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Thermal Transitions in Polymers

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CONTENTS

[Introduction](#)

[Glass transition and Melting Transition](#)

[Melting Point or First Order Transition](#)

[Glass Transition or Second Order Transition](#)

[Brittle Point](#)

[Development of Crystallinity in Polymers](#)

[Crystallization of Rubber on Cooling](#)

[Mechanism of Crystallization](#)

[Stress-induced Crystallization of Rubber](#)

[Melting of Rubber](#)

[Polymer Single Crystals](#)

[Structure of Bulk Polymers](#)

[Spherulites](#)

[Thermal Analysis](#)

Key Words

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Introduction: Polymer Morphology

Two different states or forms can be identified in which a polymer can display the mechanical or thermomechanical properties that can be associated with solids, viz., the form of a *crystal* or the form of a *glass*. It is not really the case that all polymers are able to crystallize. As a matter of fact, a high degree of molecular symmetry and microstructural regularity within the polymer chains are a prerequisite for crystallization to occur. Even in those polymers, which do crystallize in any rate, the ultimate degree of crystallinity developed is mostly less than 100%.

Studies of physical form, arrangement and structure of the molecules or the molecular aggregates of a material system relates to what is known as its *morphology*. Polymer morphology covers the study of the arrangement of macromolecules over the *crystalline*, *amorphous* and the *overlapping regions* and the overall physical clustering of the molecular aggregates.

When cooled from, the molten states, different polymers exhibit different tendencies to crystallize at different rates depending on many factors including prevailing physical conditions, chemical nature of the repeat units and of the polymer as a whole, their molecular or segmental symmetry and structural regularity or irregularity, as referred to above. Bulky pendent groups or chain branches of different lengths hinder molecular packing and hence crystallization. The nature of the crystalline state of polymers is not simple and it should not be confused with the regular geometry of the crystals of low molecular weight compounds such as sodium chloride or benzoic acid. There are polymers, which are by and large amorphous, and they have very poor tendency to get transformed into ordered or oriented structures on cooling to near or even below room temperature. Natural or synthetic rubbers and glassy polymers such as polystyrene, acrylate and methacrylate polymers belong to this class.

In a crystalline polymer, a given polymer chain exists in or passes through several crystalline and amorphous zones. The crystalline zones are made up of intermolecular and intramolecular alignment or orderly and hence closely packed arrangement of molecules or chain segments, and a lack of it results in the formation of amorphous zones.

Glass Transition and Melting Transition

On the basis of following the changes in a mechanical property parameter such as shear modulus with changes (rise) in the temperature of observation for polymer material systems, one can readily observe successively – (i) *glass transition* and (ii) *melting transition* phenomena, more easily from a graphical plot, and may also have a measure of the glass transition temperature, T_g and the melting temperature, T_m .

The glass transition and the melting transition may also be observed and ascertained from a plot of specific volume (V_{sp}) versus temperature. Let us consider the various possibilities as a melt is cooled from the position A at a high temperature that corresponds to a relatively high V_{sp} value as well, fig. 1. The path ABDG shows how the specific volume drops down as a low molecular weight compound is frozen. As the

melting temperature T_m is reached at the point B, a sharp discontinuity in V_{sp} is observed (BD). The slopes AB and DG give measures of coefficients of thermal expansion of the liquid and the solid respectively. The thermal expansion coefficient also suffers a discontinuity at T_m .

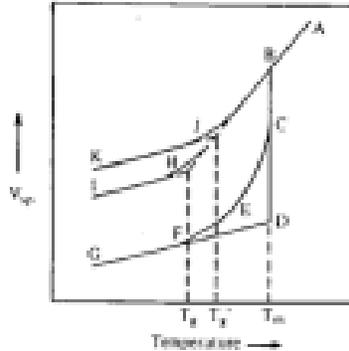


Fig.1:Schematic diagram highlighting possible changes in the specific volume (V_{sp}) of a polymer with change in temperature .

