

# Preparation and Characterization of Polyether-Based Polyurethane Dolomite Composite

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**ABSTRACT:** A polyether polyol-based two-component polyurethane composite was prepared by a reaction of polypropylene glycol (PPG) and diethylene glycol (DEG) used as a crosslinker. The final reaction for the preparation of composite is carried out with processed polyether polyol and diphenylmethane 4,4'-diisocyanate (MDI). The physicochemical properties of processed polyether polyol have been measured, such as viscosity, moisture content, and hydroxyl value. The composite has been formed with loading of inorganic filler dolomite [ $\text{MgCa}(\text{CO}_3)_2$ ] with different filler ratios. It shows good adhesive strength and mechanical properties. Composite samples have also been studied for the effects of acids and bases, swelling in solvents,

physical and mechanical properties such as compression strength, shore hardness A and D, tensile strength, and elongation. Some electrical properties have also been studied, viz. thermal conductivity, volume resistivity, and dielectric strength. A comparison of prepared polyether-based polyurethane composite with some conventional polymeric materials suggests their suitability for various applications. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2337–2342, 2007

**Key words:** polyurethanes (PUs); diethylene glycol (DEG); physicochemical properties; mechanical properties; swelling studies

## INTRODUCTION

Polyurethanes have been found in an enormously growing range of applications, such as textiles, automobiles, thermal insulation, and electrical and electronics<sup>1,2</sup> applications. Solid polymer electrolytes and organic conducting polymers are potentially useful in all solid-state rechargeable batteries. Polyurethanes become conducting by incorporating metallic the fillers<sup>3,4</sup> of different shapes and size to a nonconducting matrix. Sacher and Delmonte<sup>5,6</sup> reported metal/polymer composite and the reaction of metal powders with organic powders. Cheradame et al.<sup>7,8</sup> investigated polyethylene oxide (PEO-urethane) system in solutions of carbonates and also observed that poly(ethylene oxide) (PEO) crosslinked with urethane yields better properties as compared with pure PEO. Further research reported<sup>9</sup> good efficiency for the PEO-urethane petroleum coke composite for electrical conducting electrodes for rechargeable batteries. Several other techniques have also been used for the processing of composites.<sup>10</sup> A survey of the literature showed that polyurethanes (PUs) have excellent electrical insulation, thermal insulation, and mechanical properties; therefore, they have many versatile appli-

cations in various forms, such as foams, elastomers, cellular materials, coatings adhesive sealants, electrical cable jointing, and termination.

Linear polyurethane block copolymers are normally a condensation product of three monomers an oligomeric diol, typically a dihydroxy-terminated polyether or polyester with an average molecular weight (500–3000) and diisocyanate, i.e., generally aromatic and a low-molecular-weight aliphatic diol chain extender.<sup>1</sup> These are the copolymers that consist of hard and soft segment units. Because of incompatibility between the two structural units, it is generally, agreed that the polymer formed undergo microphase separation resulting in hard segments-rich hard domains, soft segment-rich soft matrix. Since the glass transition temperature ( $T_g$ ) of soft segments and hard segments are below and higher than the usual service temperature respectively. In thermosetting polyurethane, the properties during curing process as a function of humidity and temperature and these changes have been investigated by thermal analysis and other techniques,<sup>11,12</sup> viz. spectroscopy, dynamic mechanical analysis.<sup>12,13</sup> Several other processes have been suggested to occur concurrently I as a function of temperature. Srivastva et al.<sup>14</sup> conducted a study of the gelation of a metal-filled castor oil-based polyurethane system at different temperatures. Gelation studies can be used to provide information during the process of controlling the reaction parameters and thus help to achieve quality of polymeric products.

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Mabuse et al.<sup>15</sup> observed that two-component polyurethane has special electrical properties in a specified ratio of metal oxide/salts. Albinssan et al.<sup>16</sup> studied the ionic conductivity in polypropylene glycol complex with lithium and sodium triphosphate. Anupama et al.<sup>17</sup> studied the metal-filled castor oil-based interpenetrating networks polyurethane system. Hence, the literature surveyed on applications of polyurethane system suggested the importance of their diverse applications of polyurethanes. In the present work, we emphasize the need to keep the system as simple as possible for the formation and characterization of a polyether-based polyurethane composite with the observed properties in this study; we explore the possibility of the prepared polyurethane composite as engineering material for the devices.

