

Enhancement of low-temperature impact toughness of polycarbonate by hydroxyl terminated siloxanes and its concomitant effects on other properties

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Modification of commercial grades of polycarbonate (PC) to the specific grades required for a particular end application along with optimized processing conditions has now become inevitable keeping in view the present cost, time and technological challenges. An effective and simpler method has been developed to enhance the properties of PC by reactive blending with siloxanes terminated with a reactive group. The work presented here has very good results with respect to enhancement of low-temperature (-30°C) impact strength of PC by incorporating hydroxyl terminated poly dimethyl siloxane (PDMSOH). PC after reactive blending with PDMSOH at certain processing conditions changes properties as concentration and viscosity of PDMSOH is varied. It was observed that modification of impact toughness by this method also had concomitant effects on other properties, e.g. tensile strength, tensile modulus, optical transmittance and haze. Dependence of change in properties on both or either viscosity and concentration of PDMSOH was also observed. Impact toughness at low temperature was improved up to 655 J/m at -30°C, i.e. up to 428% by increasing both concentration and viscosity of PDMSOH whereas tensile strength and tensile modulus showed a peculiar behaviour. Optical transmittance and haze were however influenced by only < 7% and < 5%, respectively, just by changing the concentration of PDMSOH and there was hardly any change with respect to its viscosity. Results obtained may be useful in selecting and modifying PC for an end application at sub-zero temperature. The material was characterised by Izod impact tester, SEM, capillary viscometer, tensile tester, transmittance and haze tester.

Keywords: Impact toughness, Sub-zero temperature, Polycarbonate, Tensile strength, Transmittance

INTRODUCTION

Polycarbonate (PC) is a widely used engineering thermoplastic having excellent impact resistance, high optical transmittance [1] and good thermal stability. The material however starts losing its impact toughness at around -20°C temperature [2]. Enhancement of properties by blends and copolymers of PC have been extensively studied in the past few decades [3-8]. Impact modification for low temperature of PC has been attempted by researchers using different methods but they generally lead to some adverse effects on other mechanical, optical and thermal properties [9-12]. Copolymerising bisphenol-A with siloxanes of different molecular weight by interfacial copolymerisation using phosgene, had been traditionally done and a few grades of such copolymers are commercially available. These block copolymers though enhanced the impact strength of PC at sub-zero temperature because of strong separation of micro-phases of polycarbonate and siloxane blocks but there was a considerable reduction in tensile strength. Such commercially available copolymers are there only with a very few grades, probably because their requirements are quite specific and lower in volume. First reactive blending of siloxane with polycarbonate in melt state

was done by Hawkins *et al.* using carboxylic acid terminated siloxanes [11]. Later siloxanes functionalised with aryl amino group and hydroxyl aryloxy terminated PDMS were also used for reactive blending with polycarbonate [13,14]. Physical blending of siloxane with PC results in formation of larger domains of siloxane of size bigger than 10 µm whereas in reactive blending siloxane domains are much smaller and are in the size range of less than 3 µm to sub-micron sizes. Larger domain size clearly indicates the immiscibility of the two materials and the same is reflected in the end properties of the blended PC. Solubility of siloxanes in PC is very low, hence there is a clearly visible phase separation in the physical blends that can even be observed as a layer of silicon oil on the surface of PC. Miscible and immiscible blends can thus be distinguished by the morphology and domain size of siloxane blocks. Though the researchers have made good progress in reactive blending, yet there is ample scope of further work with respect to development of structure-property relationship, optimised conditions and reaction mechanism. Reactive blending as compared with conventional interfacial copolymerisation is a much simpler, less complex and efficient method to modify the properties of polycarbonate. It is also

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a very useful and cost-effective method for converting smaller volumes of PC to a grade having desired properties, as manufacturers of PC are generally conservative in developing the copolymers PC and siloxanes required in smaller quantities.

It is therefore essentially required to develop such methods that can enhance the property of a commercially available grade of PC meeting the requirement of processing and end application. Blending of PC with other polymers and additives using a compatibilizer could be one way of doing such modification but it is observed that blends of PC have adverse effects on other properties, e.g. optical transmittance, tensile strength and surface finish, etc. Phase stability and miscibility in PC blends is also very limited and generally adequate only to some extent to meet the requirement of desired property enhancement [15-17]. PC-EMA (ethylene methyl acrylate) copolymer and PC-PBT (poly butylene terephthalate) blend using different compatibilizers were studied for their mechanical and flow properties [18,19]. Impact toughening could be achieved by all these methods but at the cost of adverse effects on other properties specially the optical transmittance. Nano-fillers were incorporated in PC blends to increase the toughening by making nano-composites [20-23]. Processing of such nano-composites into a product by conventional cost-effective techniques though have some technical challenges to overcome. PC being an engineering material of vast application owing to its excellent properties as mentioned before, therefore need of an appropriate method that can take care of all the desired properties becomes imperative.

