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New Silicone Grafted Copoly(ether imide) from 4,4'-(hexafluoro-isopropylidene)diphthalic Anhydride

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A new copoly(ether imide) **1a** was synthesized from 4,4'-(hexafluoro-isopropylidene)diphthalic anhydride (6FDA) and 4,4'-bis [3'-trifluoromethyl-p-aminobiphenyl ether)biphenyl (TFBB) with 20 wt% loading of 3,5-diaminobenzoate terminated polydimethylsiloxane (DBPDMS) by solution imidization technique. The copoly(ether imide) showed a glass transition temperature of 272°C by differential scanning calorimetry and of 300°C by dynamic mechanical analysis, respectively. The polymer showed thermal stability up to 371°C for 5% wt loss in synthetic air. Dynamic mechanical analysis showed storage modulus as high as 1.62 GPa at 40°C. In the DMA plot a distinct sub T_g relaxation was observed at 130°C. The copolyimide formed tough transparent film, with tensile strength up to 47 MPa, a modulus of elasticity up to 1.83 GPa and elongation at break up to 65%. Thermal, mechanical and surface properties of the copoly(ether imide) have been evaluated and compared with the already reported analogous random copoly(ether imide) containing siloxane unit in the main chain and with the homopolyimide without siloxane unit.

Keywords: Fluorinated polyimides, thermal properties, mechanical properties

1 Introduction

Polyimides (PI) possess excellent thermal, mechanical, and electrical properties and thus have found immense applications in many technologies ranging from microelectronics to high temperature matrices and adhesives to gas separation membranes (1–4). Fluorination provides unique properties to PIs, such as reduction of dielectric constants and refractive indices, improvement of the transparency, increase in free volume, decrease of water absorption, increase in solubility, gas permeability, radiation-durability and thermal expansion coefficients (5,6).

It is well known that incorporation of fluorine in the form of pendent trifluoromethyl (-CF₃) groups enhances fractional free volume, which in turn limits chain packing density and hence increases solubility and processability. An additional positive effect of incorporating -CF₃ is reduced moisture absorption due to non-polar character of the fluorocarbon group. In electronic packaging, low dielectric constant materials minimize cross talk between the

inter-connects and maximize signal propagation speed in devices. Hence incorporation of fluorine in the form of -CF₃ groups decreases the dielectric constant due to small dipole and the low polarizability of the C-F bond (7–9). Additionally, solubility is also enhanced by incorporation of kinked linkage such as ether group (-O-) in the polyimide backbone which disrupts the planarity.

The polysiloxane component imparts a number of beneficial properties to the polymeric system into which it is co-reacted, including enhanced solubility, reduced water absorption and gas permeability, good thermal and ultraviolet stability, resistance to degradation in aggressive oxygen environments, better impact resistance and modified surface properties (10,11). These particular advantages render polysiloxane – modified polyimides attractive for aerospace, microelectronics, gas separation and other high performance applications. Connection between siloxane segments and the polyimide is often achieved through aminopropyl silane linkers. The hydrophobic nature of the siloxane segments within polyimides further reduces water uptake and dielectric constant (12).

In the present work both, -CF₃ units and grafted silicon chains, are incorporated into homopolyimides reported earlier (9). The diamine monomer 4,4'-bis (3'-trifluoromethyl-p-aminobiphenyl ether)biphenyl (TFBB) and the dianhydride 6FDA were coupled with

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3, 5-diaminobenzoate terminated polydimethylsiloxane (DBPDMS) (13) for the synthesis of fluorinated silicone grafted copolyimide. Structure–property relationship, solubility, spectroscopic characteristics as well as thermal, mechanical and surface properties has been reported in this investigation.