### MATERIALS USED

The polyurethane composite in the present study was prepared using the materials polypropylene glycol (PPG) ( $M_r$  1000), diethylene glycol (DEG)  $M_r$  106 (Fine Chemicals Ltd., Bombay, India), diphenylmethane 4,4'-diisocyanate (MDI) (Dow Chemical), silicone defoamer (Metro Ark, Calcutta, India), Pb-naphthenate (Aryavart Chemicals Ltd., Navi Mumbai, Maharashtra, India), and dry dolomite (400 mesh; Mewar Microns, Udaipur, Rajasthan, India).

### EXPERIMENTAL

Physicochemical properties of polyether polyol, such as viscosity, hydroxyl value, and moisture content, have been measured. Viscosity was measured by (Brookfield, model DV II Rheometer, USA) at 25°C and moisture content was simply determined by the oven heating method, and the hydroxyl value was measured by the method reported.<sup>18</sup>

#### Methodology of composite formation

The formation of two-component polyether-based polyurethane composite was carried out in two steps:

#### Step 1: Processing of polyol

In the first step, the reaction of polyol (PPG) was carried out in a simple reaction vessel. To a 500-mL three-necked flask equipped with stirrer, reflex condenser, thermometer, and nitrogen inlet was added 0.30 mol (w/w) polypropylene glycol and 0.15 mol (w/w) diethylene glycol. The reaction mixture was heated at  $90 \pm 5^\circ\text{C}$  for 3 h. After this processing of polypropylene glycol (PPG) and diethylene glycol (DEG), the mixture was checked for physicochemical properties. This mixture of polypropylene glycol and diethylene glycol was used as a processed polyether (polyol) for the preparation of composite. The physicochemical properties of polyol with or without filler loading are given in Table I.

#### Step 2: Processing of composite

In the second step of the experiment, component A was formulated from processed polyether polyol of step 1 for the formation of a polyurethane composite with various concentrations of inorganic filler (dolomite) loading. Before the addition, the filler dolomite was made moisture free. Component A is formulated by taking reaction ingredients parts by weight (pbw) as shown in Table II.

All the ingredients listed in Table II were mixed thoroughly for the formulation of component A. Component A was then allowed to react with component B diphenylmethane 4,4'-diisocyanate (MDI) in the corresponding ratio (1 : 1) of NCO/OH and again components A and B were mixed thoroughly. Moisture-free white paraffin wax was used as a demolding agent, and the mixture was then cast into a mold under hydraulic pressure of  $\sim 50$  lb to obtain a final polyurethane dolomite blend composite. As a precaution, mixing and casting should be complete within 20–25 min at 25°C; otherwise, after this reaction, the mixture will begin to become viscous/gelled, leading to a curing process. The molded composite samples after 6 h were demolded and placed at 70°C to post-cure for a further 4 h. The accuracy of the measurement was about  $\pm 5\%$ .

TABLE I  
Physico-chemical properties of cross-linked polyol measured with or without filler loading at 25°C

Polyol (Component A without filler)	Viscosity (cps)	Moisture content % (w/w)	OH value (mg KOH/g)
1.	1800–2000	0.22 $\pm$ 0.01	175 $\pm$ 10
2.	1820–2000	0.20 $\pm$ 0.01	176 $\pm$ 10
3.	1870–2000	0.21 $\pm$ 0.01	180 $\pm$ 10
4.	1900–2000	0.19 $\pm$ 0.01	182 $\pm$ 10
<b>Component 'A' with filler</b>			
10%	2400–2600	0.22 $\pm$ 0.01	182 $\pm$ 10
20%	2800–3000	0.24 $\pm$ 0.01	178 $\pm$ 10
30%	5200–5480	0.26 $\pm$ 0.01	178 $\pm$ 10
45%	Highly viscous paste	0.24 $\pm$ 0.01	175 $\pm$ 10

