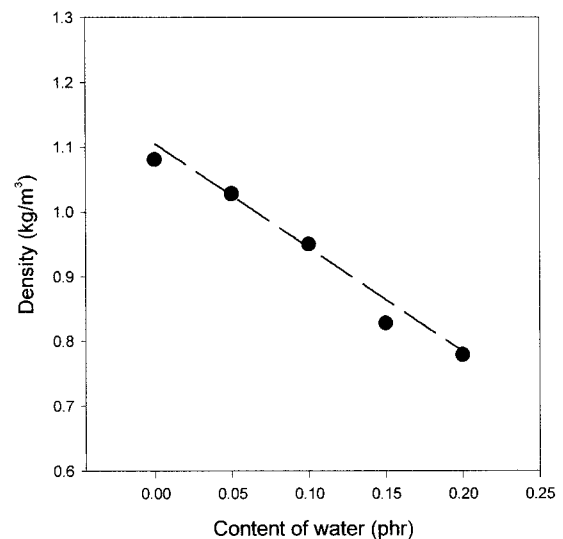
properties. In Figure 5, the arithmetic mean roughness was also measured to estimate the potentiality as a function of the water content. The arithmetic mean roughness is also a valuable property that can determine the time of the abrading process and the quality of product.

As defined in eq. (1), the lower Ra value means a smoother surface condition. As shown in Figure 5, the Ra value increased with increasing content of water because the number of garnet particles that participate in practical abrading of the surface is reduced by increasing of foaming rate. Under this experimental condition, better surface roughness was obtained of polyurethane foam composites having lower density.

The Effect of Filler

Basic properties and abrasion properties were studied with various contents and particle size

Table II   Formulation for Studying Blowing Agent Effect to Polyurethane Foam Composite

Material (phr)	B0	B5	B10	B15	B20
Polyol (FA702/					
HD 401 = 50/50)			100		
Crude MDI			60		
Garnet[a]			373		
Silicon			1.5		
Catalyst			0.5		
Blowing agent					
(water)	0	0.5	1.0	1.5	2.0

[a] Particle size is 80 μm.

Figure 1   Density of polyurethane foam composite as a function of water content.
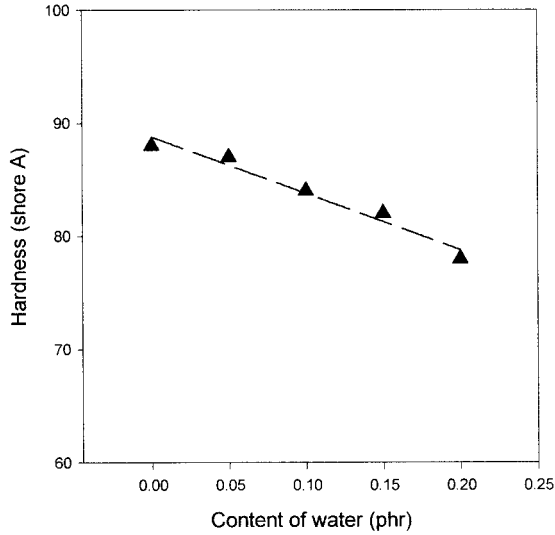
Figure 2 Hardness of polyurethane foam composite as a function of water content.
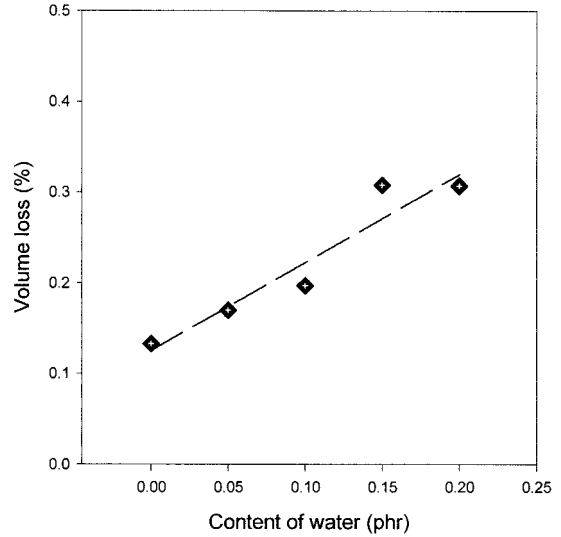
Figure 4 Percent volume loss of polyurethane foam composite as a function of water content after 5 min abrading.

of garnet. The formulation for this study is Table III.