2 Experimental

2.1 Methods

Carbon, hydrogen and nitrogen content of the compounds were analyzed by pyrolysis method. IR spectra of the polymer films were recorded with a Vertex 80V FTIR spectrophotometer instrument (Germany). $^1\text{H-NMR}$ spectra were recorded on a Bruker DRX 500 spectrometer using $\text{CDCl}_3/\text{TFA-d}$ (4:1 v/v) as solvent. The spectra were measured immediately after dissolving the polymer because the polydimethylsiloxane chain decomposes under acidic conditions. The spectra were referenced on residual chloroform ($\delta(^1\text{H}) = 7.26$ ppm). Gel permeation chromatography was performed in THF with a PL MIXED-C column (pore size $5\ \mu\text{m}$) from Polymer Laboratories at a flow rate of $1.0\ \text{mL min}^{-1}$ with linear polystyrene as a standard, using MALLS Detector from Wyatt Technologies. HPLC-Pump 64 from Knauer was used for this investigation. THF was used as the eluent at a flow rate of $1.0\ \text{ml/min}$ and calibration was carried out using low polydispersity poly (styrene) standards. DSC measurements were made on a DSC Q 1000 of TA Instruments at a scan rate of $\pm 20\ \text{K/min}$ under nitrogen. Glass transition temperature (T_g) was determined from the 2nd heating run using the half step method. Dynamic mechanical thermal analysis was performed on an Eplexor from GABO, Ahlden (Germany) under tension mode on thin film samples at a heating rate of $5\ \text{K/min}$ and a frequency of $10\ \text{Hz}$. Thermal decomposition behaviour of these polymers was investigated on a TGA Q 5000 of TA Instruments at a heating rate of $10\ \text{K/min}$ under air. Mechanical properties such as tensile strength and elongation at break of the thin polymer film ($30 \times 0.1\ \text{mm}$) was elongated at room temperature on a Hounsfield (UK) H10KS-0547 instrument under strain rate of $5\%/min$ of the sample length. Water contact angle of the flat films were measured using an OM40 micro instrument from Dataphysics, Filderstadt, Germany. The volume of the water droplets used for measurements was $2\ \mu\text{L}$.

2.2 Starting Materials

4,4'-(Hexafluoro-isopropylidene)diphthalic anhydride (6FDA) was purchased from Aldrich (USA) and was heated at 120°C overnight prior to use. The diamine monomer namely 3,5-diaminobenzoate terminated polydimethylsiloxane (DBPDMS, $n = 60$) was prepared

from the starting compound, monohydroxy terminated polydimethylsiloxane (average $M_n \sim 4670$) purchased from Aldrich, USA using the same protocol as reported in a previous article (13). The diamine monomer 4,4'-bis(3''-trifluoromethyl-p-aminobiphenyl ether) biphenyl (TFBB) used in this investigation was prepared using the procedure reported in our previous article (9). 1,2-Dichlorobenzene (ODCB) (Aldrich, USA) was used as received for the synthesis of the co-polyimide. Methanol and dichloromethane (DCM) were purchased and were used as received.

2.3 Polymerization

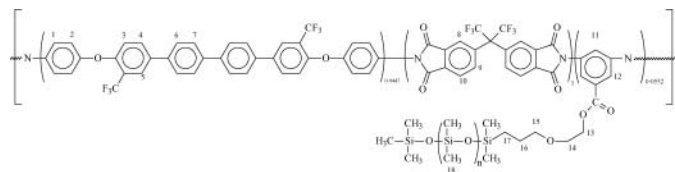
The polymerization reaction was conducted by the reaction of 6FDA with two different diamines in a random fashion. The reactions were conducted under constant flow of nitrogen. The polymerization procedure is as follows.

A $50\ \text{mL}$ three-necked round-bottomed flask equipped with nitrogen inlet, a magnetic stirrer and Dean-Stark trap fitted with a condenser was charged with $0.6675\ \text{g}$ ($1.50\ \text{mmol}$) 6FDA, $0.9322\ \text{g}$ ($1.419\ \text{mmol}$) of TFBB, $0.40\ \text{g}$ ($0.08\ \text{mmol}$) DBPDMS and $20\ \text{mL}$ of 1,2-dichlorobenzene. The reactions were carried out under constant stirring and nitrogen flow. The temperature of the reaction medium was raised slowly from room temperature to 180°C . During the course of reaction, the solution was observed to turn viscous. The reaction was continued for $6\ \text{h}$ at 180°C . The resulting viscous polymeric solution was cooled to room temperature and was precipitated from $500\ \text{mL}$ methanol. The fibrous product obtained was dried and dissolved in $20\ \text{mL}$ dichloromethane and re-precipitated from methanol. The products were dried at 120°C for $5\ \text{h}$ under vacuum and were used for further analysis.