**TABLE II**  
Physical properties and swelling effect on two components polyurethane dolomite composite in organic solvent and water at 25° C

Sample No.	Composition of polyol and filler %(w/w)	Shore Hardness A and D		Swelling (%)				
				Methyl chloride	Toluene	MEK	Water	
1.	A	100 + 0	45	65	60.0	52.0	48.0	1.0
	B	100 + 0	44	66	60.2	51.8	47.4	1.0
2.	A	90 + 10	50	60	80.0	60.0	67.0	1.0
	B	90 + 10	51	61	78.6	61.2	67.0	1.0
3.	A	80 + 20	55	75	115.0	84.0	90.0	1.1
	B	80 + 20	55	75	114.0	84.0	89.0	1.1
4.	A	70 + 30	60	85	135.0	108.0	110.0	1.1
	B	70 + 30	58	85	135.4	107.3	111.0	1.1
5.	A	55 + 45	65	90	145.0	125.0	118.0	1.2
	B	55 + 45	68	92	146.0	124.8	117.8	1.2

The reaction mechanisms of the polyurethane system exhibit a complex nature; simultaneously, various reactions occur, such as urea formation, allophanate, and biuret formation. Thermosetting polymers are formed via a crosslinking mechanism. Crosslinking and chain extension provide a mechanism of structuring for the thermosetting macromolecules.

## RESULTS AND DISCUSSION

### Characterization of composite

Characterization of the two-component polyether-based polyurethane composite is carried out with doubled samples made of the same percentage w/w dolomite filler loading to obtain the consistency of the results. The measured properties of the samples are shown in both tabular and graphic form in the present work. Changes in the properties with variation of the loading ratio of filler on the prepared two-component polyurethane composite have been studied. The stability of the chemicals of composite samples has

also been studied; the samples were weighed and allowed to remain in different concentrations of HCl, HNO<sub>3</sub>, and NaOH in an aqueous solution for 24 h at room temperature. After 24 h, these samples of composite were again weighed and, depending on their initial and final weight, the percentage absorption was calculated. Chemical absorption in dilute acid solution and solvents (e.g., ethyl alcohol and kerosene oil) has been found to be much lower, but a significant change in 5% aqueous NaOH solution is observed in Table III. Surface conditions of composite samples were also noted and the physical properties such as shore hardness A and D measured and are given in Table III.

### Swelling studies

A swelling study of two-component polyurethane composite samples has also been studied by the method of Sperling and Mihalakis,<sup>19</sup> and the percentage of swelling was calculated for each composite sample as

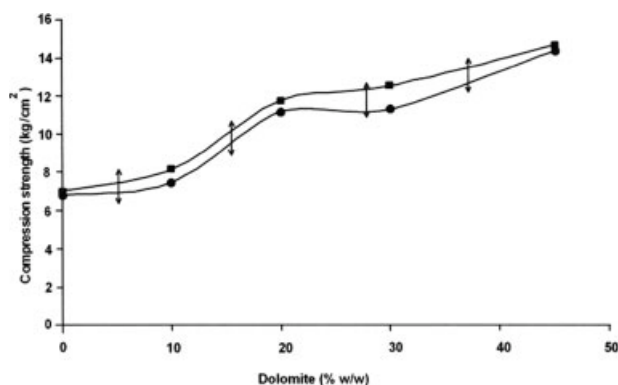
$$\text{Swelling}(\%) = \frac{(\text{weight of swollen sample} - \text{weight of dry sample}) \times 100}{\text{weight of dry sample}}$$

The swellings of composite samples have been studied in solvents (e.g., methylene chloride, methyl ethyl ketone (MEK), toluene, and water). The results are given in Table III. It is clear from the data obtained that swelling was higher in methylene chloride. The results also show the swelling order as methylene chloride > toluene > MEK > water. It was also observed that the low filler loading composite exhibits less swelling as compared with the high filler loading composite. The author assumes that in a higher filler loading composite, the flow penetration of the solvent to the polymer matrix surface is greater; this is exhibited somewhat more easily due to the

**TABLE III**  
Effect of chemicals and their absorption on two components polyurethane dolomite composite at 25° C

Concentration	Observation	Absorption % (w/w)*
5% HCl	No effect	0.020
5% H <sub>2</sub> SO <sub>4</sub>	No effect	0.018
5% HNO <sub>3</sub>	No effect	0.018
2.5% NaOH	No effect	0.024
5% NaOH	Color fade	0.200
Ethyl alcohol	No effect	0.010
Kerosene oil	No effect	0.010

\*Measurements taken after 24 h.



