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High impact thermally stable block copolyethers

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Block copolyethers characterised with high impact strengh values ($I \geq 140$ kJ/m^2) and stable physical and chemical properties for long duration under load (at 180–200°C) were obtained from 1,1-dichlor-2,2-di-(4-oxyphenyl)ethylene by acceptor catalytic polycondensation method. The dependence of the tensile and thermal properties of the block copolyethers on the molecular structure was investigated. It is shown that, after heat treatment the heat stability and the mechanical properties improved. © *2001 Kluwer Academic Publishers*

1. Introduction

Polyethers have an important place among the high molecular polycondensed polymers. In recent times many useful end products such as fibers, clays, paints and permeable materials have been obtained from this polymeric group.

The importance of aromatic polyethers is due to the combination of the high thermal stability, high tensile strength and chemical resistivity [1–3]. The polyethers may combine various properties of different polymeric materials. Linear and branched aromatic polyethers have good properties such as high physical and mechanical strength; significant dielectric properties and high thermal stability. It is obvious that non-saturated aromatic block copolyethers will have the combined good properties of aromatic and non-saturated polyethers.

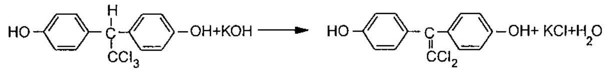
Yang et al. [4] have investigated the thermal and mechanical properties of polyethersulfone/poly (phenylene) sulfide blends. They have shown that, the impact strength was improved by the blending with poly(phenylene) sulfide while the high strength of the polyether was maintained. Another work [5] indicated that the fracture toughness of the polyether sulphone is increased by blending with thermotropic crystal polymers.

In the present work a new non-saturated block copolyether was obtained from a monomer described as 1,1-dichlor-2,2-di-(4-oxyphenyl)ethylene. The monomer was synthesised from various components of chloride which constitutes the basic ingredient of 4,4^1-dichloro diphenyl thrichloro ethane (DDT) [6, 7]. The resultant non-saturated block copolyethers were characterised by high mechanical and thermal properties. The impact strength results of the copolyethers were compared with some of the industrial polymers reported in the literature [8, 9]. The new materials differed from the convential polymers, especially, by their high impact strength properties.

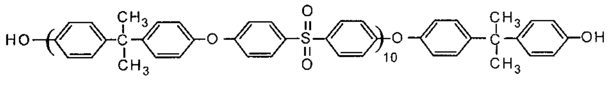
2. Experimental

2.1. Materials and processing

1,1-dichlor-2,2-di-(4-oxyphenyl)ethylene was obtained from phenol and chloride by a well-known method [10]. In this method, as the dehydrochloration was performed the monomer was cleaned by recrystallisation in a water-ethanol mixture (water/ethanol = 5/2). The recrystallized material had a melting temperature of 213°C. Dichloranyhydrides of terephthalic acids were also used.



An oligoarylensulfoneoxide (OASO) with a condensation index $n = 10$ was selected and a block copolyarylatesulfone was obtained. The structural formula of (OASO) was given as follows [11]:



Then, among the bisphenol materials (which were directly obtained from Mitsui Co. Ltd. Japan), diphenylpropane (BSP-1) and phenolphthalein (BSP-2) were chosen and combined with 1,1-dichlor-2,2-di-(4-oxyphenyl)ethylene in a molecular proportion of 1:1.

Finally, the block copolyethers were obtained by the technique of acceptor-catalytic polycondensation in dichloroethane and expressed by the following formula:

