Synthesis and Properties of Cross-linked Polyurethane Composites Materials for Passive Isolation

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Cross-linked polyurethane/filler composites based on polyester, diphenylmethane diisocyante, glycols, and glycerin were synthesized and characterized. The mechanical and thermal properties of PU/filler composites were investigated through tensile, thermogravimetry experiments. Therefore, to understand the behaviour of fillers, such as graphite, talc, $CaCO_3$, and polyamide fiber added to cross-linked polyurethane resins, several thermal and mechanical tests were conducted on samples, using these new materials. It is shown that cross-linked polyurethane composites have decreased tensile strength, improved hardness and thermal stability, relative to bulk polyurethane. The results show that the polyurethane component ratios in cross-linked polymers, the types of filler, and the amount of powder added all affect the damping behaviours and degree of phase separation of unfilled and filled cross-linked polyurethanes. The addition of filler into polyurethane composites yields an increase in the Young´s modulus and a decrease in the elongation at break.

Keywords: composite, cross-linked polyurethane, mechanical properties, filler

Urban land availability for building new structures is becoming more restrictive, thereby accelerating the trend for the new construction and other noise and vibration-sensitive structures above, or in close proximity to, existing railway lines, major roads and other "noisy" infrastructure. The acoustic vibration isolation of a building requires to the structure to be supported on a comprehensive system of isolating bearing pads designed to perform under specific operating criteria.

Polyurethane (PU) is one of the most useful three-dimensional polymers due to its unique features. It can be produced in the form of sheets, foams, adhesives, and so forth.

Most commercially available inorganic fillers contain aggregated particles that are still present after common grinding/mixing processes and these will in turn cause reduced transparency of such coatings [1, 2].

Many particles are now available, in particular SiO_2, TiO_2, ZnO, Al_2O_3 and $CaCO_3$, etc., each with various surface treatments as required. These could be incorporated into various organic polymer matrices to produce engineered composites of predetermined properties [2-7]. For example, alumina and silica having high hardnesses, are commonly used as the relevant particles to increase scratch and abrasion resistances of various coatings [8].

The effect of soft segment content and its molecular weight was studied. The results showed that the degree of cross-linking and tensile properties depends mainly on the ratio of the soft to hard segment, and is unaffected by variations in the sequence length of the soft segment at a given soft segment content [9,10].

In most composite processing techniques, the resin in liquid form must penetrate into a fiber assembly in order to produce a sound material [11-17].

Especially, if the filled inorganic material has either dielectric and/or piezoelectric properties and can transform mechanical energy into electric energy, then into heat energy and release from system, it can contribute excess damping ability to IPNs besides frictional damping ability between organic and inorganic phase, so materials with better damping properties can thus obtained effectively

This study aimed to use inorganic powder in the production of cross-linked polyurethane composite, as filler. In this study, the focus was also on the PU matrix produced from polyester diol end caped with various chain extenders and diphenylmethane diisocyanate (MDI).

Experimental part

Materials

All chemicals used in this study are listed in table 1 and were used as received from the suppliers unless otherwise

Designation	Mol. Wt.	Melting point °C	Boiling point. °C	Density g/cm^3	Refract. index	Obs.
1,5 pentane diol (PD)	104.15		242	0.994		
1,6 hexane diol (HD)	118,1	38	250	—		
glycerin	92,9		182	1,261	1.4740	
4,4' diphenyl methane diisocyanate (MDI)	250,14	42-44	152-156/ 0,2-0,3mm	—	—	
Polyethylene adipate (PEA)	2000	—	—	1.175	—	C_{OH}=56 mg KOH/g

Table 1
MATERIALS USED TO OBTAIN POLYURETHANE ELASTOMERS OF THE COMPOSITE SAMPLES FOR PASSIVE ISOLATION

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Table 2
FORMULATION AND HARDNESS OF THE OBTAINED POLYURETHANE COMPOSITES