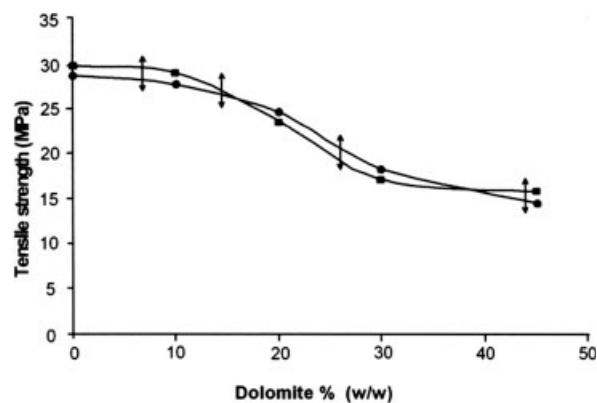
**Figure 1** Effect of dolomite loading on compression strength of two-component polyurethane composite. Sample A,  $\blacklozenge$ ; sample B,  $\blacksquare$ .

weakened bonding of the filler–polymer matrix. In the case of a low filler loading composite, the solvent flow penetration to the surface of composite may be somewhat difficult or less (strong filler–polymer bonding), hence it exhibits less penetration system of solvents flow on composite surface, thereby decreasing its swellability with the higher filler loading polyurethane composite. The composite displays resistance to water, which is proved as well by some swelling in water.

### Mechanical properties

Mechanical properties of the prepared two-component polyether-based polyurethane dolomite composite were measured with the Instron Universal Testing Machine Series 4466 (load capacity 10 KN). Appropriately sized samples of composite as per ISO/DIS 527 type I (tensile test for polymeric materials) were used to test tensile strength with the speed of testing machine crossheads adjusted at 20 mm/min. The samples of composite have been prepared in duplicate with the same filler loading. Figure 1 suggests that filler loading increases the compression strength up to a limit of filler loading, while at higher filler loading it has observed that composite samples show deformation. Thus, the composite displays better compression stability at lower filler loading, keeping mechanical properties within the range of workable conditions.

The effects of filler loading ratios on compression, tensile strength, and percentage elongation of composites are presented in Figures 1–3; it is shown that there are changes in tensile strength and elongation on increasing filler loading. It is also suggested that above 45% (w/w) filler loading, the mechanical stability of composite decreases. The composite at lower filler loading, i.e., up to 10–25% (w/w), exhibits higher tensile strength and elongation. This can also be



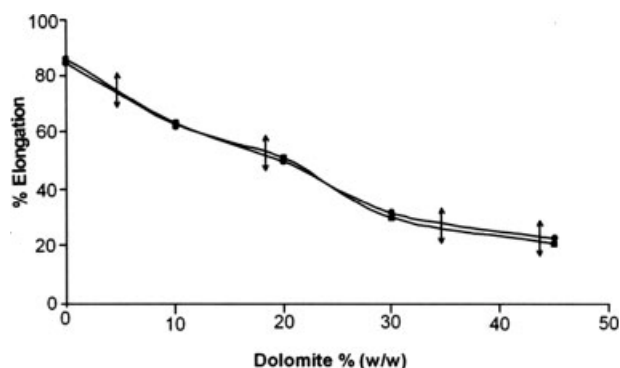
**Figure 2** Effect of dolomite loading on tensile strength of two-component polyurethane composite. Sample A,  $\blacklozenge$ ; sample B,  $\blacksquare$ .

explained by considering the fact that soft and elastomeric polyol moieties have much higher free volume, resulting in ample scope for threading of polyol with filler dolomite networks in the case of partially crosslinking where the chains are linear and have greater mobility. In contrast, in the case of the fully crosslinked polyurethane composite, the higher degree of crosslinking lowers the statistical probability of threading, thereby precluding the reinforcement of interpenetration, although it has also been observed that the prepared two-component polyurethane composite appears to have good adhesion with wood, cement, mild steel, and aluminum.