We may however, start with a molten polymer material at A and observe volume change as described by the path ABHI and there is no discontinuity notable at T_m . The liquid line AB gets further extended beyond T_m with lowering of temperature and it is seen to suffer a change in slope at a much lower temperature, T_g and finally, turns into a different linear portion (HI) of a much lower constant slope. Here, actually, the slope-change occurs over a small range of temperature (which may usually range about $5 - 10^{\circ}\text{C}$), but extrapolation of the two linear parts allows right assessment of T_g by this method. The zone HI represents the *glassy* state that ensues as the glass transition temperature is reached or just crossed as we go down in temperature. Transition to the glassy state is also commonly termed as vitrification. The region BH represents the existence of a super cooled liquid state or *rubbery* state of relatively poor dimensional stability, even under the influence of a low stress.

For all polymers, the glassy state is always attained finally on cooling, irrespective of whether the polymer being tested is crystallizable or not. Even under situations favouring crystal formation, it does not necessarily mean that crystallization occurs rapidly or completely. There still remains in most cases significant portions of amorphous zones after the *primary crystallization* process is completed.

The path ABCEFG in fig. 1 represents the case of a partly crystalline, partly amorphous polymer system. On cooling down to T_m , crystallization begins and the characteristic discontinuity in V_{sp} becomes apparent even though the sharpness at which T_m is revealed is not as pronounced for polymers as for a low molecular weight compound, and this can be appreciated from the curvature of the portion of the path BCEF. For such a system, FG represents the glassy zone and BA the melt or liquid zone and BCEF zone is by and large the amorphous rubbery (super cooled liquid) zone. The point F, where slope between the segments EF and FG changes corresponds to the glass transition point, T_g , and the polymer in such a case remains by and large amorphous. If partial crystallization

would occur on cooling below T_m , the amorphous content decreases and in that case, the change in slope at T_g may be much smaller and harder to detect.

The path ABJK may appear as a variation of the path ABHI and here, AB describes the liquid state, BJ the super cooled liquid or the rubbery state and JK describes the glassy state. The path ABHI shifts to ABJK under the condition of a higher cooling rate; it is likely that T_g is also displaced to a higher temperature (T_g') for a faster cooling rate.

Thus, the temperature response of linear polymers may be viewed as divided into three distinctly separate segments:

1. Above T_m :

In this segment, the polymer remains as a melt or liquid whose viscosity would depend on molecular weight and on the temperature of observation.

2. Between T_m and T_g :

This domain may range between near 100% crystalline and near 100% amorphous chain molecular clusters depending on the polymer structural regularity and on experimental conditions. The amorphous part behaves much like super cooled liquid in this segment. The overall physical behaviour of the polymer in this intermediate segment is much like a rubber.

3. Below T_g :

The polymer material viewed as a glass is hard and rigid, showing a specified coefficient of thermal expansion. The glass is closer to a crystalline solid than to a liquid in behavioural pattern in terms of mechanical property parameters. In respect of molecular order, however, the glass more closely resembles the liquid. There is little difference between linear and cross linked polymer below T_g .

The location of T_g depends on the rate of cooling. The location of T_m is not subject to this variability, but the degree of crystallinity depends on the experimental conditions and on the nature of the polymer. If the rate of cooling is higher than the rate of crystallization, there may not be an observable change at T_m , even for a crystallizable polymer.

The simple device used to follow volume changes upon cooling or heating is called a dilatometer, having a glass bulb or ampoule at the bottom fitted with a narrow bore capillary at the top, as in fig. 2. A dilatometer may also be used in studying progress of polymerization with time at a given temperature by following volume contraction of liquid monomer system (the polymer being formed having a higher density than the monomer being polymerized). For studies with a polymer say, polystyrene, the sample is placed in the bulb, which is then filled with an inert liquid, usually mercury and the volume changes with change of temperature (or sometimes at a constant temperature for a phase change, such as at T_m) are then registered, as in a thermometer. The expansion / contraction of mercury due to change of temperature is to be duly accounted for during experimentation for a volume change of the polymer sample. The experiments are required to be accomplished by placing the dilatometer in a thermostated bath. The

sample must be immiscible with the displacement fluid and degreased to eliminate air entrapment. Specific volume – temperature plot for polystyrene showing a distinct change in slope at 95.6⁰C, indicates glass transition temperature, fig. 3.



Fig.2:A dilatometric arrangement for measurement of volume change of a polymer with change of temperature.