In the work presented here, PC is chemically modified by siloxanes to improve its low-temperature impact strength. Different viscosity and concentrations of PDMSOH are used to modify PC and very useful observations are found with respect to low-temperature impact, tensile and optical properties. Tensile strength that generally reduces in block copolymers of PC and siloxane produced through interfacial copolymerisation interestingly gets enhanced in the PC modified by reactive blending with siloxane. The transesterification reaction that takes place between the hydroxyl group of PDMSOH and the carbonyl group of

polycarbonate is also influenced by the concentration of the catalyst KOH. Low-viscosity PDMSOH, i.e. lower molecular weight siloxane used in the reactive blending has a comparatively larger number of terminated hydroxyl groups, thus concentration of catalyst becomes important and needs to be optimised.

MATERIALS AND METHODS

Materials

Polycarbonate (PC) from the SABIC Company of grade LEXAN 144R was used for the experimental work. Two grades of hydroxyl terminated polydimethyl siloxane (PDMSOH) of viscosity 750 cSt and 3500 cSt were used of Aldrich Chemicals. Different-viscosity compositions of PDMSOH were prepared by mixing the two different grades of PDMSOH in different proportions as described in Table.1 to determine the effect of viscosity of PDMSOH on the impact strength of PC. Kinematic viscosity of PDMSOH compositions was measured at 23°C by a glass capillary U tube viscometer as per the method ASTM D445.

Sample Preparation

Reactive blending between PC and PDMSOH was done in an agitated glass reactor at 260°C in presence of KOH catalyst at 0.1 wt% concentration under an inert atmosphere of nitrogen for about 40 minutes. Both, viscosity and concentration of PDMSOH were varied to observe their impact on various properties. Viscosity variation from 750 to 3500 cSt was done by making a total of six compositions, i.e. PDMS750, A, B, C, D and PDMS3500 as shown in Table 1. Concentration of PDMSOH was changed from 0.5 to 3.0 wt% at an increment of 0.5 wt%. Physical melt blend of PC and PDMSOH (3.0 wt%) was also prepared at 260°C to compare it with reactive blended samples.

Physically blended sample (PC+PDMSOH) was prepared without KOH catalyst and mixing time was about 10 minutes to ensure a thorough mixing of the two phases. Since the reaction mass was highly viscous, both physical and reactive blending was done using pitch blade agitator at a speed of 150 to 200 rpm.

Table 1. Compositions of PDMSOH having different viscosities

Hydroxy terminated PDMS	PDMS 750	PDMS-A	PDMS-B	PDMS-C	PDMS-D	PDMS 3500
Composition [% PDMS750 : %PDMS3500]	100:0	80:20	60:40	40:60	20:80	0:100
Viscosity [cSt]	750	1210	1870	2560	3070	3500

A gas sensor was also provided at the vent of the reactor to observe the generation of CO₂ gas during reactive blending.

Characterisation

Izod impact tester was used to measure impact strength both at room temperature and at -30°C. Notched samples were prepared of size 64×12.7×3.2 mm as per ASTM-D256. Tensile strength and modulus were measured by a universal testing machine (UTM) of make Instron as per ASTM - D638. Scanning Electron Microscope of make Tescan MIRA-3 was used to observe the phase compatibility of PC and PDMSOH. UV-VIS spectrophotometer of make Chemito, India was used to characterise covalent bonding between PC and PDMSOH. Samples were dissolved in Methylene dichloride and filled in the quartz cell to characterise them by the UV-Vis spectrophotometer. Optical transmittance and haze of modified PC were measured as per ASTM-D1003.