Figure 6 shows hardness change by different garnet contents. As the content of filler increased, the hardness of the system increased, and the hardness was not much changed at a content of 373 phr or higher. It can be thought that loading of garnet having much higher hardness induces an increase of hardness of the system.

The results of measurements of the compression strength as a function of garnet content are shown in Figure 7.

Although the results of measuring compression strength show great differences as in the results of hardness, the compression strength was slightly increased with increasing content of the garnet. It might be thought that an increase of hardness can act as resistance to compression.

Abrasion character changes by garnet content were also investigated. The results of percent volume loss with various garnet contents are shown in Figure 8.
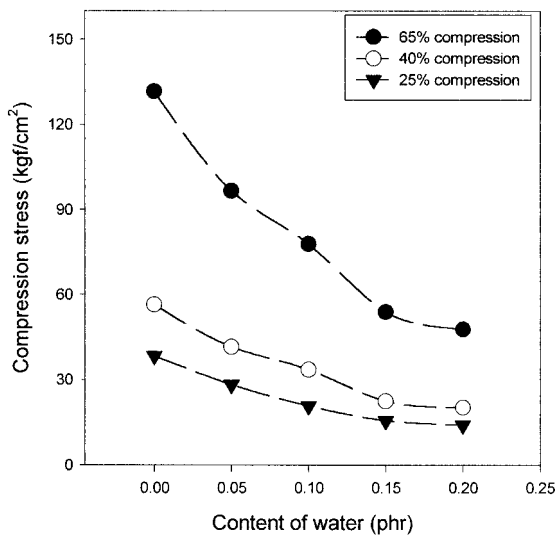
Figure 3 Compression stress of polyurethane foam composite as a function of water content at 25, 40, and 65% compression.
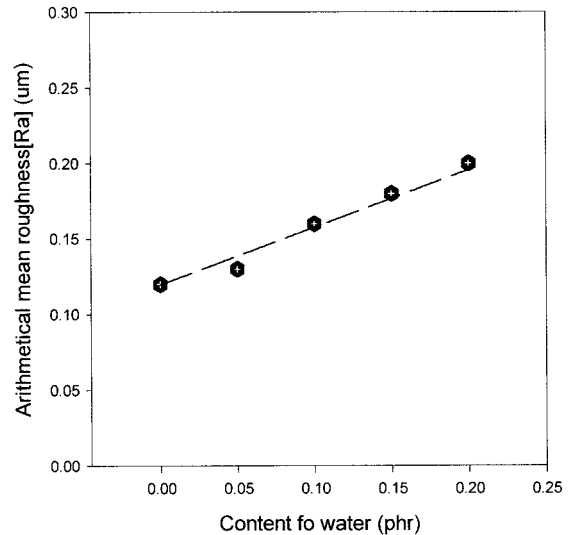
Figure 5 Five minutes abraded surface roughness of polyurethane foam composite as a function of water content.

Table III   Formulation for Studying Effect of Garnet as Filler to Polyurethane Foam Composite

| Material (phr)	G0	G40	G50	G60	G70	G75
Polyol (FA702/HD 401 = 50/50)				100		
Crude MDI				60		
Garnet[a]	0	107	160	240	373	480
Silicon				1.5		
Catalyst				0.5		
Blowing agent (water)				0.5		

[a] Particle size is 80 μm.

The nonfilled system shows definitely different results from the garnet filled system. In nonfilled systems, low percent volume loss was obtained because no abrading occurred with the system. Garnet-filled systems show far greater amounts of percent volume loss. The amount of volume loss was almost constant from a low content to 373 phr of garnet content. The reason for this difference between nonfilled and garnet-filled systems is suspected because the volume loss occurred mainly by separation of sufficiently abraded garnet particles from the system at the surface during the abrasion procedure. The reason that the G75 system shows much higher volume loss is because of its overloading of garnet, which can cause an unstable binding state for the system. Figure 9 shows the value of Ra with respect to garnet content after 5 min of abrading.