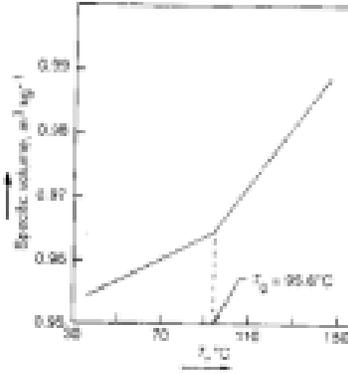


Fig. 3:Temperature dependence of specific volume for polystyrene indicating the glass transition temperature, T_g .

(Courtesy: Tata McGraw –Hill, New Delhi)

Thus, it is a common experience that raising or lowering of temperature, just as application or withdrawal of stress, greatly influences the physical structure and properties of polymers. With change of temperature a high polymer material passes through two distinct transitions characterized by (i) melting point or *first order transition*, denoted by T_m and (ii) the glass transition or *second order transition*, denoted by T_g .

Melting Point or First Order Transition

Melting of a crystalline solid or boiling of a liquid is associated with change of phase and involvement of latent heat. Many high polymers possess enough molecular symmetry and/or structural regularity that they crystallize sufficiently to produce a solid-liquid phase transition, exhibiting a crystalline melting point. The melting is quite sharp for some polymers such as the nylons, while in most other cases as for different rubbers and polystyrene, etc., the phase change takes place over a range of temperature. Phase transitions of this kind, particularly in low molecular weight materials, being associated with sharp discontinuities in some primary physical properties, such as the density or volume, V , $[V = (\partial G / \partial P)_T]$ and entropy, S , $[-S = (\partial G / \partial T)_P]$, which are first derivatives of free energy, are commonly termed *first order transitions*. Although we observe melting, a true first order transition or ideal melting in high polymers is frequently absent or missing, in view of the distribution of molecular weight and entanglements of chain molecules giving rise to the complex phenomenon of *retarded flow* or *viscoelasticity*.

Glass Transition or Second Order Transition

Glass transition or *second order transition* is not a phase transition and almost every polymeric or high polymeric material is characterized by a specific glass transition

temperature (T_g) or second order transition point (SOTP), appearing well below its (crystalline) melting point, T_m .

At T_g , the thermodynamic property parameters S, V and H merely undergo change of slope when plotted against temperature, without, however, showing sharp discontinuities as observed in the case of first order transitions, such as the idealized plot shown in fig. 4.

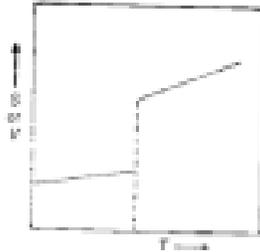


Fig. 4: First order transition showing an idealized phase transition (melting or freezing): Trend of change of volume or entropy with rise of temperature, showing discontinuity at the transition point. (Courtesy: Tata McGraw –Hill, New Delhi)

The properties that suffer discontinuities at the glass transition temperature are: heat capacity C_P , [$C_P = (\partial H / \partial T)_P$], coefficient of thermal expansion α ,

$$\left[\alpha = \frac{1}{V} (\partial V / \partial T)_P = \frac{1}{V} \cdot \frac{\partial}{\partial T} \{ (\partial G / \partial P)_T \}_P \right]$$

and isothermal compressibility K ,

$$\left[K = - \frac{1}{V} (\partial V / \partial P)_T = - \frac{1}{V} (\partial^2 G / \partial P^2)_T \right]$$

which are second derivatives of free energy and it is for this reason that the glass transition temperature, T_g is commonly referred to as the second order transition temperature, fig. 5. Refractive index (RI) also shows a sharp change at the glass transition point (T_g).

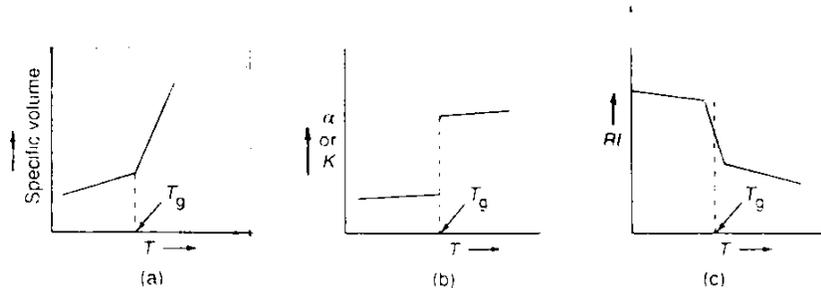


Fig.5: Trends of change in (a) specific volume, (b) coefficient of thermal expansion (α) or isothermal compressibility (K) and (c) refractive index (RI) of polymers with temperature indicating the glass transition (Courtesy: Tata McGraw- Hill, New Delhi)