RESULTS AND DISCUSSION

Reactive Blending with Siloxanes

Reaction between PDMSOH and PC chains is characterised by the Red Shift obtained in UV-VIS spectra as shown in Fig. 1. The covalent bonding between the two polymeric chains is verified in π - π^* transition of aromatic fragments of PC in the UV-VIS spectra. It can be seen that the characteristic peak of PC in UV-Vis spectra at 262 nm is not changed in the physically blended sample (PC+PDMSOH). However, for the reactive blended sample (PC/PDMSOH), there is an appreciable shift of 8 nm and the peak is found at 268 nm. The difference in the spectra of physically blended (PC+PDMSOH) and reactively blended (PC/PDMSOH) is indicative of the chemical binding between the two polymeric chains. This observation is in agreement with the results reported elsewhere [24,25]. The transesterification reaction between the carbonyl group of PC and the hydroxyl group of PDMSOH in presence of catalyst KOH takes place as shown in the proposed mechanism in Fig. 2 [12,24,25], The mechanism is also supported by the observation of an increase in the concentration of CO₂ gas in the vent of the reactor during reactive blending measured by a chemical sensor.

Influence on Low-Temperature Impact Strength

Modified Izod impact strength values of PC grade Lexan 144 R used in the experiment are tabulated in Table 2. Impact strength of the unmodified base PC resin at room temperature is 754

J/m which is drastically reduced to 124 J/m at -30°C temperature.

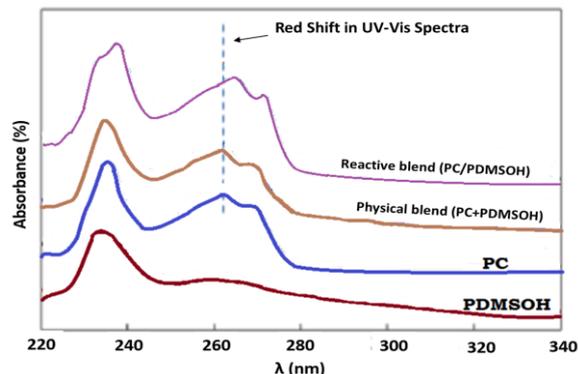


Fig. 1. UV-Vis spectra of PC, PDMSOH and their physical (PC+PDMSOH) and reactive (PC/PDMSOH) blends.

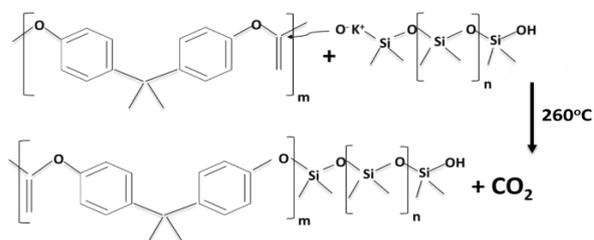


Fig. 2. Proposed mechanism of the reaction between PC and PDMSOH with KOH catalyst.

After the reactive blending with siloxane at the reaction conditions mentioned before, the impact strength at -30°C temperature increases with both concentration and viscosity of the PDMSOH, as shown in Table 2. Maximum impact strength of PC at -30°C temperature was achieved as 655 J/m at 3.0 wt% concentration and 3500 cSt kinematic viscosity of PDMSOH. The enhancement in impact strength from 124 J/m to 655 J/m is quite appreciable and is better than the values that can be achieved by interfacial copolymerization. The different impact strength values reported in Table 2 provide a range of 162 J/m to 655 J/m achieved at different concentrations and viscosities of PDMSOH. Keeping in view the effect of impact modification on other properties, specially the mechanical properties like tensile strength and modulus, an appropriate composition of the reactive blend can be selected from the reported data as may be required for a particular end application of polycarbonate. Since both viscosity and concentration of PDMSOH play role in changing the different properties of PC, data reported in this paper can be usefully applied in selection of the grade of PC. The concentration of PDMSOH beyond 3.0 wt% is not stable and it leads to phase separation. As can be seen in the SEM micrographs of Fig. 3, uniformly dispersed phases of PDMSOH are seen at 0.5 and 3.0 wt% concentration

in Fig. 3(a) and 3(b), respectively, whereas phase separation is observed in Fig. 3(c) at 3.5 wt% concentration. Uniformly dispersed siloxane domains from 2 μm to sub-micron sizes are seen in Fig. 3(a) which are miscible with the reactive blend of PC and PDMSOH. This phenomenon occurs upto the concentration of 3.0 wt%. As shown in Fig. 3(b), domain sizes of 1 to 3 μm are found uniformly dispersed in the bulk PC blend. Unevenly dispersed siloxane domains of sizes bigger than 10 μm are shown in Fig. 3(c) at 3.5 wt% concentration which verifies that siloxane is immiscible and unstable beyond 3.0 wt% concentration. Immiscibility of siloxanes could also be seen visually as an oil-like layer on the surface of PC as a separated phase at higher concentrations of PDMSOH.