The results of Fig. 9 show that the Ra of nonfilled system does not change after abrasion, and the Ra of the garnet-filled system was decreased with increasing the garnet content. The reason that higher garnet-loaded systems show a lower Ra is due to more particles participating in the abrading surface.[9,10] The G75 system showed much lower Ra because the garnet was overloaded. The overloaded garnet particles can easily secede from the system on the abrading surface, and they participate in abrading. Polyurethane foam composites having various particle sizes (9, 16, and 30 μm) were prepared to investigate the effects of garnet particle size on abrasion properties. They were formulated based on G70 in Table III, and their particle sizes of garnet were altered to 9, 16, and 30 μm. Table IV shows the Ra of polyurethane foam composites at different garnet particle sizes. Table IV gives the results of Ra as a function of garnet particle size that are opposite with respect to the abrading time.
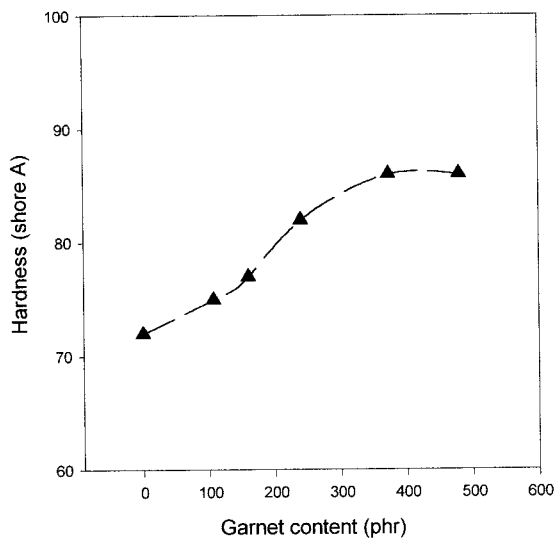
Figure 6 Hardness of polyurethane foam composite with different amounts of garnet.
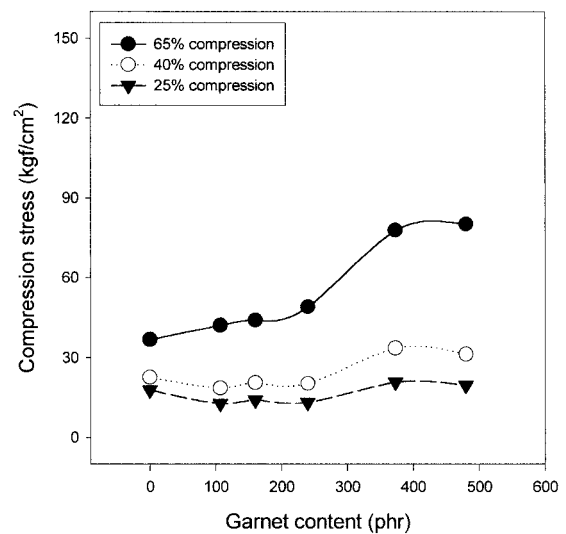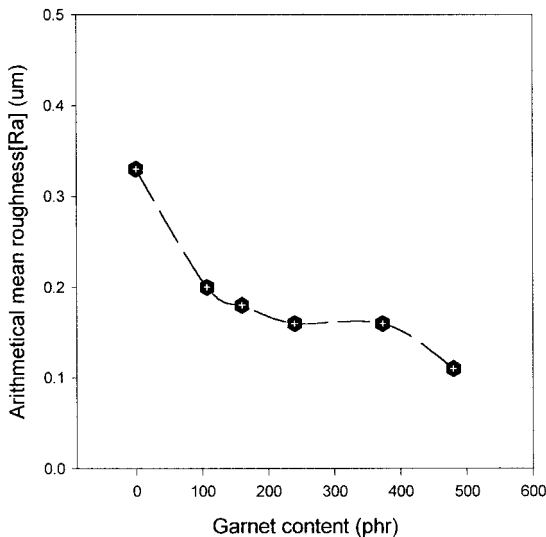