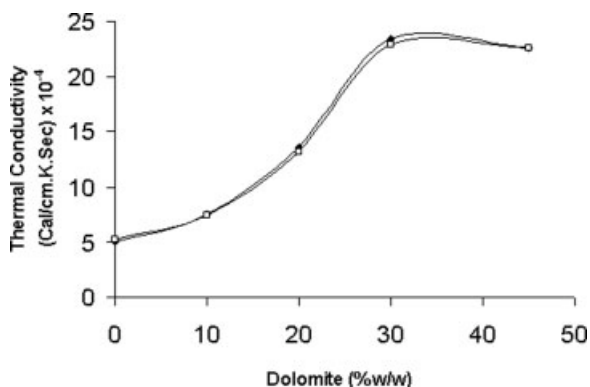
### Electrical properties

#### Thermal conductivity

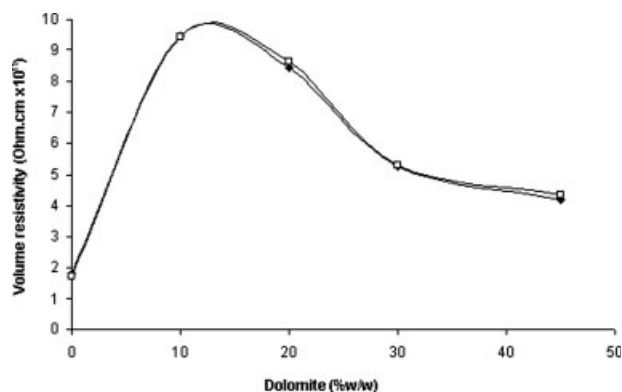
Thermal conductivity ( $\lambda$ ) of prepared composite samples with different dolomite loading, such as 0%, 10%, 20%, 30%, and 45% w/w, has been measured by the two-slab guarded hot plate method (Montac Instruments, Chandigarh, India). Appropriately sized



**Figure 3** Effect of dolomite loading on elongation of two-component polyurethane composite. Sample A,  $\blacklozenge$ ; sample B,  $\blacksquare$ .



**Figure 4** Thermal conductivity of two-component polyurethane dolomite composite with different filler loading. Sample A,  $\blacklozenge$ ; sample B,  $\blacksquare$ .



**Figure 5** Volume resistivity of two-component polyurethane dolomite composite with different filler loading. Sample A,  $\blacklozenge$ ; sample B,  $\blacksquare$ .

samples with a known area and thickness were placed between the source and sink, plates of instrument, maintained at a constant temperature. We have applied voltage of 7.16 volts and a current of 6.2 amperes, to test the samples. Depending on the temperature of source and sink, plates of instrument thermal conductivity ( $\lambda$ ) was calculated using the following equation:

$$\text{Thermal Conductivity}(\lambda) = \frac{VIL}{A(T_{SO} - T_{SI})}$$

where L is the thickness of sample; A is the cross-sectional area of the sample;  $T_{SO}$ ,  $T_{SI}$  are the temperature of source and sink, respectively; V is the voltage applied; and I is the current (in Amperes).

Figure 4 shows the relationship between thermal conductivity ( $\lambda$ ) and filler loading of polyurethane prepared composite. It shows that up to 30% (w/w) filler loading thermal conductivity ( $\lambda$ ) increases; above this, thermal conductivity remains almost constant, suggesting that filler loading up to 30% (w/w) yields an optimized value of thermal conductivity, above which there is no major use of the composite in view of thermal conductivity. As Figure 2 also suggests, above 30% (w/w) or higher filler loading, the composite does not promise of good mechanical properties. Hence, thermal conductivity of prepared polyurethane composite can also be affected on higher filler loading due to the formation of weak bonds between filler and polymer matrix. The accuracy in the measurements of thermal conductivity was  $\pm 5\%$ .