Nr	Designation samples	Rate Polyester/ Diisocyanate/ Chain extenders	Diisocyanate	Chain extenders Glycerin +	Filler %	Hardness Shore A
1	PUP_g 1	1:3:2	MDI	PD	Graphite 1%	68
2	PUP_g 5	1:3:2	MDI	PD	Graphite 5%	70
3	PUP_g 10	1:3:2	MDI	PD	Graphite 10%	74
4	PUP_c 1	1:3:2	MDI	PD	$Ca\ CO_3$ 1%	64
5	PUP_c 5	1:3:2	MDI	PD	$Ca\ CO_3$ 5%	65
6	PUP_c 10	1:3:2	MDI	PD	$Ca\ CO_3$ 10%	71
7	PUH_t 1	1:3:2	MDI	HD	Talc powder 1%	67
8	PUH_t 5	1:3:2	MDI	HD	Talc powder 5%	70
9	PUH_t 10	1:3:2	MDI	HD	Talc powder 10%	73
10	PUH_p 1	1:3:2	MDI	HD	Polyamide 1%	82
11	PUH_p 5	1:3:2	MDI	HD	Polyamide 5%	85
12	PUH_p 10	1:3:2	MDI	HD	Polyamide 10%	89

stated. Polyester and chain extenders were checked for the content of moisture and, if necessary, dried under a vacuum until the content of water was below 0.03%.

Preparation of polyurethanes

Typically, synthesis of PU was done by the following procedure, and the moles of the added reagents for the various PU were shown in table 2.

The synthesis of PUs was performed in a one liter glass reactor at normal pressure, under nitrogen blanket and vigorous agitation. The NCO/OH ratio of all formulations was 1.03-1.05. The PU composite was produced by a prepolymer process. In the case of the prepolymer procedure, filler was first mixed with polyester, followed by the addition of MDI at 80°C for 1 h to yield a prepolymer that was mixed in the second step with a chain extender to 90°C for 10 min. The resulting material was poured into a mold and left to cure at 100°C for 20 h, post-curing TPU at laboratory temperature for 7 days. Under these conditions the addition of catalyst was not necessary. The polyurethane sheets thus prepared were used for the determination of mechanical and physical properties and for the resistance study.

Samples were produced by molding, using cross-linked polyurethane resins doped with talc powder having ~ 0.05 mm sized particles, and composites containing ~ 0.07 mm sized graphite and $CaCO_3$ grains.

Infrared Spectroscopy (FT-IR) was done using a VERTEX 7 Instruments equipped with a Golden Gate single reflection ATR accessory, spectrum range was 600-4000 cm^{-1}.

The *thermal stability* of polyurethanes was performed on a DERIVATOGRAF Q-1500 D apparatus (Hungary). The rate of the TGA scans was 10°C /min in air atmosphere. The initial weight of the samples was about 50 mg and the temperature range 30-700°C.

Mechanical Property. The PU block copolymers were molded into tensile specimens with 6 mm thickness depending on the hard/soft segment content, and the prepared PU specimens were used for tensile test. A tensile test was performed using a TIRA test 2161 apparatus, from Germany, with a dumbbell-type specimen. Measurements were run at an extension rate of 10 mm/min, at 25°C. At least five specimens were tested, and the average was plotted.

Hardness was measured on Instron Shore Durometer using scale-A.

Results and Discussion

IR Spectroscopy

FTIR spectra of the raw materials are shown in figure 1. The absorption of -NCO groups at 2273 cm^{-1} in IR spectra of PU was not observed in the resulting composite sheets, indicating the absence of free -NCO groups. Comparing with the broad absorption of -OH stretching vibration in the range from about 3350 to 3450cm^{-1} for the raw materials, the peaks for the sheets narrowed and shifted to higher than 3400 cm^{-1}, implying the contribution of –NH stretching vibration from PU. It was noted that the peaks at 1746 cm^{-1} (stretching vibration of urethane carbonyl groups), [18] 1640 cm^{-1} (Amide I), and 1560 cm^{-1} (Amide II) occurred in PU, displaying the formation of urethane bonds in the sheets.