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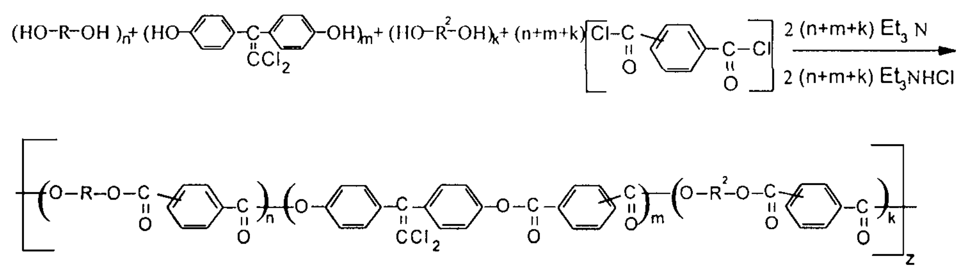
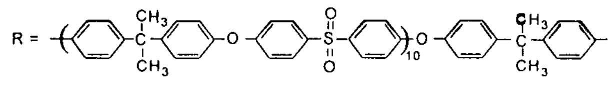
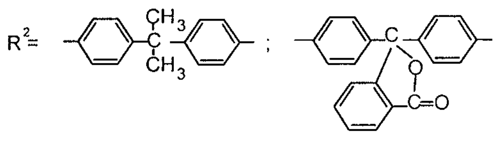
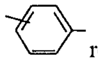


where,





 represents the remnants of dichloranyhydrides.

The two different R^2 values correspond to diphenylpropane and phenolphthalein. The synthesis was processed in dichloroethane media for an hour. Triethylamine was used as an acceptive catalyser.

The copolyethers based on diphenylpropane and and phenolphthaleine were labelled as (BSP-1) and (BSP-2), respectively.

2.2. Test methods

2.2.1. Heat treatments

The sheet test specimens were obtained by pouring the polymeric solution onto a surface and letting dichlorethane to evaporate. Then the resultant polymeric sheet was put into an SPT-200 oven under vacuum at 100°C for two hours and dried.

The sheet specimens were heat treated as a function of time and temperature. First, the specimens were heat treated at 200°C for different times (from 1.8×10^5 up to 7.2×10^5 s). Secondly, the temperature changed between 200–300°C while the heat treatment time kept at 1.8×10^3 s. After this heat treatment the molecular structure of the copolymers were identified by IR-spectroscopic methods.

Finally, the specimens were heat treated at 200°C for different times up to 36×10^5 s. Then the as-moulded and heat-treated specimens were subjected to mechanical and thermal tests.

2.2.2. Viscosity measurements

The viscosity measurements were made according to GOST 10028-81 (Russian State Standards) using an Ubbelohde viscometer with a diameter of 0.56 mm. The experiments were conducted at room temperature (20°C) and the density of the solution was 5×10^3 g/m^3. Dichlorethane was used as a solvent.

2.2.3. Molecular structure and weight measurement tests

The properties of block copolyethers (BSP-1 and BSP-2) were investigated by various methods. The molecular structure of block copolyethers was identified by a "Perkin-Elmer" IR-spectrometer. The molecular weight of linear block copolyethers was measured by sedimentation method on an ultracentrifugel 317 V-MOM (made in Hungary) machine by equilibrium approaching method. In this method the cell is rotated at a relatively low speed (5000–10,000 rpm) until an equilibrium is attained whereby the centrifugal forces balance the tendency of the molecules to diffuse back against concentration gradient developed. Measurements are made of the equilibrium concentration profiles for series of solutions with different initial polymer concentrations so that the results can be extrapolated to $c = 0$, where c is zero concentration [12].

2.2.4. Mechanical tests

The measurement of the mechanical properties of block copolyethers was carried out according to GOST (Russian State Standards) 17-316-71 by using film specimens ($100 \times 10 \times 0.1$mm) on a tensile test machine MRS-500 with a constant deformation rate of 40 mm/min at 20°C.

The specimens for impact tests were obtained by moulding the doughy polymer at a temperature of 290°C (BSP-1) and of 340°C (BSP-2). The copolymers were pressure moulded into test specimens of $4 \times 6 \times 50$ mm^3 and prepared for the notched impact tests. A notch depth of $a = 0.5$ mm was obtained by means of a sharp blade held by a special fixture. While the blade penetrated into the polymer, a positive stop prevented the blade moving further inside the specimen. The specimens were striked edge-on in three point bending mode on a support of 40 mm. The impact testing was done on pendulum impact testing machine IT-1/4 equipped with a piezoelectric load sensor and an immediate signal output to the recording oscillograph C 8-13. Such a unit allowed us to obtain the 'load-time' (p-t) diagrams from which all the necessary mechanical characteristics were calculated.