The glass transition is not a phase transition and therefore, it involves no latent heat. Below this temperature normally rubber – like polymers lose flexibility and turn rigid, hard and dimensionally stable and they are then considered to be in a glassy state, while above this temperature, all normally rigid, stiff, hard glassy polymers turn soft and flexible, become subject to cold flow or creep and as such turn into a rubbery state. The difference between the rubbery and glassy states lies not really in their geometrical structure, but in the state and degree of molecular motion.

Below the glass transition temperature, T_g , the chain segments or groups, as parts of the chain molecular backbone, can undergo limited degrees of vibration; they do not possess the energy required to rotate about bonds and change positions with respect to segments of the neighbouring chains. At or slightly above T_g , rotation sets in, particularly of side groups or branch units, and it is conceivable that only *short range* molecular segments rather than the entire high polymer molecule would rotate at this point. The much higher coefficient of thermal expansion just beyond T_g is indicative of much greater degree of freedom of rotation.

At the respective glass transition or second order transition temperatures, different polymers may be viewed to be in an isoviscous state, and in reality, T_g is a common reference point for polymers of diverse nature, below which all of them behave as stiff rigid plastics (*glassy* polymer) and above which they appear *leathery* and *rubbery* in nature. As we understand, a useful rubber is a polymer having its T_g well below room temperature, while a useful plastic is one whose T_g is well above the room temperature. Table 4.1 lists the T_m and T_g values of some common polymers.

Table 1: T_m and T_g Values of Several Polymers

Polymer	Repeat Unit	$T_m, ^\circ C$	$T_g, ^\circ C$
Polyethylene	– CH ₂ – CH ₂ –	137	-115,-60
Polyoxymethylene	– CH ₂ – O –	181	-85,-50
Polypropylene (isotactic)	– CH ₂ – CH (CH ₃) –	176	- 20
Polyisobutylene	– CH ₂ – C (CH ₃) ₂ –	44	- 73
Polybutadiene (1, 4 cis)	– CH ₂ – CH = CH – CH ₂ –	2	- 108
Polyisoprene (1, 4 cis), (NR)	– CH ₂ – C(CH ₃) = CH – CH ₂ –	14	- 73
Poly (dimethyl siloxane)	– OSi (CH ₃) ₂ –	- 85	- 123
Poly (vinyl acetate)	– CH ₂ – CH (OCOCH ₃) –	---	28
Poly (vinyl chloride)	– CH ₂ – CH Cl –	212	81
Polystyrene	– CH ₂ – CH (C ₆ H ₅) –	240	95
Poly (methyl methacrylate)	– CH ₂ – C(CH ₃)(COOCH ₃) –	200	105
Poly tetrafluoroethylene	– CF ₂ – CF ₂ –	327	126
Poly caprolactam (Nylon 6)	– (CH ₂) ₅ CONH –	215	50
Poly(hexamethylene adipamide) (Nylon 66)	–HN(CH ₂) ₆ -NHCO-(CH ₂) ₄ CO –	264	53
Poly (ethylene terephthalate)	– O(CH ₂) ₂ – OCO – (C ₆ H ₄) CO –	254	69
Poly (ethylene adipate)	– O(CH ₂) ₂ – OCO – (CH ₂) ₄ CO –	50	-70

Molecular weight and molecular weight distribution, external tension or pressure, plasticizer incorporation, copolymerization, filler or fibre reinforcement, and cross linking are some of the more important factors that influence the glass transition temperature, melting point or heat – distortion temperature of a matrix polymer. The comparative lowering of T_m and T_g for modification of polymer by *external plasticization* (plasticizer incorporation) and by *internal plasticization* (comonomer incorporation) is shown in fig. 6. Generally, a comonomer incorporation i.e. copolymerization is more effective than external plasticization in lowering the melting point, while the latter process (external plasticizer incorporation) is more effective than the former (copolymerization) in lowering the glass transition temperature. Cross-linking causes significant uprise in T_g , as cross-links hinder rotation of chain elements, thus necessitating a higher temperature for inception of rotation of segments between cross-links. Likewise, higher molecular weight, leading to complex, *long range* chain entanglements, restricts scope for segmental rotation and thereby causes a rise in the T_g value with a notable levelling off effect for molecular weight $> 10^5$.