The mechanism of impact toughening can be understood by the fact that siloxanes have extremely low glass transition temperature and also they are much softer material compared to the base PC resin.

Impact stress on PC is transferred to the softer siloxane modifier that results in enhanced toughness and also low temperature ductility due to the sub-zero glass transition temperature of PDMSOH. Incorporation of siloxane in the PC matrix with uniformly dispersed phases, good compatibility and adherence are a few factors that result in appreciable modification in low-temperature impact strength and it could only be achieved by reactive blending between the two phases.

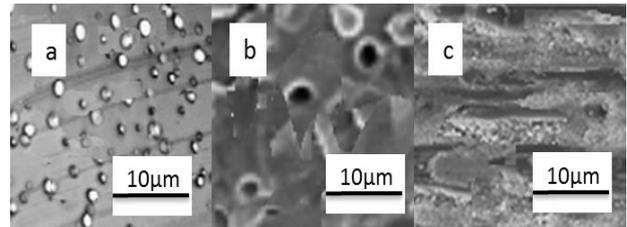


Fig. 3. SEM of PDMSOH-PC blend (a) 0.5 wt% (b) 3.0 wt% (c) 3.5 wt%.

Table 2. Change in Izod impact strength at different concentrations and viscosities of PDMSOH

PDMSOH concentration [wt %]	Izod Impact Strength [J/m] at -30°C					
	PDMSOH 750	A	B	C	D	PDMSOH 3500
0.5	162	170	174	178	181	185
1.0	220	223	226	228	232	235
1.5	316	321	331	339	346	355
2.0	395	406	414	428	446	460
2.5	415	426	440	477	508	540
3.0	445	490	525	585	615	655