2.2.5. Thermomechanical and other tests

Thermomechanical analyses of the polymers was conducted in the room (atmospheric) conditions. The tests were carried out on a Pribor thermomechanical analyser. The temperature was increased at the rate of 4°C/min and the load was kept to give a constant stress value of 0.05 MPa. The thickness and the width of the test specimens were 0.1 mm and 8 mm, while the distance between the clamps were 80 mm. A thermal chamber with a diameter of 30 mm and length of 150 mm was employed. The temperature gradient in the thermal chamber was 2°C along the length and 0.1°C along the diameter. The deformation of the specimen was measured by a strain gauge. The temperature and deformation were recorded on a x-y recorder.

Thermogravimetric analyses of the as moulded and heat treated copolymers was carried out by an electronic "Setaram" type thermo-balance (the temperature was increased at the rate of 10°C/min in argon).

Investigation of the polydispersity of the block copolymers were conducted by turbidimetrical titration method on a FEC-56M device. The principle of titration is that the diluted polymeric solution will become turbid if a precipitator is added and will have a different optical density from the original solution. The turbidity increases with the amount of the precipitator until the polymeric solution forms a stable suspense. The resultant optical density and corresponding precipitator volume are related to the dispersity of the polymer. In the present work dichloroethane and isopropanol were used as solvent and precipitator, respectively.

The fire resistivity of the polymers was evaluated by the oxygen index method. Dielectric properties of the polymer were investigated by dielectric weight loss method on a Kumetre VM-560 Tesla machine at a frequency of 10^6 Hertz and in the temperature range of 20–300°C.

Chemical resistivity of BSP-1 and BSP-2 was investigated in concentrated and diluted solutions of acids (H_2SO_4) and alkalis (NaOH).

3. Results and discussions

3.1. Molecular structure and weight measurement tests

The data obtained from the elemental analysis, IR-spectroscopy and turbidimetrical titration were used to confirm the given chemical structure the polymers. The molecular mass of BSP-1 and BSP-2 were 74,000 and 62,000, respectively.

The IR-spectra results showed that the resultant bands of absorption peaks correspond to different bonds and groups. The presence of absorption bands (see Fig. 1) which corresponds to ether bonds, (920–940 cm^{-1}), ester bonds (1000–1300 cm^{-1}), isopropylidene groups (1350–1360,1385,2875,2970 cm^{-1}) and C=O groups (1600–1700 cm^{-1}) and the absence of hydroxyl groups (3600 cm^{-1}) points to the fact that the polycondensation of the copolymers and dichloranhydrides of isophthalic and terephthalic acids were completed and their properties were manifested.

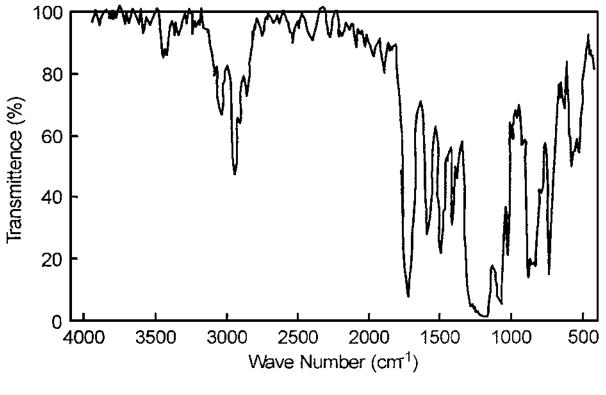


Figure 1 IR spectrum of BSP-1.