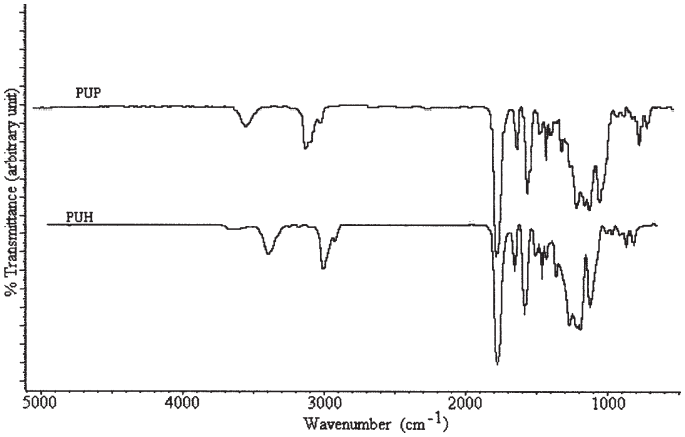

Fig. 1. IR spectra of cross-linked polyurethane samples synthesized with PD and HD

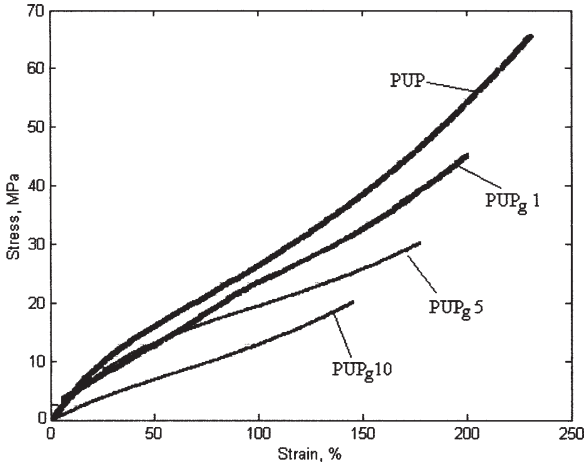

Fig. 2. Stress-strain curves of polyurethane prepared with PD and graphite

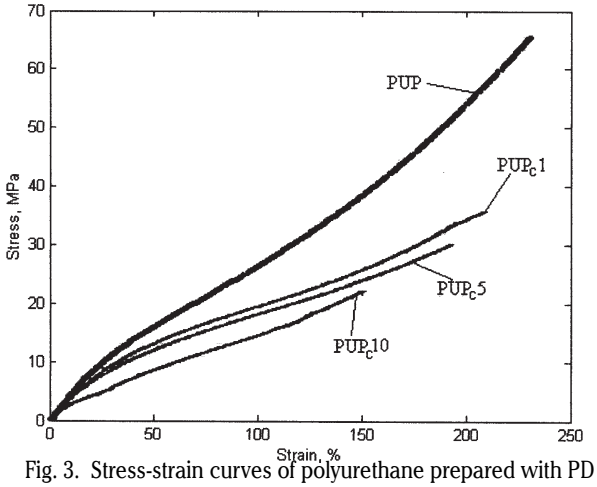

Fig. 3. Stress-strain curves of polyurethane prepared with PD and Ca CO_3

Mechanical properties

Table 2 shows the results of the hardness tests on the Shore A scale for composite samples measured at five different points in each sample. As can be seen, the hardness of the cross-linked resin containing inorganic filler in varying mass proportions was similar to that of the polyurethane resin containing polyamide filler what was higher with increase of amount filler.

Urethanes composites are of interest in part because of the wide range of properties available by appropriately selecting raw materials. Figure 2-4 presents the stress-strain curves of PU/inorganic filler blends containing 1-10 wt % filler, in which the crosslink density was constant.