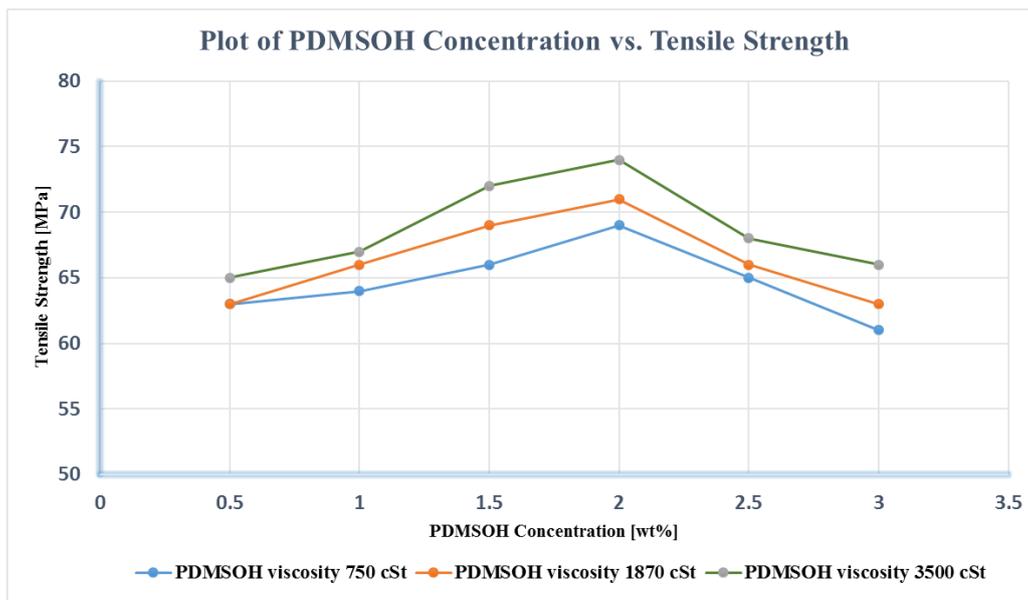


Fig. 4. Effect of PDMSOH concentration on tensile strength of PC

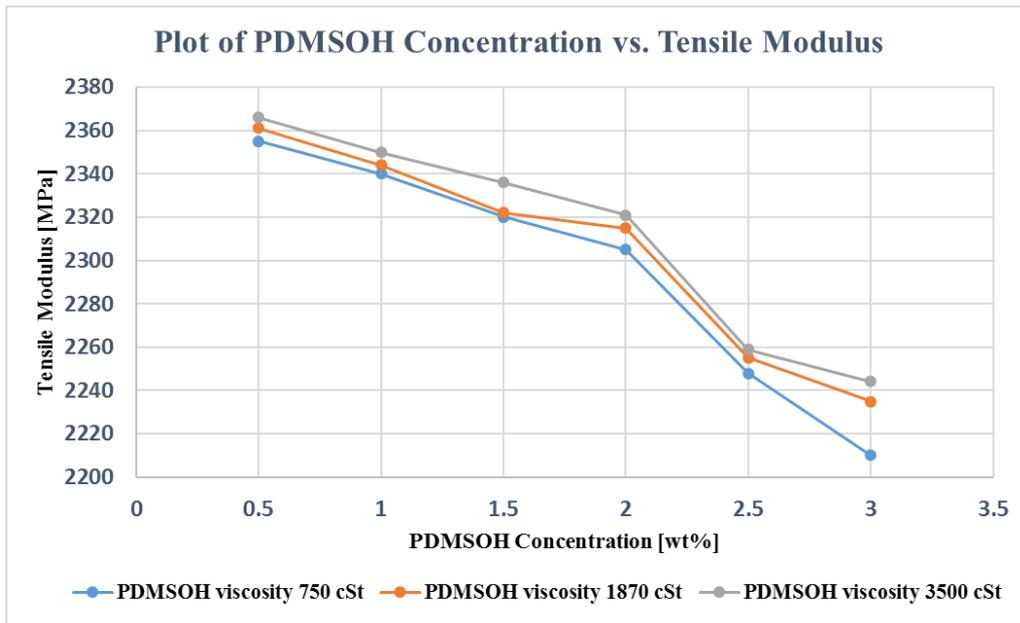


Fig. 5. Tensile modulus of PC at different concentrations and viscosity of PDMSOH

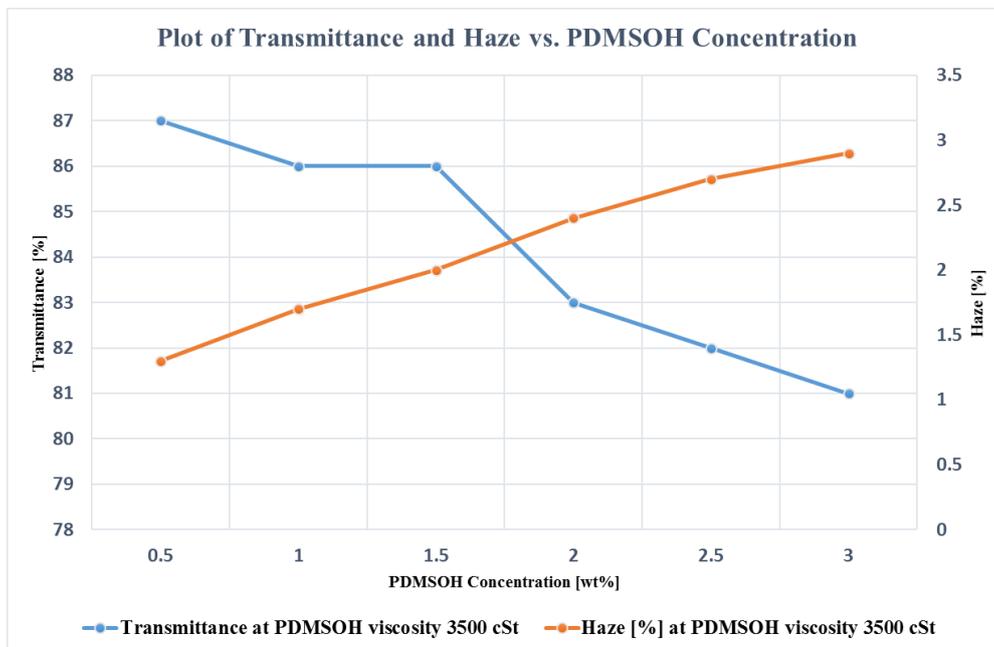


Fig. 6. Influence of PDMSOH concentration on transmittance and haze

Concomitant Effects on Other Properties

Tensile strength and modulus are also very important mechanical properties required for a particular application of PC. While modifying PC it is essentially required to observe the influence of modifier on these properties. As shown in Fig. 4, tensile strength of modified PC initially increases upto 2.0 wt% concentration of PDMSOH and then keeps decreasing upto 3.0 wt%. Improvement in tensile strength is achieved by the enhanced adhesion between the polymer chains by PDMSOH. Lower molecular weight chains of siloxanes in PDMSOH of viscosity 750 cSt are more evenly dispersed in the