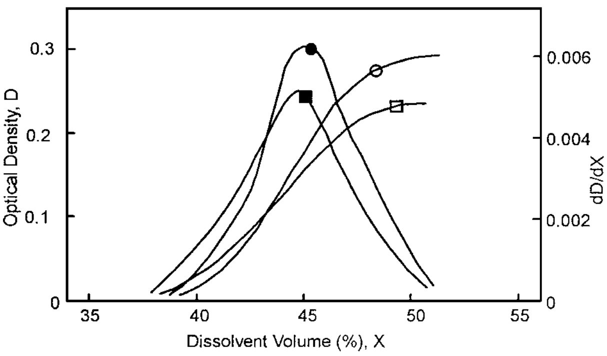


Figure 2 The turbidimetric titration curves (●, ■—differential curves and ○, □—integral curves) of molecular mass dsitribution for (●, ○) BSP-1 and (■, □) BSP-2.

The results of turbidimetrical titration confirmed the structure of the above mentioned copolymers (see Fig. 2). The differential curves for both copolymers show only a single maximum which means that the reactants of the copolymers are statistically mixed. They are characterised by low polydispersity.

The block copolymers easily dissolved in organic solvents such as dimethylformamide (DMFA) and tetrahydrafuran (THF) and did not dissolve in alcohol and acetone.

3.2. Mechanical tests

Block copolyethers show good impact toughness. Fig. 3 indicates that the impact strength of BSP-1 and BSP-2 is about 140 kJ/m^2 and 100 kJ/m^2, respectively. Such a high impact value is not very common among polymers. Fig. 4 clearly shows the superior impact properties of the new copolymers compared with polycarbonate (PC) and ABS [9].

The effects of heat treatment on the impact beahviour of both coplymers are presented in Fig. 3. Both copolymers showed a decrease in impact strength following heat treatment. The decrease in impact strength for bisphenol-A based copolyether (BSP-1) was about 29%. It decreased from 140 kJ/m^2 (no heat treatment) to 100 kJ/m^2 (heat treated at 200°C for 6×10^6 s). The change in impact strength for phenolphthalein based copolyether (BSP-2) was also similar. It showed a

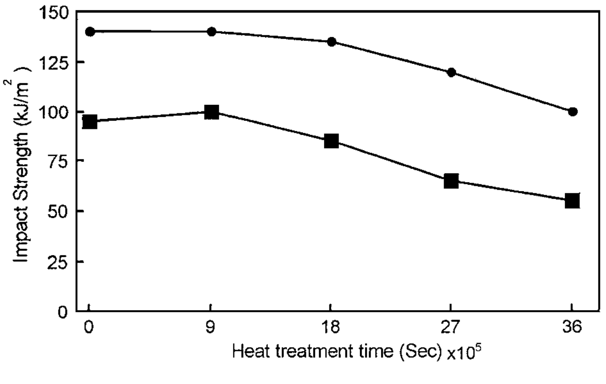


Figure 3 The impact strength vs. heat treatment time.

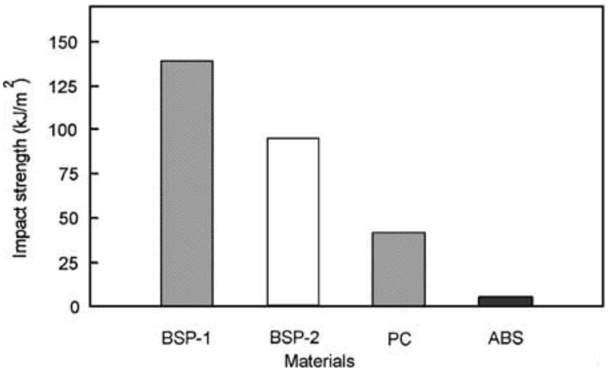


Figure 4 The comparison of Impact strengths of the two copolyethers with injection moulded PC and ABS (the last two values were taken from the reference [9]).

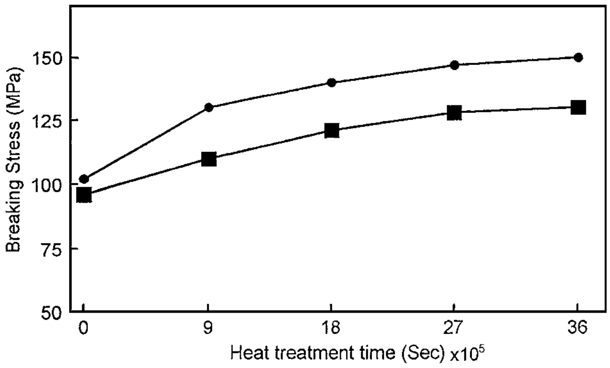


Figure 5 The breaking stress vs. heat treatment time.