Polymer film was prepared from a $15\ \text{wt}\%$ polymer solution in DCM. The polymer solution was poured in a flat bottom Petri dish to obtain polymer film. The Petri dish was covered and the solvent was allowed to evaporate at a controlled rate at 30°C overnight. Finally, the Petri dish was kept in a vacuum oven; the temperature of the oven was slowly raised to 120°C and kept under continuous vacuum for $5\text{--}6\ \text{h}$ to remove any trace of solvent. The Petri dish was placed in boiling water to remove the film.

2.4 Copolyimide 1a

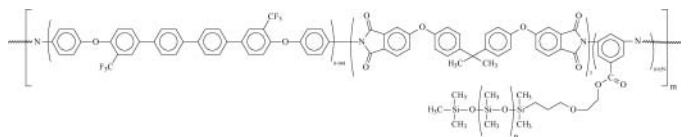
Elemental analysis for: $(\text{C}_{62.63}\text{H}_{48.55}\text{O}_{9.42}\text{F}_{5.66}\text{N}_2\text{Si}_{3.42})_n$ ($1184\ \text{gmol}^{-1}$)_n: C, 63.54%; H, 4.13%; N, 2.36%; Found: C, 63.97%; H, 4.54%; N, 2.49%.



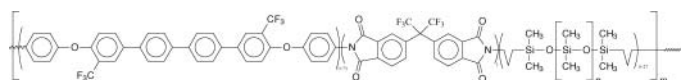
IR (KBR) (cm^{-1}): 2963 ($-\text{CH}_3$ group present in DBPDMS); 1780 and 1730 (asymmetric and symmetric $-\text{CO}-$ stretch); 1616 ($\text{C}=\text{C}$ ring stretching band); 1504 (band due to $\text{C}-\text{F}$ absorption); 1377 (asymmetric $\text{C}-\text{O}-\text{C}$ stretch); 1094 and 1020 ($\text{Si}-\text{O}-\text{Si}$ stretching); 800 ($\text{Si}-\text{C}$).

$^1\text{H-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOD}$, 4:1 v/v): 8.27(s, H^{12}), 8.11(d, H^{10}), 7.98 (s, H^5 , H^8), 7.96(d, H^9), 7.93(s, H^{11}), 7.79(d, H^4), 7.70(d, H^6), 7.59(d, H^7), 7.4(d, H^1), 7.22 (d, H^2), 7.17(d, H^3), 4.62(t, H^{13}), 3.99(t, H^{14}), 3.68(t, H^{15}), 1.67(m, H^{16}), 0.52(m, H^{17}), 0.09(s, H^{18}).

2.5 Copolyimide 1b⁽¹³⁾



2.6 Poly(imide siloxane) 1c⁽¹⁴⁾



3 Results and Discussions

The reaction scheme and polymer structure is shown in Figure 1. The polymer was prepared by conventional one pot solution imidization method. A high boiling non polar solvent is preferred; in the present synthesis 1,2-dichlorobenzene (ODCB) was used as solvent with a solid content of 20 wt%. The reactants; diamines and dianhy-

ride were mixed together, the polymerization temperature was raised to 180°C and continued for 6 h. During the course of reaction, water formed due to imidization was removed azeotropically by ODCB and accordingly the fresh solvent was added to make up for the solvent loss. After completion of 6 h at 180°C the reaction temperature was brought down to room temperature and the fibrous polymer was isolated via precipitation. Free standing film was prepared from dichloromethane solutions (15 wt%) of that polymer by first slow solvent evaporation over night at 30°C and subsequent heating to 80°C under continuous vacuum for 5–6 h to remove any trace of solvent.