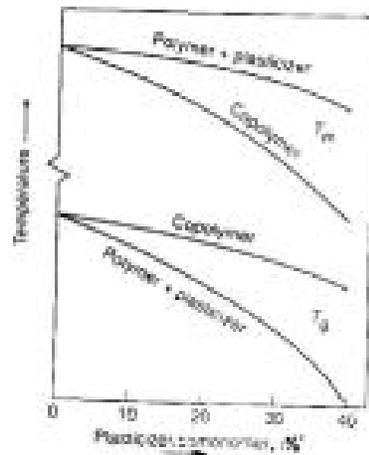


Fig. 6: Schematic plots showing relative lowering of T_m and T_g of a polymer by separately incorporating (a) an external plasticizer and (b) a comonomer by copolymerization. (Courtesy: Tata McGraw –Hill, New Delhi)

Brittle Point

A polymer is also characterized by a temperature called the brittle point¹ or brittle temperature (T_{br}) which is close to or somewhat higher than its glass transition temperature (T_g) for most high polymers. As the temperature of the polymer in its rubbery state is lowered, the flexible nature and rubbery properties are gradually lost and the polymer stiffens and hardens; at an intermediate stage, a temperature called the brittle point is attained at or below which the polymer specimen turns brittle and breaks or fractures on sudden application of load.

For comparison of brittle points of different polymers, it is necessary to do the testing under specified conditions, including specified sample size and thickness, degree and rate of cooling, etc. as the test is empirical in nature. The brittle point corresponds to a temperature at which the time interval of load application just matches or equals that needed by the test specimen to undergo the necessary deformation. At a lower

temperature, the specimen is unable to deform as rapidly, and hence it fails to withstand the load and thus breaks; above the brittle temperature, the time of load application is more than adequate for the specimen to absorb the applied energy and deform to escape fracturing or breakage. Lower molecular weight limits the scope for long-range molecular interactions and chain entanglements and hence leads to a higher brittle temperature. Changes in T_g and T_{br} with polymer molecular weight, as schematically illustrated in fig. 7, clearly shows that the trends of change for the two parameters are just the opposite. The difference between the two is much narrower in the higher molecular weight range, but it gets progressively wider as the molecular weight decreases.

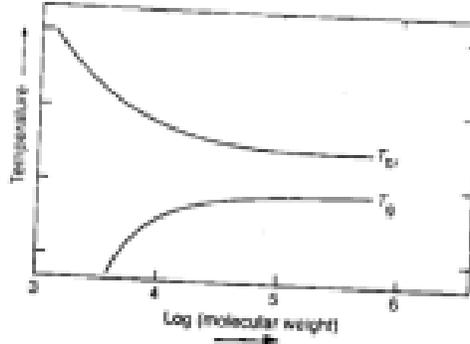


Fig. 7: Typical plots showing dependence of brittle temperature (T_{br}) and glass transition temperature (T_g) on polymer molecular weight. (Courtesy: Tata McGraw –Hill, New Delhi)

Development of Crystallinity in Polymers

Polymer morphological studies primarily relate to molecular patterns and physical state of the crystalline regions of crystallizable polymers. Amorphous, semi-crystalline and prominently crystalline polymers are known. It is difficult and may be practically impossible to attain 100% crystallinity in bulk polymers. It is also difficult according to different microscopic evidences, to obtain solid amorphous polymers completely devoid of any molecular or segmental order, oriented structures or crystallinity. A whole spectrum of structures, spanning near total disorder, different kinds and degrees of order and near total order, may describe the physical state of a given polymeric system, depending on test environment, nature of polymer and its synthesis route, microstructure and stereo – sequence of repeat units, and thermomechanical history of the test specimen. Further, the collected data for degree of crystallinity may also vary depending on the test method employed. The degree of crystallinity data shown in Table 2 must therefore be taken as approximate.

