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RESEARCH ARTICLE

A REVIEW ON: GLASS TRANSITION TEMPERATURE.

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Abstract

When heat is applied to the material like polymer, the molecules of polymer get energy and they start to move around .When heat energy is enough to change the amorphous rigid structure to the flexible structure some point. The polymer molecules start to freely move around each other. This caused transition point of the polymeric material is caused the glass transition temperature. The physical properties of the polymer depend on this temperature value. The use of polymer above the transition value depends on what properties are needed for the polymer. At ambient material which exists in flexible, rubbery state shows typically transition value in 0^0C to -150^0C range. When rigid, glassy polymer is being used below the Tg it means polymer has high strength in such areas as tension, compression, shear etc.

Introduction:-

As the temperature increases polymer undergoes transition and marketed changes in material properties are observed. The temperature at which these changes observed is known as glass transition temperature. By knowing the Glass transition temperature (T_g) one can get the idea about physical properties of particular polymer (Champion D, et al., 2004). By identifying the Glass transition temperature we can determine the existence of material in crystalline or amorphous state, viscous rubbery, super cooled liquid, and less viscous liquid form.

In glassy state polymers are characterized by their hardness, stiffness, and brittleness. Below the glass transition temperature lower polymer movement of the polymer observed and above the glass transition temperature higher polymeric movement is observed. When low polymeric movement observed material found in rubber like polymer with lose flexibility and turn rigid, hard and, dimensionally stable, and when polymeric movement observed high then material is in amorphous form (Maynihan C T, 1976).

Phenomenon of glass transition is shown by both crystalline and amorphous solids. When solid substance heated they get melt, and instead of crystalizing they get converted to amorphous solid if quench cooled. When polymer in molten state is cooled and reaches to its glass transition temperature, change in polymer from elastic material to brittle one due to change in change mobility occur i.e. The mechanical property change in polymer is observed(Jenkins M, 2007). Below this temperature material is in glassy state, while above this temperature they turns into rubbery state and becomes subject to cold flow or creep. At glass transition temperature greater molecular mobility results in sticky behavior when viscosity of the amorphous material decreases considerably (Roth C B, et al., 2006).

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Below glass transition temperature material can undergoes limited degree of vibration they do not have the required energy to rotate about the bond and with respect to neighboring chain segment change in position is observed (Billmeyer F W, 1994). Above the glass transition temperature or at this temperature rotation set towards or moves to the particular side group and only short range molecular segment instead of high polymer segment would rotate at this segment.

The glass transition is the gradual transition and not a sharp transition which is the mid value of temperature region of transition between brittle and soft (Maynihan C T, 1976). The transparency and brittleness below the glass transition temperature is characterized by the vitreous state or glassy state.

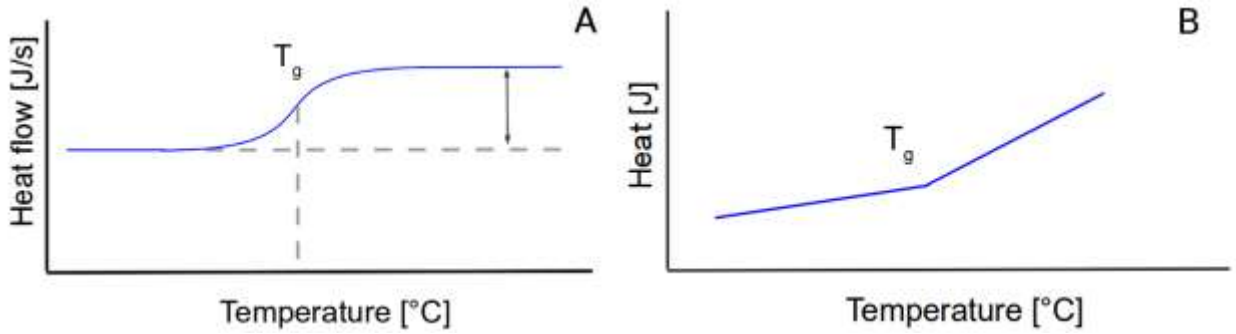


Fig no:- 1 Plot A: Heat flow versus temperature showing gradual transition that occur over a range of temperature. Plot B: Middle value of the slopped region taken as a glass transition.