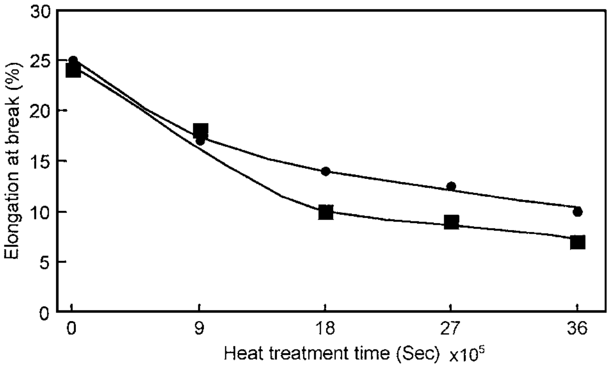


Figure 6 The elongation at break (%) vs. heat treatment time.

decrease rate of 42% with heat treatment (from 95 kJ/m^2 to 55 kJ/m^2).

Linear types of polyethers may undergo plastic deformation and have high strength values. Figs 5 and 6 show that BSP-1 has a breaking stress of 102 MPa and about an elongation rate at break of 25%. The breaking stress of BSP-2 was 96 MPa while elongation at break was 24%.

The relationship between breaking stress and heat treatment is presented in Fig. 5. Both copolymers showed an increase in breaking stress with heat treatment time at 200°C. The breaking stress BSP-1 showed a 47% increase in breaking stress with heat treatment. It increased from 102 MPa (no heat treatment) to 150 MPa (heat treated at 200°C for 6×10^6 s). The change in breaking stress for BSP-2 was also similar. It showed an increase rate of 35% with heat treatment (from 96 MPa to 130 MPa).

The relationship between the elongation at break, ε (%) heat treatment is presented in Fig. 6. Both copolymers showed similar reductions in elongation at break with heat treatment. The elongation at break for BSP-1 showed 60% reduction with heat treatment (it is reduced from 25% for no heat treated specimens to 10% for the heat treated specimens for 36×10^6 s). The change BSP-2 was also similar. The elongation at break showed a reduction of 70%. It was reduced from 24% to 7% upon following heat treatment.

It is clear that heat treatment significantly affected the mechanical behaviour of the copolymers. It is important to identify whether these changes in mechanical properties are caused by the crosslinking of the copolymers or by some other effects. The higher values of breaking strength and lower values of elongation at break for the heat-treated specimens meant that the heat treatment could have introduced crosslinking, because crosslinking is expected to impart a stronger mechanical behaviour. The crosslinking of the molecules renders elongation more difficult and hence enhance the modulus of elasticity and breaking stress. The highly crosslinked polymers are usually rather brittle with small elongation at break. Therefore, the reason for the observed mechanical deterioration after heat treatment is probably the cross linking of the copolymers caused by heat treatment. The significant reductions in impact strength also supports this conclusion. The cross linked rigid materials show a brittle failure rather than ductile failure under impact loads.

In order to thoroughly assess the causes of the improved mechanical behaviour of the copolymers further work was carried on. It is supposed that the double bonds between C and CCl_2 ($C{=}Cl_2$) which were initially present along the main chain of the linear polymers were broken and the copolymers were converted into three dimensional networks after heat treatment. This conversion introduced a saturation into the copolyethers which also increased the oxidative stability. In order to confirm this hypothesis of three dimensional restructuring, the kinetic structure of sheet specimens were investigated as a function of time and temperature. A typical IR spectrometric result for an as-moulded and heat-treated specimen (at 300°C for 1.8×10^3 s) was presented in Fig. 7. The maximum absorption peak of the copolymers due to the double bond group $C{=}CCl_2$ was observed to be around 980 cm^{-1} before heat treatment. This result (J) was