Polymers showing degrees of crystallinity $> 50\%$ are commonly recognized to be crystalline. The cellulosics (cellulose acetate) and also regenerated cellulose (viscose) used as fibres have crystallinity degree lower than that of native cellulose, the base fibre. The predominantly linear chain molecules of high-density polyethylene (HDPE) show a degree of crystallinity that is much higher than any other polymer known (even substantially higher than that for the low-density polyethylene (LDPE). For HDPE, the attainable crystallinity degree is close to the upper limit (100%). Atactic polymers in

general (including those of methyl methacrylate and styrene bearing bulky side groups), having irregular configurations fail to meaningfully crystallize under any circumstances.

Table 2: Approximate Degree of Crystallinity (%) for Different Polymers.

Polymer	Crystallinity (%)
Polyethylene (LDPE)	60 – 80
Polyethylene (HDPE)	80 – 98
Polypropylene (Fibre)	55 – 60
Nylon 6 (Fibre)	55 – 60
Terylene (Polyester fibre)	55 – 60
Cellulose (Cotton fibre)	65 – 70
Regenerated cellulose (Viscose rayon fibre)	35 – 40
Gutta Percha	50 – 60
Natural rubber (Crystallized)	20 – 30

Figure 8 provides a comprehensive idea about crystallization rate (volume change with time) at different selected temperatures. For high density polyethylene (HDPE), as the temperature is lowered, the volume changes proportional to the rates of crystallization rapidly increase and well below the actual melting point (127°C), the volume change soon becomes so rapid that measurements and observation become uncertain and difficult, if not practically impossible. The obvious consequence of the very high rate of crystallization in polyethylene is that it is virtually impossible to obtain and isolate the polymer in the amorphous state at room temperature i.e., under ambient conditions. Sudden chilling or quenching of the melt to below room temperature results in a material which is still largely crystalline, though expectedly with the likelihood of a somewhat lower degree of crystallinity than otherwise developed on normal melt – cooling. The reason for this state of affairs is that the time required for crystallization is far shorter than the time taken for cooling the test polymer specimen.

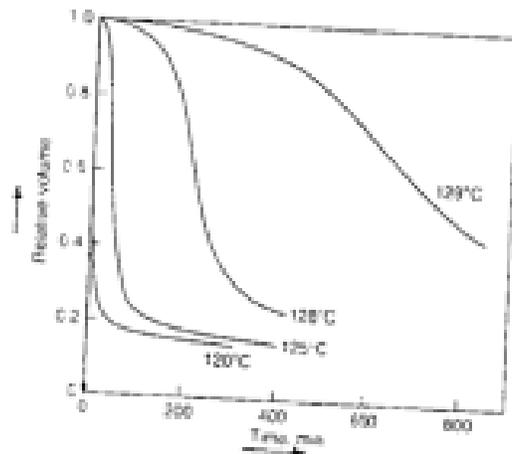


Fig. 8: Plot of relative volume with time (min) showing densification of polyethylene on development of crystallinity at different specified temperatures.
(Courtesy: Tata McGraw –Hill, New Delhi)

For practical reasons, therefore, the process of polymer crystallization is very conveniently studied and measured with confidence using a polymer that is by and large amorphous; natural rubber is one such polymer. The merit of using rubber as a model material for study of polymer crystallization is that the crystallization process is slow to allow due measurements with easy manipulations and it takes place in a convenient range of temperature.

It is worthy of mention that all rubbers (particularly those which are copolymers) are not crystallizable. Only those built up of chains characterized by chemically identical and regular repeat units, such as natural rubber, 1, 4 cispolyisoprene and certain grades of polychloroprene are capable of crystallization.

Crystallization of Rubber on Cooling

If unvulcanized natural rubber (NR) is held at a fixed low temperature, say 0°C , it slowly gets somewhat stiffened and hard, and loses flexibility and softness proportionately. However, the material still retains some degree of flexibility and toughness. The observed physical change is also associated with some enhancement in density or lowering in volume; the associated changes are consequences of slow development of crystallinity in the material.

Crystallization in an ordinary low molecular weight liquid on cooling to or below the freezing point takes place very rapidly, consequent to ready and fast molecular rearrangement from a disordered state to a very regular state of packing. A polymer melt system is, however, much more complicated due to chain entanglements, restricting free mobility of the chain segments, and consequently, hindering and delaying the desired rearrangement process on cooling. For rubber – like polymers, the time scale of crystallization is commonly much longer than for liquids of low molecular weight materials.

