POLYURETHANE ELASTOMERS WITH IMPROVED THERMAL CONDUCTIVITY
PART I: ELABORATING MATRIX MATERIAL FOR THERMAL CONDUCTIVE COMPOSITES

[1]SOMDEE PATCHARAPON, [2]MAROSSY KÁLMÁN, [3]LASSÚ-KUKNYÓ TÍMEA, [4]KÓNYA CSABA

[1,2]Institute of Ceramics and Polymer Engineering, University of Miskolc, Miskolc, Hungary
[3,4]BosodChem Zrt.,Kazincbarcika, Miskolc, Hungary
E-mail: [1]somdee_patch@hotmail.com, [2]polkal01@uni-miskolc.hu

Abstract - Cross-linked polyurethane elastomer matrix was evaluated for thermal conductive composites with magnesium oxide powder (MgO). MgO as one of the cheapest materials for high thermal conductivity,seems to be useful for incorporation in polyurethane elastomer increasing thermal conductivity of the composites. Possible matrix polyurethane elastomers were fabricated. The effect of MgO contents from 1 to 30 %wt were investigated bothin flexible and in rigid polyurethane elastomers. First experimental aim is investigating the structure of the polymer intended for application. Improving thermal conductivity was first not achieved but the causesof the poor results were discovered. After that differential scanning calorimetry (DSC) and thermally stimulated discharge (TSD) methods were used to examine the structure of polyurethane elastomers. Furthermore, hardness measurements were carried out for estimating the effect on mechanical properties. Then, morphology of theMgO particles was observed using scanning electron microscope (SEM). Resultsshowed that thermal conductivity of the composites both of flexible and rigid polyurethane elastomers did not significantly change with loading MgO contents less than 30 %wt. In case of structure examinations, DSC thermogramsregistered a small transition around -62 °C of flexible polyurethane elastomers and their composites while the small transition of rigid polyurethane elastomers were hard to evaluate because the DSC technique is not sensitive enough for detecting a glass transition in these rigid polyurethane elastomer chains. Therefore, TSD technique was used to investigate chain relaxation. Pure flexible and rigid polyurethane elastomers show the same glass transition temperatures of soft segments around -65 °C. The incorporation of MgO less than30 %wt in both flexible and rigid polyurethane elastomer did not significantlyaffect hardness properties. Moreover, the smallest MgO particle observed were around 400 nm by SEM technique.

Keywords - Polyurethane Elastomers, Magnesium Oxide, Thermal Conductivity

I. INTRODUCTION

Polyurethanes (PU) are versatile polymeric materials that can be used in wide range of applications such as elastomers, coatings, foot wear, furniture, foams, packaging, adhesives, automotive finishes, electronics and so on. It has several advantages consisting of high impact strength, good elasticity, high elongation, abrasion resistance, excellent resistance to oilsand solvents, good tear resistance, etc. Moreover, polyurethanes can be usedin both rigid and flexible form, easy to process and could be used in electronic applications. Polyurethanes are formed by chemical reaction between a di- or poly isocyanate and a diol or polyol, forming repeating urethane groups usually in presence of chain extenders, catalysts and other additives. Often ester, ether, urea and aromatic rings are also present along with urethane linkages in the polyurethane backbone [1]. The general structure or bond that forms the basis of this chemistry is the urethane group shown in Fig. 1. Polyurethane elastomers (PUs) are widely used in various industries because they have excellent chemical, physical and mechanical properties such as oxidation stability, low temperature stability, radiation resistance and abrasion resistance. In order to further improve mechanical properties for specific industrial applications, the addition of various fillers or additives into polyurethane to prepare composites is a possibility[2].

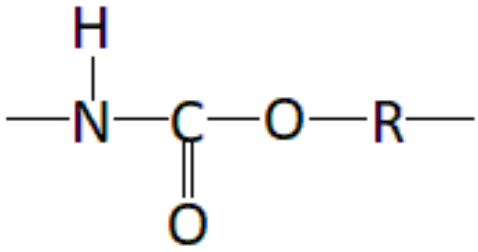


Fig.1 Urethane group

Magnesium oxide is a kind of high thermal conductivity filler. The nanometer sized MgO has been used in great demand in recent years with a broad range of applications such as a bactericide, ceramic material, catalyst, material for toxic waste remediation and refractory material. Furthermore, the morphology and the size of the final MgO product depend on the polymer or surfactant used in the precursor material [3]. MgO has a high electrical resistivity greater than $10^{15}\Omega$cm at 600 K. In addition, it has a high physical strength and stability and a melting point of 2852 °C [4]. Moreover, magnesium oxide has high thermal conductivity; 40-60 W/mK. Effect of MgO filler on thermal conductivity, thermal properties and mechanical properties of polyurethane elastomer composites were investigated in this study while the

structure of pure polyurethane elastomers were examined by TSD technique. SEM technique was used to observe the morphology of MgO powders.