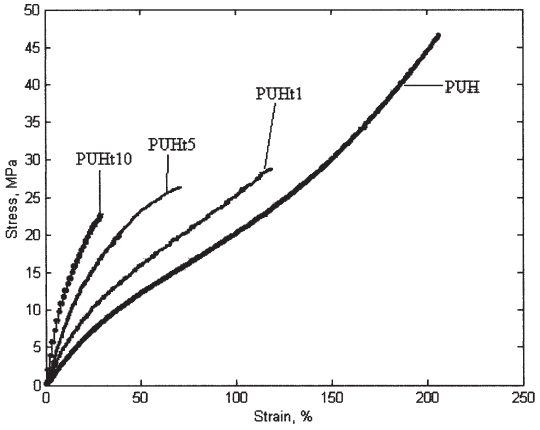

Fig. 4. Stress-strain curves of polyurethane prepared with HD and talc powder

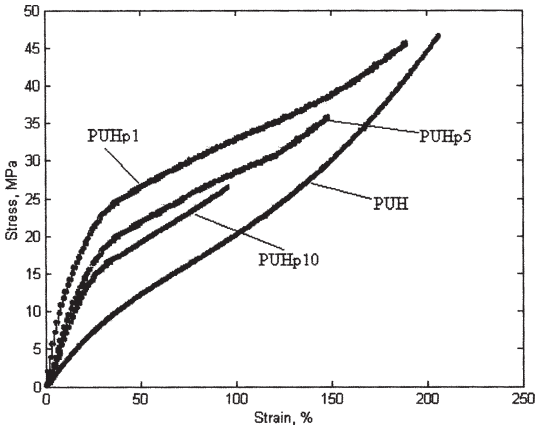

Fig. 5. Stress-strain curves of polyurethane prepared with HD and polyamide fiber

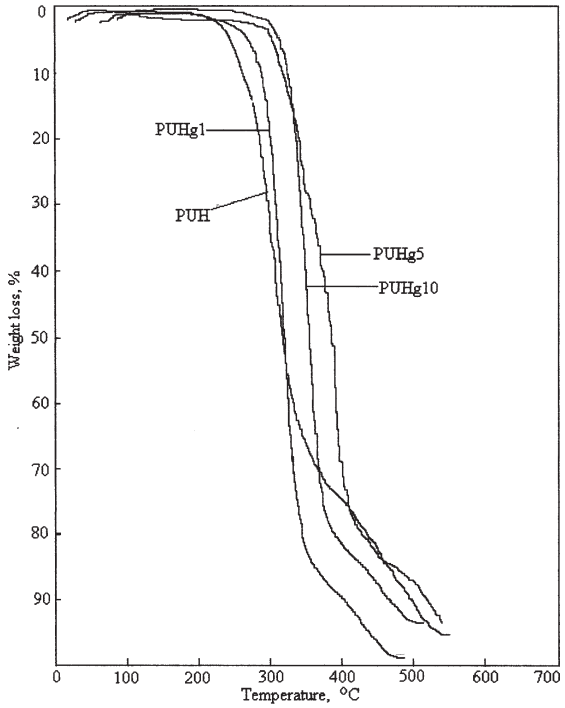

Fig. 6. TG curves of polyurethane with PD and graphite

The stiffness [modulus of elasticity] increases with filler content, filler type, and chain extender type. In all cases, mechanical properties decreased dramatically with filler content. This difference is most significant at the extremes of the composition range studied.

This factor may contribute, in part, to the large variation in mechanical properties found in the materials produced from the fillers. Instead, the results suggest that accessibility

Table 3
TENSILE PROPERTIES OF POLYURETHANE COMPOSITES OBTAINED WITH VARIOUS FILLERS AND COMPOSITIONS

Designation samples	E_1 MPa	L1 %	FR MPa	AR %	FM MPa	AM %	E MPa
PUPg 1	12.8	72	44.5	199	44.6	198	32
PUPg 5	14	61	28.7	173	28.7	173	35
PUPg 10	16	58	18	148	18.5	148	42
PUPc 1	11	75	34.6	210	35	210	29
PUPc 5	14,4	60	27	195	27.3	194	35,8
PUPc 10	15.2	43	18	149	18	149	45
PUHt 1	10	31,4	29	128,6	29	128	48,7
PUHt 5	13.2	29	26.8	78	27	78	52
PUHt 10	15	27.6	23.6	32	24	32	58
PUHp 1	20	17,7	45,8	189	46	189	72,5
PUHp 5	24	16	37	150	37	150	84
PUHp 10	27	15	35	98	35	98	96

E_1 – effective modulus to first transformation of phase; L1- elongation to first transformation of phase; FR- tensile stress at break; AR- elongation at break; FM- tensile stress at maximum; AM – elongation at maximum; E- modulus

of the interior structure of the filler wall may play a much more important role in determining composite properties.