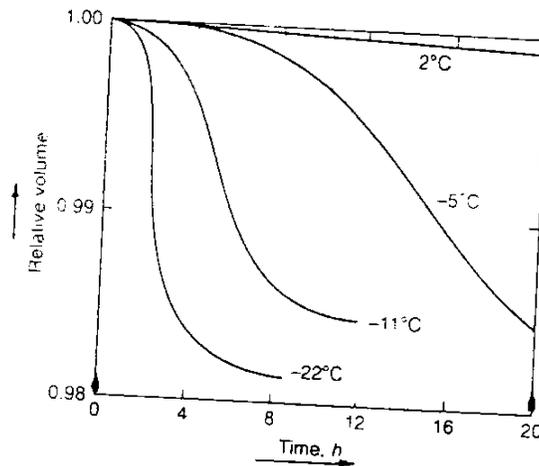


Fig. 9: Densification on crystallization of natural rubber, plot of relative volume vs. time (hour) at different temperatures. (Courtesy: Tata McGraw –Hill, New Delhi)

Trends of change in relative volume of natural rubber (NR) with time due to crystallization at different low temperature are shown in fig. 9. The attainable maximum crystallinity and the time span required for this to happen are very much dependent on the temperature of observation⁶. In each case, the volume contraction rate is relatively slow initially; the volume contraction (or crystallization) rate shows an increasing trend with time, passes through a higher steady zone at an intermediate time period and then finally drops down, decays or levels off giving a maximum attainable development of crystallinity degree at a given temperature. Lowering of temperature causes enhancement in the steady rate of crystallization of NR till about -25°C , where the steady rate vs. temperature plot, fig. 10 passes through a maximum. Further reduction in the temperature of crystallization causes a falling trend in the steady rates of crystallization as in fig.10. The crystallization is (nearly) completed in about five hours at -25°C . In natural rubber, the degree / extent of crystallinity under the most favourable situation does not exceed 30%.

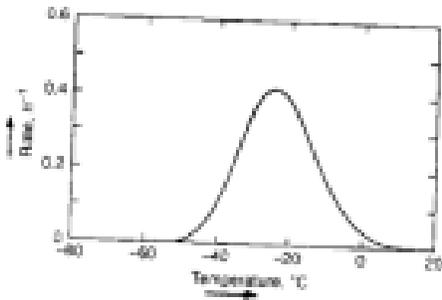


Fig. 10: Plot indicating trend of change in steady rate of crystallization with change in temperature for natural rubber (Courtesy: Tata McGraw –Hill, New Delhi)

Mechanism of Crystallization

As the polymer melt is kept at a temperature close to or slightly above its melting range, the initial slowness in crystallization rate build up (delayed crystallization) is linked with the initial process of nucleation. Growth of crystallites is contingent upon the development and existence of a certain number of very tiny growth centers or nuclei for the deposition of oriented chain segments. The growth centers are initially formed on extended cooling or holding of the melt at the specified temperature by coming together of a small number of chain segments in the course of their random motion (micro Brownian motion) under the prevalent situation. Nucleation is, however, common to all processes that turn an initially homogeneous medium into a heterogeneous system as a consequence of deposition of a separate phase.

As the growth is sustained and continued, the opposing effect of chain entanglements becomes increasingly severe and ultimately critical, thus imparting severe restrictions on the mobility of chain segments and thus making it difficult for them to get to a position for attachment to any one of the crystallites formed. Beyond this stage, the crystallization rate diminishes sharply and finally, the process dies down.

Lower temperature favours nucleation and lower thermal energy of the chain segments makes it less likely that a nucleus once formed would disappear again, the net result

being a gain in the number of nuclei and an increase in the overall rate of crystallization with progressive lowering of temperature. At progressively lower temperatures, however, the overall energy of the polymer system including that available to chain segments tend to get so much lowered that the segments seem to practically lose much of their mobility and hence their deposition on a nucleus formed is progressively hindered much more effectively and there appears a sharp dropping trend in the rates of crystallization. For natural rubber, the crystallization process gets effectively frozen out below -50°C , fig. 10.