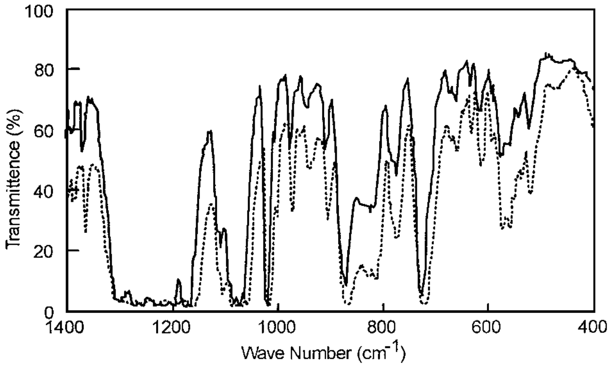


Figure 7 The IR-spectrometric results of as-moulded (——) and heat-treated (....) polyethers (at 300°C for 1.8×10^3 s).

TABLE I The thermal and flow properties of the copolyethers

Heat treatment time (sec)	Intrinsic viscosity (m^3/kg)	Temperature (°C) Glass transition temperature T_g (°C)	Temperature (°C) Melt temperature T_m (°C)	Mass loss (%2)	Mass loss (%10)
0	0.102*	210	270	372	402
	0.084	250	320	362	402
9×10^5	0.116	220	302	377	412
	0.085	255	320	372	407
18×10^5	–	227	–	387	417
	0.8	257	330	382	412
27×10^5	–	227	–	395	422
	0.75	257	330	382	407
36×10^5	–	227	–	402	422
	0.7	257	330	377	392

*Upper value is for BSP-1 and lower value is for BSP-2.
–The material degraded.

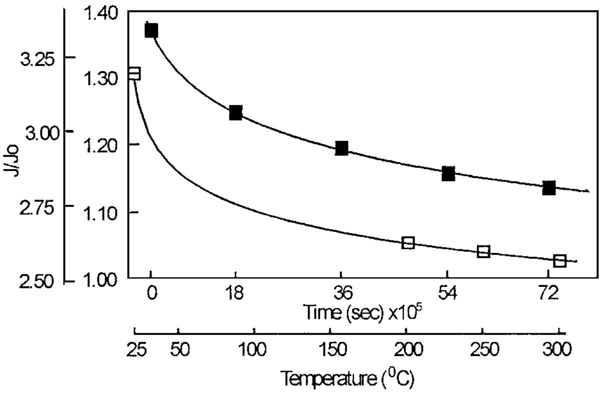
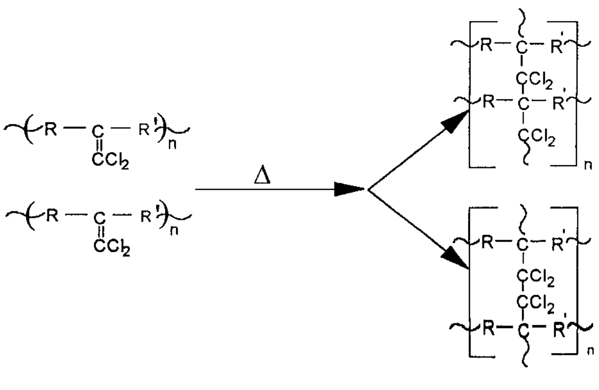


Figure 8 The dependence of absorption intensity of C=CCl_2 groups on heat treatment as a function of (■) heat treatment time (at 200°C) and (□) heat treatment temperature for 1.8×10^3 s.

used to assess the mechanism of the structure. The intensity results which obtained by using the absorption peak of double bond aromatic ring at 900 cm^{-1} (J_0) were used as a reference point. It is shown in the Fig. 8 that, the absorption intensity ratio J/J_0 falls abruptly as the annealing time and temperature increase. This fact clearly confirms that the heat treatment causes changes in the structure of double bond C=CCl_2.

The results confirm that the molecular structure of the block copolyethers changes after heat treatment at 200°C and as a result of this, the thermal resistivity and mechanical properties improved.