base polycarbonate resin which results to maximum enhancement in tensile strength. However, as the molecular weight of PDMSOH chains increases with the higher viscosity, dispersion is adversely affected, probably due to the tendency of polymer chains to clutter and entangle more with the longer chain lengths. Beyond 2.0 wt% concentration of PDMSOH, there is reduction in tensile strength due to the weakening of interface beyond a certain concentration of the siloxane modifier in PC, however, at lower concentrations it improves the inter-chain binding in PC. Higher viscosity has a lesser impact on tensile strength as shown in Fig. 4 as

PDMS molecules of longer chain lengths tend to lump instead of adhering on PC chains whereas siloxane molecules of shorter chain lengths spread more evenly and uniformly at the PC-PDMS interface. Contrary to tensile strength, tensile modulus slightly decreases up to 2.0 wt% concentration of PDMSOH as shown in Fig. 5. This mechanical behaviour is attributed to incorporation of a softer material, i.e. siloxane in PC which increases the strain as the material loses its stiffness. Modulus further sharply decreases up to 3.0 wt% concentration of PDMSOH as shown in Fig. 4. Decrease in tensile strength and increase in strain at higher concentrations of siloxanes are the main cause of the substantial reduction in the tensile modulus of modified PC. One of the most useful properties of polycarbonate is its excellent optical property. Optical transmittance of the material is comparable to glasses and in the base PC resin, it is in the range of 86-88% [26]. Modification of PC for its enhanced mechanical properties generally has concomitant effects on its optical property. This effect is observed mainly because of difference in the refractive indices of polycarbonate and siloxane. The extent of optical transmittance and haze affected by siloxane also depends on the morphology, dispersion and concentration of siloxane. As shown in Fig. 6, the optical transmittance mildly decreases upto 1.5 wt% concentration of PDMSOH and then sharply decreases up to 3.0 wt%. This phenomenon can be understood by the fact that at lower concentrations, PDMSOH is finely dispersed in PC and its domain sizes are mostly less than 1-micron size as shown in SEM Fig 3(a). It therefore does not have much impact on the path of incident light and not much decrease in transmittance is found. However, at higher concentrations, when phase boundaries are bigger, as shown in Fig.3 (b), the material's optical property is substantially affected due to large aberration in the path of incident light and thus transmittance is reduced to 82% (Fig.6). Haze consistently yet mildly increased (Fig.6) as concentration was increased from 0.5 to 3.0 wt%. Effect of viscosity on both optical transmittance as well as haze was not observed and it was almost the same for all the viscosities of PDMSOH. Influence on optical properties of siloxane modification however calls for a detailed study so that the application of PC where both mechanical and optical properties are equally important, can be observed as per the requirement. There is a good scope of further research on the optical properties of PC simultaneously with modification of mechanical properties specially where higher concentrations of impact modifier are

needed. Siloxane itself has good transmittance and its incorporation in PC only mildly affects the optical property. Thus, modified PC maintains its usefulness for many optical applications of PC like snow goggles, bulletproof glass and visors.

CONCLUSIONS

- Low-temperature impact toughness of reactive blends of hydroxyl terminated siloxanes with polycarbonate is substantially enhanced from 124 to 655 J/m at -30°C and the method developed for impact modification is simple and cost-effective.
- This work also gives good insight about the concomitant effects on other properties, i.e. tensile strength, modulus, optical transmittance and haze while carrying out impact modification.
- Modification of impact toughness by the method reported here also has a good effect on tensile strength contrary to conventional blending with impact modifiers where impact strength is enhanced at the cost of reduction in tensile strength.
- Chemical linkage of siloxane by transesterification not only provides the advantage of copolymer of PC and PDMS but also acts as compatibilizer for additional amount of siloxane that may have to be added in the PC matrix for a particular application.
- Very useful and interesting results for tensile strength variation were also obtained which can be used to optimise the siloxane incorporation in order to achieve desired mechanical properties at both room temperature and sub-zero temperature.
- Optical properties of the modified PC do not change much and are well in the range of properties required for low-temperature optical application of PC, e.g. snow goggles, visors and bullet proof glasses, however there is ample scope of further detailed research on the optical properties of polycarbonate along with its impact modification.

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