For comparison, a grafted copoly(ether imide) containing 20% loading of DBPDMS (**1b**) (13) and also a poly(imide siloxane) in the main chain with same siloxane loading (**1c**) is incorporated in this study prepared as described previously (14) (structure see exp. part).

3.1 Spectroscopy

The formation of the copoly(ether imide) was confirmed by FTIR spectra which showed absorption bands at about 1780 cm^{-1} ($\text{C}=\text{O}$ asymmetric stretching), 1730 cm^{-1} ($\text{C}=\text{O}$ symmetric stretching), 1377 cm^{-1} ($\text{C}-\text{N}$ stretching) and 722 cm^{-1} ($\text{C}=\text{O}$ bending) which are characteristic of the imide rings. The strong absorption bands at 1094 , 1020 cm^{-1} ($\text{Si}-\text{O}-\text{Si}$ stretching) and 800 cm^{-1} ($\text{Si}-\text{C}$) are the characteristic for the siloxane group. The $^1\text{H-NMR}$ spectrum of the polymer confirms the expected structure.

The number average molecular weight ($M_n \sim 56,800$ g/mol) of the silicon containing graft copoly(ether imide)

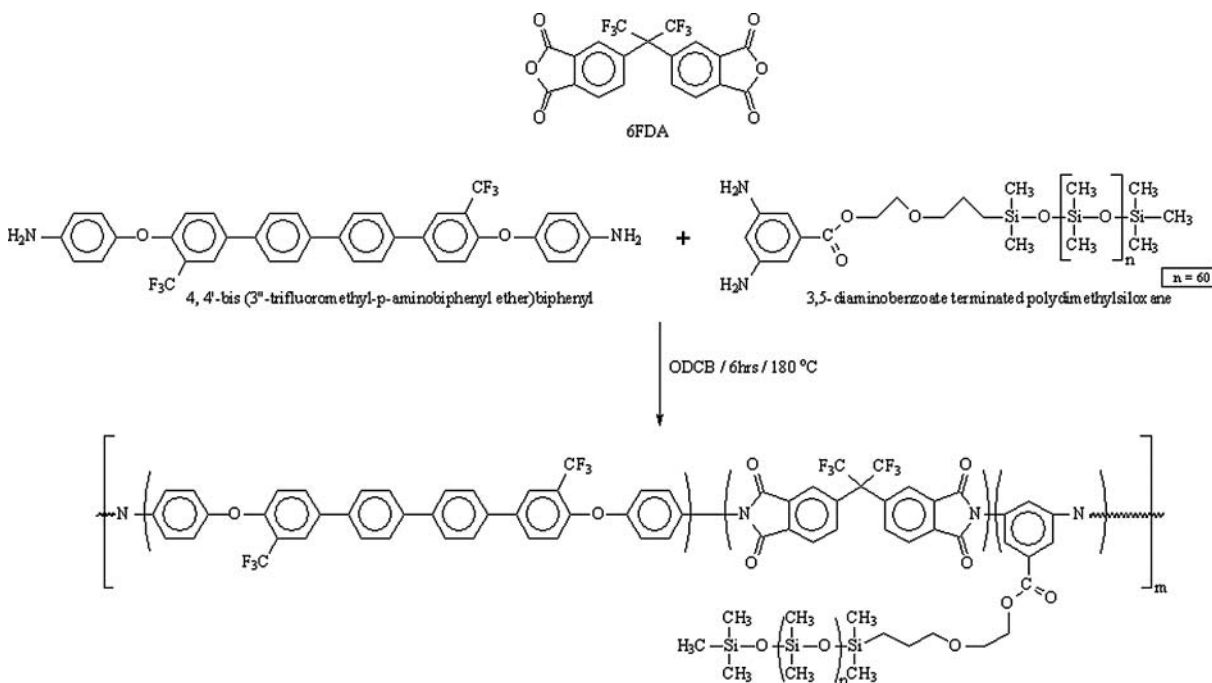


Fig. 1. Reaction scheme and structure of copoly(ether imide) 1a.