A vitreous form of carrier which solubilizes the drug molecule in a homogeneous system is known as a glass solution. Major advantage of this glass solution over solid solution is as a true solid they do not possess the strong lattice hence do not present this barrier to rapid dissolution (Kulkarni P, et al., 2011). Again major disadvantage of glass solution is that they are present in metastable state and do not in crystalline state hence, depending on storage condition and physiochemical properties a glass can convert to crystalline solid. This change in physical conditions or physiochemical properties may lead to problem in dissolution phenomenon.

Measurement of glass transition temperature (T_g):-

The glass transition temperature estimated by the Fox equation is given below. This Fox equation can be applicable for random copolymer, dry formulations, and amorphous mixtures. Value can be calculated by following equation, again this T_g value of copolymer usually fall between those of homopolymer (Hak-Kim C, et al., 2004).

The relationship of two homopolymer estimated as given below:

$$1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

Where,

W_1 and W_2 are the weight fraction of homopolymer 1 and 2.

T_{g1} and T_{g2} are the glass transition temperature of homopolymer 1 and 2.

This glass transition temperature also characterized as the second order transition. The value and characteristics of particular polymer structure closely related to the stiffness and intermolecular forces. In a binary solid water mixture the glass transition temperature of such system depends strongly on the water concentration T_g can be determined if the moisture content is known. The equation to determine T_g, model proposed by Gordon and Taylor (Gaula A M, and Adamopoulos K G, 2010).

$$Tg = \frac{(1 - Xw).Tgs + k\,.Xw.Tgw}{(1 - Xw) + k.Xw}$$

Where,

T_g is Glass transition temperature of mixture and T_{gs}, T_{gw} are the glass transition temperature solid and water respectively.

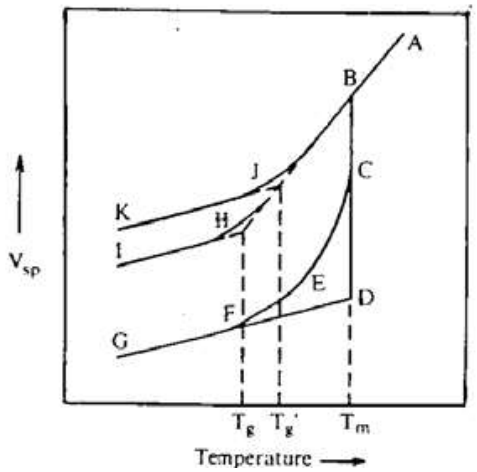
X_w-mass fraction of water,

k-Gordon- Taylor parameter.

Glass transition temperature measurement techniques:-

- Dynamic Mechanical Measurement (Aloul F, et al., 2006).
- Thermal Expansion Measurement (Martin A, et al., 1991).
- Elastic Hardness (Martin A, et al., 1991).
- Differential Scanning Calorimetry (Aloul F, et al., 2006).
- Specific Heat Measurement (psic.ws/mactest/tg 2007).
- Isothermal Compressibility (Martin A, et al., 1991).
- Refractive Index (Billmeyer F W, 1994).
- Broad line NMR (Billmeyer F W, 1994).
- Thermomechanical Analysis (Martin A, et al., 1991).
- Micro heat transfer measurement (Paradkar A R, et al., 2003).

Graph 1:- Specific volume against temperature for solids forming glass.



Below T_g:

Polymer material observed is rigid hard and viewed as glass material is closer to a crystalline solid. Rate of cooling determines the location of T_g.

Between Tm and T_g:

The rubber like physical behavior of the polymer in this intermediate segment depending on the polymer structural regularity and on experimental condition polymer material may range between near 100% amorphous chain polymer cluster.