Figure 7 Compression stress of polyurethane foam composite with different amounts of garnet.
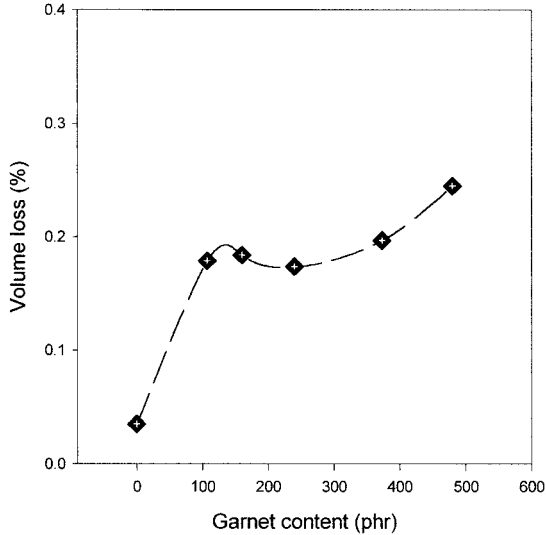
Figure 8 Percent volume loss of polyurethane foam composite with different amounts of garnet.

In 5 min of abrading, the Ra of the system was decreased with increasing garnet particle size, but in 15 min of abrading, the system, which has smaller garnet size, shows a lower Ra. Five minutes were not enough time to cause sufficient abrasion for the systems having smaller particles (16 and 30 μm). On the contrary, it was sufficient time to make enough abrasion for systems having relatively larger particles (80 μm). In terms of critical value of Ra, which means the least value of Ra each particle size can reach, smaller particle

Figure 9 Five minutes abraded surface roughness of polyurethane foam composite with different amounts of garnet.

Table IV   Arithmetical Mean Roughness (Ra) of Polyurethane Foam Composite with Respect to Particle Size of Garnet at Different Abrading Time

Average Particle Size	9 μm	16 μm	30 μm	80 μm
Arithmetical mean roughness (Ra) after 5 min abrasion (μm)	0.29	0.24	0.17	0.16
Arithmetical mean roughness (Ra) after 15 min abrasion (μm)	0.27	0.08	0.11	0.14

size has a lower value.[9,10] For that reason, when enough time (15 min) was applied to the system, the system containing smaller particles showed a lower Ra. The results of Table IV show that 5 mins can be regarded as sufficient time for G80, not for G16 and G30, but 15 min is all right for all systems applied in this study. The results of Table IV show that all systems except G9 exhibited good abrasion properties as an abrasive. In the case of the G9 system, it showed higher Ra value because the mixing of polymer and garnet was poor due to a high surface area.

The Effect of Polyol

Polyol is an important component that determines the main chain structure of the polyurethane. Its main chain structure, the hydroxyl value, and functionality of the polyol can also affect its physical properties. In this study, a few types of polyols having various hydroxyl values were prepared, and the physical properties of the polyurethane foam composites were measured with respect to formulation of their blend systems. Formulation for that purpose is shown in Table V.

Table VI shows the physical properties of polyurethane foam composites follows the formulation in Table V.

In these systems, hardness and compression strength were increased with increasing contents of polyols containing more OH groups in the polyol blend. That is a typical tendency for all kinds of polyurethane foams, not only for these systems.[1-8] As the number of OH groups increase, the crosslinking density of the polyurethane is higher. The percent volume loss also showed a similar tendency with regard to hardness and compression strength. Because the ap-

Table V   Formulation of for Studying Effect of Polyol to Polyurethane Foam Composite