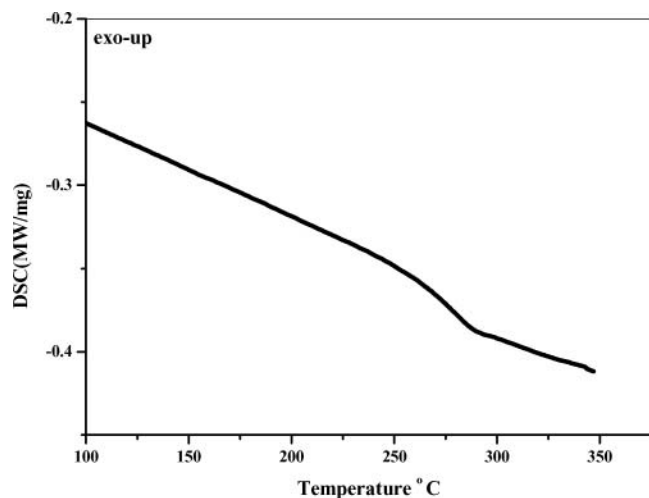


Fig. 2. DSC plot of the 1a.

as obtained by GPC indicates formation of high molar mass with a polydispersity value of 2.2.

3.2 Polymer Solubility

The solubility of the resulting copoly(ether imide) was investigated in different organic solvents. Despite of its rigid aromatic backbone, the copolyimide exhibits very good solubility (10 wt%) in common organic solvents such as N-methyl-2-pyrrolidinone (NMP), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAc), tetrahydrofuran (THF), chloroform (CHCl₃) and dichloromethane (CH₂Cl₂) due to the presence of polydimethylsiloxane unit in the side chain. The polymer was observed to be insoluble in dimethyl sulphoxide and acetone.

3.3 Glass Transition Temperature vs. Polymer Structure

DSC curve of the copoly(ether imide) is shown in Figure 2. The glass transition value is given in Table 1. Interestingly, the siloxane grafted copoly(ether imide) shows high glass transition temperature comparable to that of the homopolyimide made from 6FDA and TFBB with a T_g value of 273°C, whereas a comparable block copoly(ether imide) polymer **1b** with the siloxane moiety in the backbone has a T_g value of only 208°C (14). This finding clearly indi-

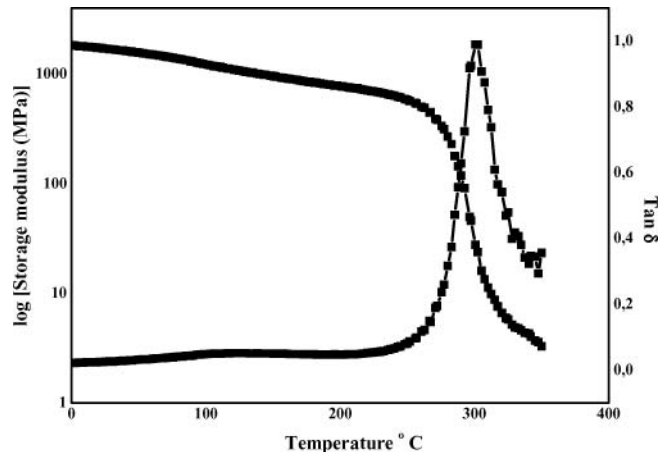


Fig. 3. DMA plot of 1a.

cates that the siloxane moiety in the main chain has a pronounced effect on lowering the glass transition temperature of the polymer in comparison to the siloxane grafted polymer for the same loading. This interesting feature can be attributed due to the fact that the silicon grafted polyimide contributes slightly or in no way to the flexibility of the polyimide chain as that observed for the linear analogue, rather the T_g value was nearer towards the T_g of homopolyimide without siloxane moiety (9). It is also worth noting that the present grafted copoly(ether imide) show higher glass transition temperature in comparison to the previously reported grafted copoly(ether imide) which show a value of 209°C where 4,4'-(4,4'-Isopropylidenediphenoxy)bis(phthalic anhydride), BPADA was used as a dianhydride unit. This is due to the two flexible ether linkages present in the dianhydride unit of BPADA (13).