Above T_m:

Above T_m value in this segment, the polymer melts or remains in liquid state; viscosity of polymer in this state depends on the molecular weight of a polymer.

Table 1:- Reported glass transition temperature of some drug molecules.

Drug molecules	**Glass Transition Temperature (^{0}C)**
Albendazole	60
Ketoconazole	44.85
Felodipine	42.7
Indomethacin	42
Saquinavir	107
Itraconazole	57.85
Mefenamic acid	57
Nimodipine	20
Omeprazole	57
Nifeipine	48
Etoricoxib	40.8

Celecoxib	58.1
Ibuprofen	-45.27
Inulin	155
Meglumine	18.9
Acetaminophen	25.85
Glafenine	63
Oridonin	126
Griseofulvin	88
Flurbiprofen	-4.65
Ketoprofen	-14
Carbamazepine	61
Carvedilol	42
Fenofibrate	17.15
Indomethacin	44.85
Dipyridamole	40
Naproxen	29
Felodipine	41
Chlorpropamide	15.39
Cloperastine HCL	41.17
Melatonin	20.12
Propranolol HCL	43.45
Quinidine	68.35
Terfenadine	69.05
Tolbutamide	13.16
Diazepam	46
Hesperetin	82
Metolazone	109
Valsartan	76
Telmisartan	127.85
Tadalafil	147
Nimesulide	20
Cimetidine	36

Table 2:- Reported glass transition temperature of some polymers.

Name of polymer	**Glass transition temperature**
Povidone K17	126
Hydroxy Propyl methyl cellulose	172
Povidone K25	152.4
Eudragit L 100	67
Povidone K12	101
Povidone K 17	136
Povidone K 30	156
Povidone K 90	177
Copovidone	105 to 108
Eudragit E 100	45
Eudragit RS 100	64
Eudragit RTM S100	160
Eudragit L 100-55	110
Eudragit RTM L 100	150
Eudragit RTM E	50
Eudragit FS 30 D	48
Eudragit NE 30 D	9
Eudragit NM 30 D	11

Poly acrylic acid	106
Poly methyl acrylate	8
Polyhydroxy butyrate	-55
Polyethylene Terephthalate(amorphous)	65
Carbopol 934	67.89
HPMC Acetate succinate	113
Polyethylene Terephthalate 133	87
Polyethylene Terephthalate 135	82
Polyethylene Terephthalate 163	92
Poly ethylene oxide	-67
Poly vinylpyrollidone	168
HPMC Pthalate	143
Pluronic F 127	56
Polyglycolide	35-40
Poly(P-dioxanone)	-10 to 0
Polylactide (PLA)	63.8
Poly caprolactum (PCL)	-60
Poly butylene Succinate	-45 to-10
Poly hydroxybutyrate-co-hydroxyvalerate(PHBV)	-5 to 20
Chitosan	203
Methylcellulose	184 to197
Hydroxy propyl cellulose	105
Hydroxy propyl methyl cellulose E 5	150
Hydroxy propyl methyl cellulose E 15	154
Hydroxy propyl methyl cellulose E 50	164
Poly vinyl acetate	28
Poly vinyl alcohol	85
Poly vinyl chloride	87
Poly oxyethylene	-67
Poly oxymetylene	-55
Polyethylene glycol 4000	45
PVP Vinyl Acetate	106
PVP K 12	117
PVP K 29	176
PVP K 90	181
Kollicoat	45
Soluplus	70
Plasdone S-630	106

Factor affecting Glass transition temperature:-

Molecular structure:-

Substitution of a bulkier group in material or the insertion of inflexible side group increases the T_g of a material due to decrease in mobility observed (Jenkins M, 2007 and Champion D, et al., 2004)**.**

eg. Substitution of bulkier group (carbazole) in Poly-N- vinyl carbazole shows increased value of glass transition temperature (T_g).