This impact on interfacial structure and morphology would be clearly represented in ultimate properties of the composites. It should not be surprising that a strong correlation exists between filler content and the mechanical property of interest in virtually all instances.

When blended with 5–10 wt % filler, the strengths and elongation decreased, but since the moduli has improved, the toughness of the blend increased.

The effects of filler content on the tensile strength, elongation at break, and Young's modulus (*E*) of the sheets are shown in figures 2- 5, and table 3 respectively. It exhibited a decreased tensile strength and low elongation at break, implying that filler composition greatly contributed to the toughness of the composites. With an increase of filler content, the Young's modulus increased, whereas that of elongation at break and tensile strength decreased.

Composites with smaller polyamide size fiber displayed higher strength than those with inorganic filler. This is expected because smaller size fiber gives a larger surface area for the interaction with polyurethane matrix. This result is in agreement with other studies [19 – 22] where composites with smaller size fillers produced higher tensile strength than those of larger size.

Thermogravimetric analysis

Thermal degradation curves of the raw materials and the sheets are shown in figures 6 and 7. These show that, unfortunately, the variation of the proportion of filler added to the resins failed to influence the thermal characteristics. There were three distinct stages of decomposition in the curves.

The sheets and raw materials decomposed slowly in the first stage from room temperature to 300°C. In the second stage, the sheets decomposed quickly in the temperature range of 300 to 450 °C with a weight loss of 65 to 75%.

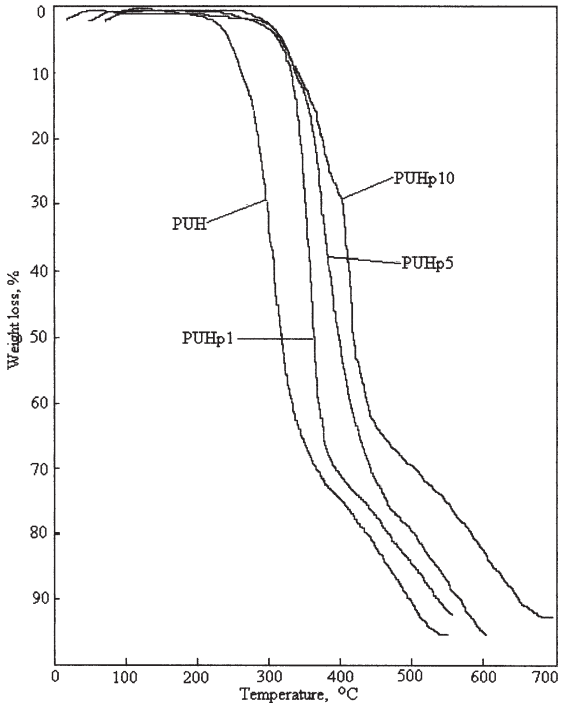

Fig. 7. TG curves of polyurethane with HD and polyamide fiber

In the former two stages, the thermal stability of composites sheets was higher than that of the raw materials. In the third stage, the weight loss of the sheets was larger than that of corresponding raw materials and increased with an increase of filler content.

The TGA curves clearly show that the cross-linked polyurethane composite exhibited enhanced thermal stability compared to bulk PU. When the filler content was increased, thermal stability enhancement increased.

Conclusions

A maximum toughness of PU composites can be achieved by introducing 10 wt % of a properly crosslinked polyurethane (having an OH mole ratio of diol to triol of 1 to 1). The toughness thus achieved is an order of magnitude higher than that of pure PU. Optimum toughness is a result of a balance between the compatibility of the cross-linking polyurethane with fillers and the stiffness of this network.

The inorganic fillers added these polyurethane resins significantly alter the thermal and mechanical properties of the composites compared to those of the pure resins. Measurements, however, reveals that the polymer's viscous elastic characteristics changed according to the mass proportion of filler, showing increased moduli of storage elasticity and loss.

The small amount of filler, can improve the damping properties without a significant sacrifice phase continuity but large amount of inorganic phase indicating large phase separation in system.

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