3.4 DMA Measurements

The DMA plot of the polymer predicts the properties of a polymer in real application under stress and this helps in designing a polymer for a particular application. Thus, it is not only possible to gain information on the T_g of a polymer but DMA also provides the storage modulus value of the polymer and its change with temperature. Figure 3 shows the dynamic mechanical analysis plot of the copolyimide **1a**. The T_g is taken from the tan δ peak at 10 Hz. The tan δ

Table 1. Comparison of thermal, mechanical and surface properties of the polymers

Polymer	M_n (g/mol)	PDI	Siloxane ^a (%)	T_g^b (°C)	T_d^c (°C)	TS (MPa)	EB (%)	YM (GPa)	CA (°)
Homo-polyimide	24760	1.87	—	273 ⁽⁹⁾	526 ⁽⁹⁾	109 ⁽⁹⁾	21 ⁽⁹⁾	2.1 ⁽⁹⁾	90 ⁽¹⁴⁾
1a	56800	2.20	18.14	272	371	47	65	1.8	102
1b ⁽¹³⁾	32500	2.60	17.07	209	396	46	62	1.25	101
1c ⁽¹⁴⁾	18700	2.08	17.38	208	416	51	30	1.2	96

PDI; Polydispersity index, a) determined from ¹H-NMR; b) from DSC; c) 5% weight loss temperature in air, TS; tensile strength, EB; elongation at break, YM; Young modulus, CA; average contact angle

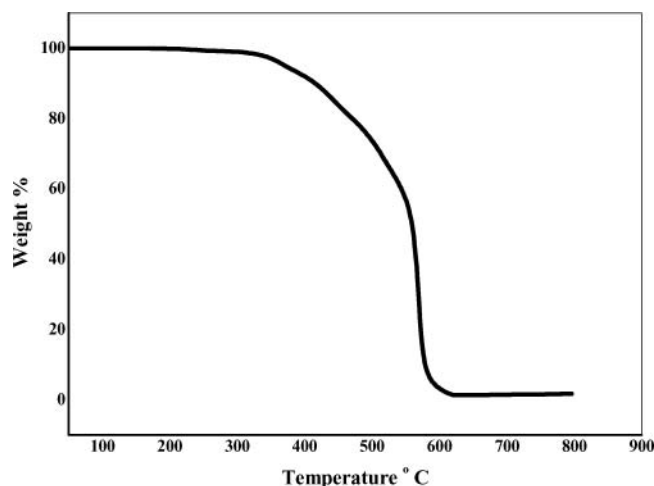


Fig. 4. TGA plot of 1a.

values show a maximum at a particular temperature, which in turn indicates the T_g of the polymer at 300°C. The value is in good agreement with the DSC T_g accounting for the common shift of about 20°C for the DMA measurement. The co-polymer showed storage modulus as high as 1.62 GPa at 40°C.

3.5 Thermal Stability

The thermal property of the grafted copoly(ether imide) was evaluated by TGA. The TGA thermogram is shown in Figure 4 recorded in air atmosphere and the thermal properties of the polymer are summarized in Table 1. The 5% weight loss temperature of the newly synthesized poly(imide siloxane) **1b** containing siloxane unit in the polymer backbone is detected at 371°C in air atmosphere. Compared to the homopolyimide and the grafted copolyimide **1b** with isopropylidene unit which shows a value of 396°C at 5% weight loss, the copolyimide **1a** shows lower thermal stability. The low thermal stability of the copoly(ether imide) **1a** may be attributed due to the presence of weak polydimethylsiloxane side chain.