Molecular weight:-

Increase in molecular weight in case of straight chain of polymer decreases in chain end concentration. This results in increased glass transition temperature (T_g). Change in molecular weight of material changes with respect to stronger interaction and decreased end group concentration and increased value of T_g (Zeng X M, et al., 2001, Montserrat S and Colomer P, 1984, Roth C B, et al., 2006).

Addition of moisture content:-
Increase in moisture content shows decrease in the T_g value observed. The plasticizing effect of water is due to weakening of hydrogen bonds and intra, inter-macromolecular dipole-dipole interaction due to shielding of their attractive forces shown by the water molecule. (Gaula A M, and Adamopoulos K G, 2010).

Chemical Cross linking:-
Increased value of glass transition temperature observed with increase in crosslinking hence decreased mobility of the material (Billmeyer F W, 1994).

Side group length:-
Polymer chain moves apart from each other with increase in length of side group. As the increase in free volume in the molecule results in decreased value of T_g (Jenkins M, 2007 and Champion D, et al., 2004).
eg. with increase in chain length polyvinyl n-butyl ether showed decreased T_g.

Thickness of Polymer film:-
As increase in the thickness of polymer film increased value of T_g observed, and as decreased in the thickness of polymer film decreased value of T_g (Roth C B, et al., 2006 and Forrest J A, et al., 1996).
eg. decreased in film thickness of polystyrene decreased value of T_g observed.

Addition of Plasticizer:-
Addition of plasticizer to the polymer decreases the T_g of a polymer. Above result observed due to increase in free volume in a polymer (Honary S, et al., 2002 and psic.ws/mactest/tg 2007).
eg. polyethylene glycol- plasticizer.

Rate of cooling:-
Slower the rate of cooling of molten solid mass then obtained T_g value is low, and higher the rate of cooling of solid molten mass observed T_g value is high (HSU C L, et al.,2003, Maynihan C T, 1976 and Ediger M D, et al.,1996).
eg. cooling rate of sucrose shows the above effect.

Presence of double bond in backbone:-
Double bond presence in back bone decreases the rotation of bond, Hence increase in free volume and decreased Tg observed (Jenkins M, 2007).
eg. low T_g value of polybutadiene as compared to polybutane containing side chain double bond.

Presence of Polar group:-
Increase of intermolecular forces due to presence of polar group, cohesion and inter chain attraction leads to decrease in free volume. As decrease in free volume results in increased value of T_g (Martin A, et al., 1991).

Branching:-
There is decreased mobility of polymer chain with increase in branching, as branching increases rigidity of polymer increases. Increase in rigidity increases T_g value (Cory W C, et al., 2010, Sartomereurope 2007, Mahlin D, et al., 2013).

Table: - 3 Case studies reported.

Drug	**Polymer**	**Method**	**Significance of Glass transition temperature**
Acetaminophen (T_g-25.85^{0}C)	PovidoneK17 (T_g-126^{0}C)	Spray drying	Polymer Tg and stabilization of formulation found inverse relationship. Amorphous drug show increase in oral bioavailability by 26.4 fold.
Ibuprofen (T_g-45.25^{0}C)	PVP (polyvinyl pyrrolidone) (T_g-168^{0}C)	Solid dispersion	Single Tg value of the formulation observed which shows that complete miscibility of the PVP and Ibuprofen.Increases in the Tg value observed as the plasticizing effect of PVP increases with increase in its own