II. MATERIALS AND METHODS

In this paper, diphenylmethane-4,4'-diisocyanate (MDI) was used for isocyanate. ONGRONAT XP1147 is an acidified MDI blend based on ONGRONAT 2100; MI50 and pure4,4'MDI. Average molecular weight is 266 g/mol and equivalent weight is 127.33 g/mol. ALCUPOL D4011 is used for polyol blend in this study. It is a reactive polypropylene glycol (PPG-4000) compound with ethylene oxide. Monoethylene glycol (EG) is used as chain extender. The EG content was changed between 7 and 34 %wt. Catalyst in this reaction is Jeffcat TD33A. It is a 33.3 %wt solution of triethylenediamine in dipropylene glycol. Moreover, air release additive BYK A500 was also added. It is a silicone free air release additive for unsaturated polyester resins as well as polyurethane systems. Moisture scavenger is Finmasorb430. It is a molecular sieve paste on castor oil basis with 50% solid content; used for absorbing water in moisture sensitive systems. Furthermore, magnesium oxide particle size less than 250 μm was used to prepare the polyurethane elastomer composites.

The A components were prepared by weight fraction that consist of polyol blend, chain extender, catalyst, air release additive, moisture scavengerand magnesium oxide particles as shown in Table 1. After that, the A mixtures were mixed with the specific MDI blend. In the first step, each MgO contents were hand mixed into PPG, monoethylene glycol, catalyst, air release additive and moisture scavenger for 5 min. Then, the A mixtures were homogenized using an ultrasonic atomizer. After that, ONGRONAT XP1147 is an acidified MDI blend (B mixture), it was added in mixture and shear mixed for 8-12 sec at 35% of machine capacity (6000 rpm). The mixtures were poured into the hot mold of 70 °C for 30 min to prepare polyurethane elastomer composites sheet. The length, width and thickness of the mold are 200, 100 and 1-4 mm, respectively. After completion the process, properties of the polyurethane elastomer composites were investigated.

Pure flexible and rigid polyurethane elastomers and polyurethane elastomer composites with MgO were prepared. Both flexible and rigid polyurethane elastomers were prepared by using different chain extender contents; 7 and 34 %wt. Furthermore, MgO filler with different contents from 1 to 30 %wt were added in both flexible and rigid polyurethane elastomers. Thermal conductivity was measured using a C-THERM thermal conductivity analyzer (TCi). Hardness was investigated according to ISO868 standard (Shore A was used for soft and shore D for rigid materials). DSC of pure polyurethane elastomers and polyurethane elastomer composites weremeasured on a METTER TOLEDO model DSC 823 with a heating rate of 10 °C/min from -100 to 250 °C.Moreover, thermally stimulated discharge technique was used to examine the structures of both flexible and rigid polyurethane elastomers. Glass transition (α relaxation) of polyurethane elastomers wasdetermined via the TSD technique. Sample disks of 26 mm diameter were cut by die-cutting for TSD tests.Polarizing field was 500V/mm and temperature was used in the range of -120 to 10 °C. Cooling and heating rates were 5 °C/min.Morphology of MgO powder was investigated by SEM technique.

Description	Trade Name	Weight (phr)
Polypropylene glycol copolymer (PPG)	ALCUPOL D4011	100
Monoethylene glycol (chain extender)	EG	7 and 34
Catalyst	Jeffcat TD33	0.3
Air release additive	BYKA500	0.3
Moisture scavenger	Finmasorb 430	10
Filler	MgO	0 to 30

Table 1 Ingredient of A components

III. RESULTS AND DISCUSSIONS

For this experimental, chain extender content at 7 and 34 %wt were used to prepare polyurethane elastomer composites with MgO, because we would like to prepare both flexible and rigid polyurethane elastomer composites. Fig. 2(a) shows the variation of thermal conductivity of polyurethane elastomers. It is slightly increasing with increasing amount of MgO filler. The highest thermal conductivity is observed of 7 %wt EG with 20 %wtMgO at 0.280 W/mK. This might be attributed to the amount and quality of dispersion of the MgOfiller in the polyurethane matrix. The decrease of thermal conductivity is causedby formation of air bubbles during curing, when the uncured polyurethane mixture has high viscosity [5]. In case of 34 %wt EG, result did not significantly change with MgO from 1 to 30 %wt as shown in Fig. 2(b). This may be due to many tiny air bubbles inside the rigid polyurethane elastomer sample. The other concern of the importance of the filler dispersion is relatively low, because the densely packed fillerparticles are in direct contact with each other at high filler concentrations [6].