It can be stated that after heat treatment, the initial structure of the copolymers changes into a three dimensional cross linked structure as follows:



3.3. Thermomechanical and other tests

Although the intrinsic viscosities were not very high for both copolymers, they increased upon heat treatment (see Table I).

Block copolymers BSP-1 and BSP-2 showed high thermal resistance. These properties increased by 20–30°C with heat treatment. The results for the Seteram thermobalance are given in Table I. The results confirm that the molecular structure of the block copolyethers changes after heat treatment at 200°C and as a result of this, the thermal resistivity increases. The mechanism which was responsible for the improvement of the tensile mechanical behaviour after heat treatment is also responsible for the increased thermal stability. The heat treatment introduced cross linking on the copolymers, which in turn hindered breakage of the molecules and thus increased the thermal resistivity.

The results of the thermomechanical tests have shown that copolyethers possess comparatively high glass transition temperature (T_g) and melt temperature (T_m). This may be due to the fact that, the saturation of the polymeric chain by flexible simple ethereal bonds is accompanied by the increased density of the chain packing. This, in turn, causes a decrease in the mobility of the macromolecules. Thermomechanical properties strongly depend on the structure of the molecular orderings. Heat treatment increased the glass transition temperature of BSP-1 and BSP-2 by 17°C and 7°C, respectively. This is an expected result. The transition from glassy state to a plastic state is mainly due to the hastened molecular motion accelerated by the temperature increase. Since the heat treatment introduced cross linking, the molecular motin of the main chains of the copolymers are hindered and consequently T_g increased. Therefore it can be concluded that the cross linking introduced by heat treatment was responsible for the improved thermomechanical behaviour.

Block copolyethers BSP-1 and BSP-2 have high stable dielectric properties too. These values were shown to be about dielectric constant, $e^1 = 3$-3.3 dielectric loss factor, $t_g\delta = 0.01$–0.02 and volume resistivity, $\rho_v = 3.6 \times 10^5$–4.3×10^5 ohm · cm. These properties of polyethers did not change at the temperature range of 20–300°C.

TABLE II The environmental effects of different acid and bases on the copolyethers at 20°C

No.	Time (sec) $t \times 10^4$	(%) mass loss in NaOH (10%)	(%) mass loss in NaOH (40%)	(%) mass loss in H_2SO_4 (10%)	(%) mass loss in H_2SO_4 (96%)
1	8.6	+0.06	−2.63	+0.08	−57.4
		+0.1	−5.32	+0.17	–
2	43.2	−0.23	−12.7	−0.05	–
		−5.4	−25.7	0	–
3	86.4	−0.54	−21.4	−0.13	–
		−7.8	−42.6	−014	–
4	129.6	−1.17	−30.3	−0.32	–
		−11.3	−62.3	−0.24	–
5	172.8	−1.99	−46.2	−0.46	–
		−14.9	–	−0.41	–
6	216	−3.05	−61.9	−0.59	–
		−22.9	–	−0.55	–
7	259.2	−3.87	−80.6	−3.58	–
		−29.2	–	−0.86	–

*Upper value is for BSP-1 and lower value is for BSP-2.
–The material completely dissolved.

The block copolyethers are chemical and fire resistive. The oxygen index for the polymers is around 35.5–36%. According to these figures it can be shown easily that the polymers are not flammable. When the block copolyethers were inserted into diluted acids and alkalis, they were observed to be resistive to the chemical environmental effects (see Table II). These properties were further improved with the structural changes caused by the heat treatment.

4. Conclusion

The block copolyethers BSP-1 and BSP-2 have demonstrated high impact strength values, good thermal electrical and chemical properties. The thermomechanical properties and tensile strength were improved upon heat treatment, while the ductility and the impact strength decreased. These changes in the magnitudes of thermal and mechanical proprieties are due to the restructuring of the aromatic $C{=}CCl_2$ bonds into three dimensional networks because of heat treatment. Therefore these two materials are recommended to be used as sheet plastics and high strength construction materials.

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