**Volume resistivity**

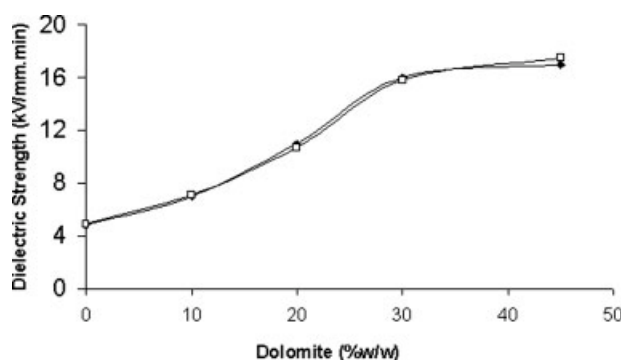
Volume resistivities ( $\rho$ ) of the composite samples have been measured by Keithley Measuring DC source (model 237, Germany) by applying 1000 volts. The samples were prepared according to the shape of the electrodes of the instrument by cutting in a 5-cm

diameter sphere of 0.2-cm thickness; the volume resistivities ( $\rho$ ) were measured using the equation:

$$\rho = 22.9 V/t_c I,$$

where V is the voltage applied; I is the current (in amperes); and  $t_c$  is the thickness of the sample.

Volume resistivities of the dolomite blend polyurethane composite samples are presented in Figure 5 (samples A and B), which show that the volume resistivity of composite decreases as the dolomite concentration increases, but at a higher concentration, i.e., 30–45% (w/w), there is no major change in volume resistivity. It also explains the nature of polymer filler matrix and the effect of material strength on the resistivity. We assume that the decrease in volume resistivity is due to the ionic nature of filler (dolomite). Dielectric strength has also been measured at 22°C and 80°C. Figure 6 demonstrates the effect of filler loading on the dielectric strength of the composite, showing that the trend at a lower range, i.e., 10–30% (w/w) filler loading, increases the dielectric strength. This also suggests that the higher filler containing composite decreases the dielectric properties due to



**Figure 6** Dielectric strength of two-component polyurethane composite with different dolomite loading. Sample A,  $\blacklozenge$ ; sample B,  $\blacksquare$ .

weak bonding of the polymeric matrix or by breakdown of the voltage process, which may occur at high filler loading. In addition to the electric properties of polymeric materials, it has already been reported that no polymeric material ensures a perfect insulator. Various factors, such as water treeing, thermal breakdown, physical defects, voids, and filler impurities, can affect the properties of composite. Conclusively, all these factors influence the structure of polymeric materials. It has also been observed that the prepared polyurethane composite displays an elastomeric nature with low filler loading. The elastomeric nature results from the two-phase morphology of the hard and soft segments. The hard and soft segments depend on crosslinking and chemical reaction processes. The primary intermolecular interaction that occurs in pure urethane is hydrogen bonding between the urethane C=O group of one unit with the urethane N—H group of another that possesses a strictly highly ordered structure. This highly ordered structure composite enhances molecular packing and the maximum degree of H-bonding between the urea >NH and >C=O groups. This theoretical interpretation leads to the conclusion that the properties of polymeric material also depend on the molecular weight distribution as well as the orientations of the hard and soft segments. Thus, the overall conclusion is that not only the concentration of filler loading of dolomite, but also its morphology, structural effects, strain, and time, are the parameters that influence the resistivity.

### CONCLUSIONS

The present study establishes that the prepared two-component polyurethane composite exhibits good thermal stability at the usual service temperature. Chemical absorption studies have also shown that samples of prepared polyurethane composite are stable in dilute acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, ethyl alcohol, and kerosene oil, but that they deteriorate in concentrated acid and base solutions. Swelling studies also confirm the good stability of composite in water. Thermal conductivity increases with increasing filler up to 30% (w/w) loading. All the above facts prove that this material has promising suitability for cable jointing, electrical insulation, and electronic potting compounds. Stress-strain behavior also confirms

that ductility of composite material was due to elastomeric property of base matrix. These composite material samples with dolomite filler have sufficient mechanical strengths and can be used as engineering materials.

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