For the flexible (7 %wt EG) sample Shore A and for rigid (34 %wt EG) Shore D method was used for hardness testing. To measure the hardness one needs to have a sample that is at least 4-5 mm thick and has a large enough surface for the base of the durometer to rest on. For the most accurate measurements, a dead load instrument should be used [7]. The variations of hardness Shore A and D values for each formulation of the flexible polyurethane elastomer/MgO composites are shown in Fig. 3(a) and 3(b). It is observed that both hardnesses of Shore A and D values did not significantly change with the increasing in magnesium oxide content. Results show between 52-60 Shore A

and between 10-15 Shore D. Although MgO content was increased, however the incorporated MgO particles act as inactive fillers in the polyurethane elastomers therefore shall have no or no significant affect on the hardness properties.

When incorporating MgO in polyurethane elastomer matrix at 34 %wt EG, Shore A hardness results show no significant change with the increase in magnesium oxide content; between 94-98 Shore A as shown in Fig. 4 (a).

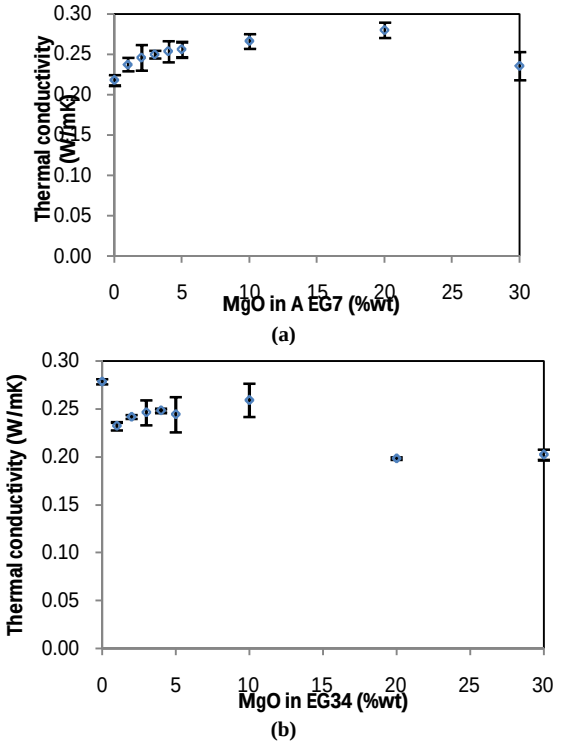


Fig. 2 Thermal conductivity of polyurethane elastomers at 7 %wt EG (a) and 34 %wt EG (b) with variousMgO from 0 to 30 %wt

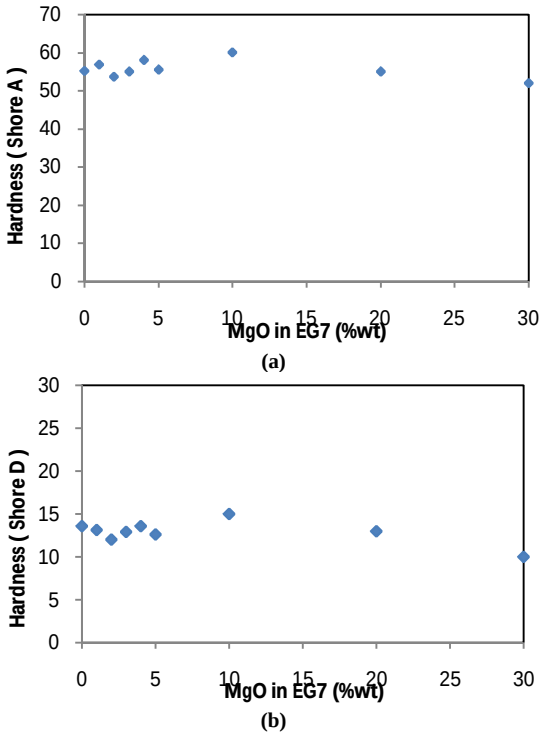


Fig. 3 Hardness Shore A (a) and D (b) of polyurethane elastomers at 7 %wt EG with various MgO from 0 to 30 %wt