3.6 Mechanical Properties

The mechanical properties of the copoly(ether imide) film were tested at room temperature and exhibited tensile strength at break of 47 MPa and elongation at break of up to 65% as shown in Table 1 in comparison with the related homopolyimide and block co-poly(imide siloxane). The stress-strain plot (Figure 5) of the grafted copoly(ether imide) showed the behavior of a typical engineering thermoplastic. The tensile modulus value of 47 MPa as found for the 20 wt% fluorinated silicon grafted copolyimide **1a** is fully comparable to that of the linear siloxane containing analogue (14) and is lower than that of the fluorinated homopolyimide without siloxane moiety (109 MPa) (9). It is interesting to note that the elongation at break for the flu-

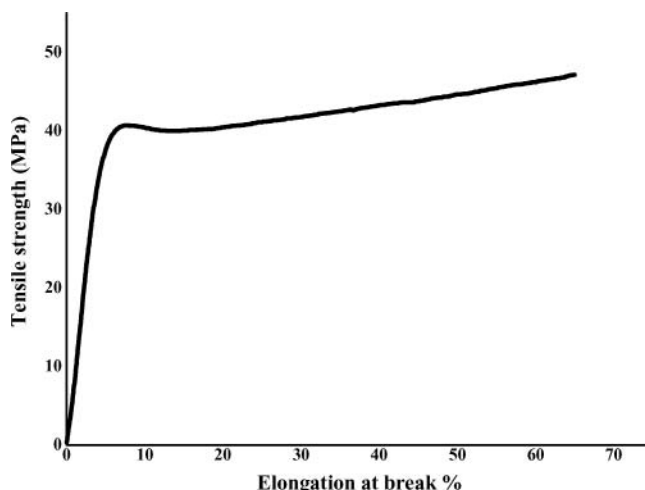


Fig. 5. Stress-strain plot of 1a.

orinated siloxane grafted copoly(ether imide) is up to 65% which is very high compared to the linear analogue (14) and fluorinated homopolyimide without siloxane moiety (9) indicating very high toughness. The value of newly synthesized grafted copoly(ether imide) is similar to the previously reported grafted copoly(ether imide) with isopropylidene unit (13) which showed tensile strength at break value of 46 MPa, elongation at break 62% and Young's modulus value of 1.2 GPa (13).

3.7 Contact Angle Measurement

The contact angle measurements provide information about the surface energies of the system. Contact angle is an important parameter which is often used as a measure of the hydrophobicity of a polymer surface. Contact angle of the siloxane grafted co(polyether imide) was measured using water as a medium to investigate surface wettability. Contact angle was measured as average value over a large number of measurements on the flat film and the mean of the entire values namely mean contact angle (CA) has been reported. The value of 102° found is significantly higher than that of the homopolyimide due to siloxane incorporation, but is also higher than that of the block copoly(ether imide) since the grafted siloxane chains have higher mobility for better surface segregation. The present contact angle value of siloxane grafted co(polyether imide) is comparable with the previously reported contact angle value of 101° where BPADA was used as dianhydride unit (13).

4 Conclusions

A new fluorinated silicon grafted copoly(ether imide) has been synthesized by solution imidization. The resulting polymer exhibited a high glass transition temperature of 271°C comparable to that of the homopolyimide without siloxane moiety but moderate thermal stability in air.

The polyimide film has good mechanical strength, a high Young's modulus, is very tough and exhibits a very high water contact angle. Thus, with the siloxane grafted copolyimide one can design materials having better processability without affecting the glass transition temperature together with high modulus as well as high strain at break maintaining a significant improvement in toughness. Thus, the effect of the previously reported graft structure with isopropylidene unit with same loading of polydimethylsiloxane as side chain is similar for elongation at break and contact angle value but the incorporation of hexafluoroisopropylidene group enhances the T_g and Young's modulus significantly. Such copoly(ether imide) containing both fluorine and silicon in the backbone can be of great interest for surface modifications, cable insulation and for gas separation membranes.

Acknowledgments

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