Compounds (phr)	CMDI (phr)	Polyol (100)				Garnet (phr)
		GP1000	GL3000	FA702	HD401	
PH91	53	90	—	—	10	356
PH82	59	80	—	—	20	371
PH73	66	70	—	—	30	387
PH64	72	60	—	—	40	401
PH55	78	50	—	—	50	416
PH46	84	40	—	—	60	430
LH91	26	—	90	—	10	294
LH82	35	—	80	—	20	315
LH73	45	—	70	—	30	338
LH64	54	—	60	—	40	359
LH55	63	—	50	—	50	380
LH46	72	—	40	—	60	401
FH91	21	—	—	90	10	282
FH82	31	—	—	80	20	305
FH73	41	—	—	70	30	329
FH64	50	—	—	60	40	350
FH55	60	—	—	50	50	373
FH46	70	—	—	40	60	396

GP1000:OH value: 168, functionality = 3, GL3000: OH value: 56, functionality = 3, FA702 OH value: 35, functionality = 4, HD401: OH value: 400, functionality = 3, catalyst = 0.5 phr, silicon = 1.5 phr, water = 0.1 phr, Index ([NCO]/[OH]) = 1.

Table VI   Physical Properties of Polyurethane Foam Composites with Various Polyols and Their Mixing Ratio

Compounds (phr)	Hardness (sore A)	25% Compression Stress (kgf/cm^2)	40% Compression Stress (kgf/cm^2)	65% Compression Stress (kgf/cm^2)	Percent Volume Loss (%)	Arithmetical Mean Roughness (Ra)
PH91	61	4.43	8.61	18.40	0.63	0.15
PH82	68	4.24	9.68	23.28	0.41	0.14
PH73	83	11.17	24.71	58.26	0.30	0.16
PH64	89	33.19	53.35	107.40	0.24	0.16
PH55	93	74.19	89.60	147.10	0.11	0.19
PH46	96	100.10	111.40	168.40	0.13	0.18
LH91	45	3.32	6.23	12.13	1.25	0.08
LH82	47	3.48	5.44	11.75	1.22	0.08
LH73	57	3.72	6.49	15.19	0.58	0.12
LH64	68	5.45	10.33	29.61	0.32	0.15
LH55	74	12.71	22.48	61.98	0.29	0.17
LH46	89	41.16	58.56	121.32	0.22	0.16
FH91	49	2.33	6.52	13.99	1.05	0.07
FH82	52	2.75	6.10	12.68	0.62	0.11
FH73	61	3.68	7.63	18.11	0.46	0.13
FH64	75	8.62	16.70	42.62	0.28	0.16
FH55	86	20.83	33.64	77.98	0.20	0.16
FH46	93	34.69	69.13	121.50	0.12	0.15

plications of these systems are for abrasives, higher crosslinking density can be regarded as an advantageous factor in terms of a lifetime. As the results of Ra value changes, lower Ra values were shown with decresing content of polyol having more OH groups in the polyol blend. The reason for this can be thought of because lower hardness and compression strength derived from lower crosslinking density can make efficient contact between the system and the abrading surface, and a high percent volume loss has more garnet particles that are separated from the system.

CONCLUSION

Polyurethane foam composites filled by garnets, a typical abrasive for glass display panels, were prepared, and the effects with various formulations to its basic and abrading properties were studied.

In the case of blowing agent and filler, a tendency of basic physical properties (density, hardness, compression strength) with respect to their content was quite similar to that of typical polyurethane foams. In abrading properties, increasing water content induced an increase of percent volume loss, and the Ra was not advantageous for application. Increasing of garnet content results in an increase of percent volume loss and a decrease of Ra. At different particle sizes of garnets, the Ra of the system containing smaller garnets was lower when abraded for a sufficient amout of time, but the Ra of the system containing larger garnets was lower when abraded for an insuffi-

cient time. At different polyol formulations, the basic properties also showed almost the same tendency as other polyurethane foams. An increase in the hydroxyl value in the polyol blend results in a percent volume loss, but the Ra was increased. The considered application as an abrasive, a lower water content, and more garnet loading with stable mixing are advantageous in terms of both lifetime and surface roughness, but a higher hydroxyl value in the polyol blend are advantageous for a lifetime, but disadvantageous for surface roughness.

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