In case of Shore D tests, the results show increase of hardness whit increase ofMgO content up to 3 %wt of 64 Shore D then hardness starts to decrease with increasing MgO content as shown in Fig. 4(b).This result indicates that dispersion and agglomeration of MgO particle in rigid polyurethane elastomer matrix influence on stiffness of polyurethane elastomer composites. The indentor of Shore D instrument is a pin of very small area, the stress is high. The indentorof Shore A instrument is a truncated cone, the stress is much lower.

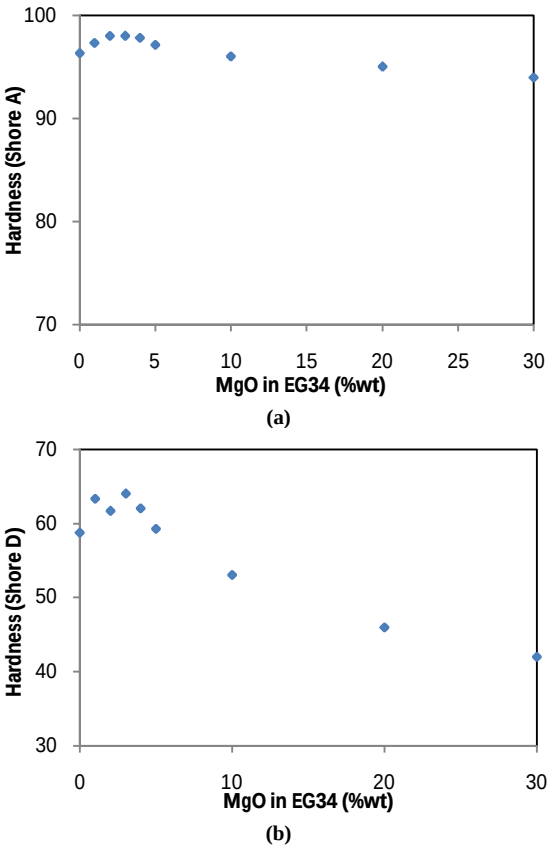


Fig. 4 Hardness Shore A (a) and D (b) of polyurethane elastomers at 34 %wt EG with various MgO from 0 to 30 %wt

Tiny air bubbles occurring inside the polyurethane elastomer samples having an influence on the thermal conductivity and some mechanical properties as discussed above. These results show low values at high filler concentration. These are due to the bubbles mentioned above. Polyurethane elastomers lose the continuous matrix phases. Bubbles occuring inside the sample may be due to the polyurethane elastomer matrix having high moisture and water content and together with the effect of moisture on the MgO powder.

Differential scanning calorimetry measurements were carried out for the characterization of the polyurethane elastomer/MgO composites. Samples were sealed in aluminum pans. The samples were heated from -100 to250 °C with a heating rate of 10 °C/min in order to obtain the thermograms. Polyurethane elastomers at 7

and 34 %wt EG were prepared with various MgO contents of 0, 5, 10, 20 and 30 %wt. The DSC thermograms of polyurethane elastomer/MgO composites at 7 %wt EG areshown in Fig. 5. The small transition observed at around -62 °C may be the glass transition of the soft segments of the polyurethane elastomers. Adding MgOin different amounts did not significantly affect the position of the small transition of the polyurethane elastomer matrix. This indicates that theMgO particles d not influence the PPG polyol segment. Normally, the incorporation of nanoparticles constrains the movement of the molecular chains; leading to the increase of glass transition temperatures. On the other hand, nanoparticles can also disturb the entanglement network of the polymer chains thus leading to a slight decrease of glass transition temperatures [8].