			concentration in the formulation.
Ibuprofen (T_g-45.25^{0}C)	Pluronic F 127 (T_g-56^{0}C)	Physical mixture	Solubility of the drug found increases with increase in the concentration of the Pluronic F127.Hence used in the solubility enhancement of the drug in the formulation.
Fenofibrate (T_g-17.15^{0}C)	Kollicoat (T_g-45^{0}C)	Film freezing	Rapid diffusion of the drug molecule due to low Tg value of the polymer. This leads to lower level of supersaturation due to drug crystallization.
Celecoxib	Pluronic F 127 (T_g-56^{0}C)	Spray drying	Powder becomes sticky and may cause sticking of the powder to the side wall of the drying temperature exceeds polymer Tg.
Mupirocin calcium (T_g-59.10^{0}C)	Eudragit RS (T_g-56.30^{0}C)	Spray drying	Detection of transition being overlapped with desolvation. Plasticizing effect of residual methanol (1.4%) on spray dried drug. Residual methanol has no effect on polymer transition. Drug found in amorphous form after characterization of thermogram.
Felodipine (T_g-42.7^{0}C)	PVP (polyvinyl pyrrolidone) (T_g-168^{0}C), PEG (polyethylene glycol) (T_g-45^{0}C)	Solid dispersion	Drug shows lower melting temperature than the Tg of the PVP, and melts above the melting temperature of the PEG. Dissolution effect observed close or above the glass transition temperature of the polymer. When DSC of the formulation was carried out only the glass transition of Felodipine and PVP detected. Above result gave an indication that prepared system was immiscible system in which drug is dispersed in PVP matrix.
Ketoconazole (T_g-44.85^{0}C)	Pluronic F 127 (T_g-56^{0}C)	Solid dispersion	Reduction in crystalline nature was observed. This transition phenomenon observed at Tg value. Amorphous nature increases the dissolution rate, but nature of drug is less Amorphous than the solid dispersion of drug with PVP K 30 which shows complete amorphous nature of drug.
Ketoconazole (T_g-44.85^{0}C)	PVP K 30 (T_g-156^{0}C)	Solid dispersion	Drug was found in completely amorphous nature indicated by X-ray powder diffraction and DSC. Amorphous nature of drug due to transition at Tg shows increased dissolution rate. It shows more (complete) amorphous nature of drug than the solid dispersion of drug with the Pluronic F 127.
Hesperetin (T_g- 82.^{0}C)	PVP (polyvinyl pyrrolidone), (T_g-168^{0}C), PEG (polyethylene glycol) (T_g-45^{0}C)	Solid dispersion	Drug melts above the melting temperature of the PEG. When PVP used in the
Hesperetin (T_g-82.^{0}C)	PVP (polyvinyl pyrrolidone) (T_g-168^{0}C)	Physical mixture	Drug melts 70^{0}C above the Tg value of the PVP and not by any moisture effect. Dissolution of drug induced by these interaction results in drastic effect on its melting.
Clotrimazole	Poly ethylene oxide (T_g-67.^{0}C)	Hot melt extrusion	Increase in the concentration of the PEO increases the Tg value of the formulation. Brittle failure of the film observed when the Tg of the formulation was above the storage or testing temperature

Ketoconazoe (T_g-44.85^{0}C)	PVP K 30 (T_g-156^{0}C), Pluronic F 127 (T_g-56^{0}C)	Physical Mixture	Both the polymer have higher Tg value than the pure Drug. Rate of dissolution was observed higher than the pure Ketoconazole drug.
Mupirocin calcium (T_g-59.10^{0}C)	Eudragit RS (T_g-56.30^{0}C)	Solid dispersion	Complete miscibility for all drug polymer ratios were found because of single glass transition temperature was observed.
Felodipine (T_g-44.85^{0}C)	PVP (polyvinyl pyrrolidone) (T_g-168^{0}C)	Physical mixture	Enhanced dissolution occur above the glass transition temperature of the polymer. Two materials were miscible with each other in molten state. Absorbed moisture during drug dispersion in PVP increases the free volume and decreases the Tg of PVP. Macromolecular chain motions begin at low temperature hence results in drug polymer interactions. DSC is the sensitive technique to characterize transition phenomenon.

Conclusion:-

This article includes review of literature for glass transition temperature (T_g). The T_g value of the material gives its existence in crystalline or amorphous state. The effect of glass transition temperature on the physical characteristics of polymers and use of polymer material according to the value above and below transition temperature can be useful in the development of drug delivery system. Various T_g ranges of drug and polymer reported in case studies will be beneficial for further study related to change in physical characteristics and effect of drug polymer interaction on T_g values was studied.

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