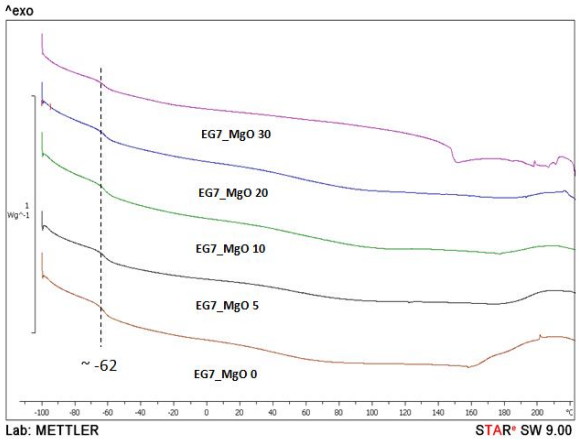


Fig. 5 DSC thermograms of polyurethane elastomers at 7 %wt EG with various magnesium oxide content from 0 to 30 %wt

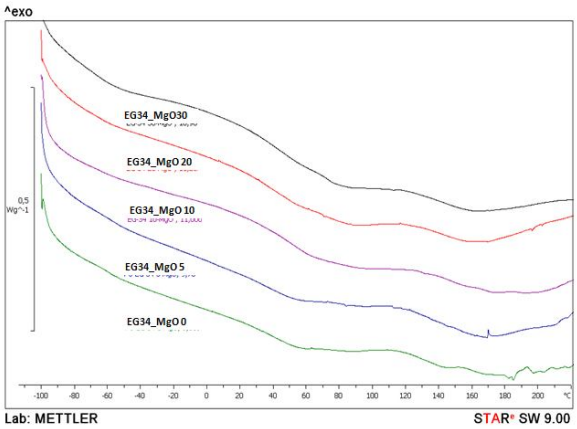


Fig. 6 DSC thermograms of polyurethane elastomers at 34 %wt EG with various magnesium oxide content from 0 to 30 %wt

Fig. 6 shows the DSC thermograms of polyurethane elastomer/MgO composite at 34 %wt EG with various MgO contents. The small transition of the soft segment is not clearly observed when adding MgO from 5 to 30 %wt. However, it may be expressed that theMgO content did not effectthe cross-linking and chain decomposing of polyurethane elastomers. However, changing theMgOcontent from 5 to 30 %wtthe $T_g$could not beeasily detected by the DSC technique in this study.

TSD technique can confirm the glass transition temperatures. Both curves of flexible and rigid polyurethane elastomers show the same transition temperatures for the soft segments at around -65 °C as shown in Fig. 7. The small intensity peaks of the rigid polyurethane elastomersrelated to the transition in DSC curves aredifficult to evaluate. Moreover, it can be indicated that they originate from the polyol and also can be proved that the hard and soft segments in polyurethane elastomers form an incompatible mixture.

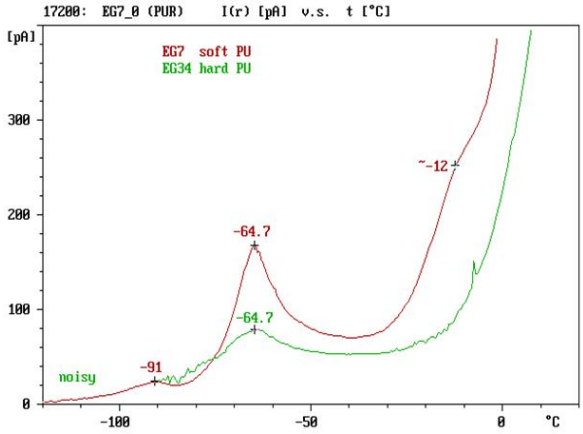
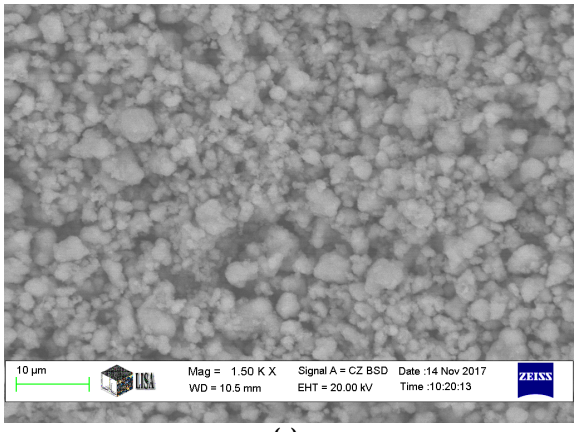
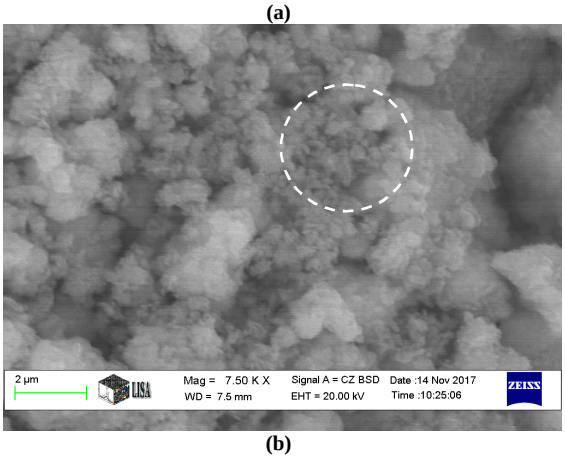


Fig. 7 TSD thermogram of pure polyurethane elastomers at 7 %wt EG and 34 %wt EG



(a)



(b)

Fig. 8 SEM image of MgO powder with nominal magnification of 1500×(a) and 7500×(b)

The morphology of the MgO particles was studied using the SEM technique. Fig. 8 shows SEM micrographs of MgO with nominal magnification of 1500× and 7500×. The SEM images show aggregation of many small particles. Sizes of the aggregates are less than 10 μm. In case of 7500×, the image shows the smallest particle in the range of nanometers at around 400 nm as shown in dashed circle line.

CONCLUSION

Both flexible and rigid polyurethane materials were produced containing 1 to 30 % by weight magnesium oxide filler contents. The magnesium oxide particles did not affect significantly the thermal conductivity. The reason of this observation was that the polyurethane matrix was slightly foamed and the air bubbles significantly decrease the thermal conductivity.

Magnesium oxide did not improve the mechanical properties therefore MgO is inactive filler in polyurethane.

Low temperature (around -65 °C) glass transition region was observed by DSC and TSD methods; the glass transition temperatures were the same, independent of the hardness and MgO content. This transition originates from the segmental motion of the polyol. Because the intensity of this transition depends on the polyol content the less sensitive DSC method shows these transitions clearly for the soft polyurethane only. TSD method undoubtedly proves the presence of this transition in the rigid material too.

SEM images show the primary and aggregated particles at around 400 nm and 10 μm.

ACKNOWLEDGMENTS

This research was supported by the European Union and Hungarian State, co-financed by the European Regional Development Fund in the framework of the GINOP-2.3.4-15-2016-00004 project, aimed to promote the cooperation between the higher education and the industry. The research was also supported by Institute of Ceramics and Polymer Engineering, University of Miskolc and BorsodChemZrt. Company.

REFERENCES

[1] E. Sharmin and F. Zafar. (2012). Polyurethane : An Introduction. InTech. Retrieved from http://dx.doi.org/10.5772/51663

[2] T. Thomson. (2005). Polyurethanes as Specialty Chemicals Principle and Applications. Retrieved from http://s1.downloadmienphi.net/file/downloadfile3/206/1396439.pdf

[3] R. T. De Silva, M. M. M. G. P. G. Mantilaka, S. P. Ratnayake, G. A. J. Amaratunga and K.M. Nalin de Silva. Nano-MgO reinforced chitosan nanocomposites for high performance packaging applications with improved mechanical, thermal and barrier properties. (2016). Carnohydrate Polymers.Doi:http://dx.doi.org/doi:10.1016/j.carbpol.2016.10.038

[4] I.M. Alwaan, A. Hassan and M.A.M. Piah.Effect of zinc borate on mechanical and dielectric properties of metallocence linear low-density polyethylene/rubber/magnesium oxide composite for wire and cable applications. Iran Polym J, 24 (2015), pp. 279-288

[5] S. Benli, U. Yilmazer, F. Pekel, S. Ozkar. Effect of Fillers on Thermal and Mechanical Properties of Polyurethane Elastome.Journal of Applied Polymer Science, (1998).Doi: 10.1002/(SICI)1097-4628(19980516)68:7<1057::AID-APP3>3.0.CO;2-E

[6] K. Kim, M. Kim and J. Kim. Enhancement of the thermal and mechanical properties of a surface-modified boron nitride-polyurethane composites. Polym. Adv. Technol, 25(2014), pp.791-798

[7] I.R. Clemitson. (2015). Castable Polyurethane Elastomers. Retrieved fromhttp://www.ebook777.com/castables-polyurethane-elastomers-second-edition/

[8] S.Y. Gu, L.L. Liu and B.B. Yan. Effects of ionic solvent-free carbon nanotube nanofluid on the properties of polyurethane thermoplastic elastomer.J Polym Res, 21:356 (2014).Doi: 10.1007/s10965-014-0356-0

★★★