Stress – Induced Crystallization of Rubber

It is a common knowledge and a matter of wide experience that stretching of a strip of vulcanized rubber makes it develop a temporary crystallinity by axial orientation of the chain molecules along the direction of stretching and that the orientational effect disappears instantly on withdrawal of the stretching force. A strip of raw or unvulcanized rubber also develops crystallinity when subjected to high extensions on application of a stretching force, but it remains more or less in the extended state (in view of the absence of restraining cross links) without notable retraction to its original state on stress release. However, when heated carefully in the subsequent stage, such as by dipping the test strip into slightly warm water (temperature $> 30^{\circ}\text{C}$) the crystals melt and allow the strip to revert largely to its unstrained state.

The cross links in the vulcanized rubber act as points of reinforcement and are responsible for accumulation of the strong retracting or restoring force that comes into play in breaking the stress – induced orientation (or the crystalline structure) on withdrawal of the applied stress. In the unvulcanized system, the absence of cross links allows varied degrees of chain uncoiling if not chain slippage on low/moderate extensions and whatever elastic restoring force accumulates is far too insufficient or inadequate to break the crystalline structure and induce dimensional recovery. Raising the test strip temperature to 30°C or slightly above this level, allows melting of the axially oriented crystallites, causing the rubber chain molecules to coil up and the test strip to retract to its initial or near initial (random / unoriented) state.

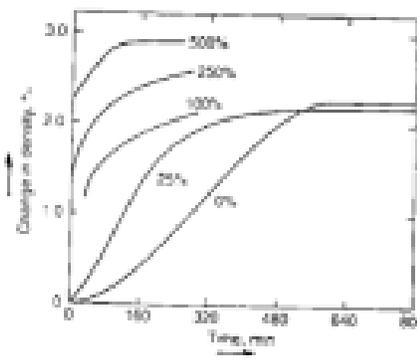


Fig. 11: Time-dependency of stress-induced crystallization (densification) of unvulcanized rubber held at 0°C for different indicated orders of fixed extensions, plot of density change (%) vs. time (min). (Courtesy: Tata McGraw –Hill, New Delhi)

Fig.11 shows the time-dependency of crystallization of unvalcanized rubber at a low temperature (here 0°C) on application of different fixed extensions revealing trends of % change (increase) of density with time of specified stretch application. Moderate extensions produce effects as observed for lowering of temperature. For extensions > 100%, however, the crystallization rates are very high, such that only final stages are practically observable.

Melting of Rubber

Much like crystallization, the opposite process, i.e., melting in polymer systems too is distinctive, diverse in nature and more complex than in low molecular weight material systems. The melting curves of a typical rubber (natural rubber) of low degree of crystallinity and of a typical plastomeric polymer (high density polyethylene, HDPE) of very high degree of crystallinity are shown in fig.12 and 13 respectively. For rubber, the curve shows the trend of change in volume with rise of temperature beginning at 0°C, fig.12. The beginning of melting is indicated by a steep rise in volume with rise of temperature and the melting process is seen to span over more than a range of 10°C for rubber crystallized at or slightly below 0°C, till the melting process is complete or over. Beyond this point, further enhancement in temperature gives a linear plot much in tune with the thermal volume expansion of the amorphous rubber.

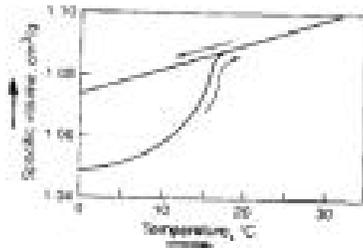


Fig.12: 'Melting curve' showing increase in specific volume (cm^3/g) vs. temperature ($^{\circ}\text{C}$) for natural rubber

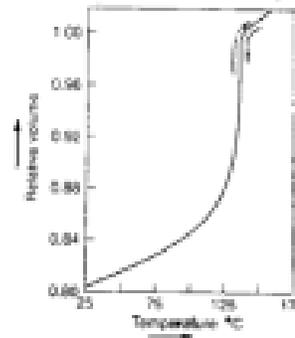


Fig. 13: Melting curve showing a plot of relative volume vs. temperature for rise for polyethylene.

(Courtesy: Tata McGraw –Hill, New Delhi)

The melting curve of the highly crystalline polymer polyethylene characteristically shows a sharp volume change and the temperature of the beginning and end of the melting process is usually limited well within a range of 10°C or to be more precise, within a span of 5°C. If after melting the rubber, the temperature is lowered again, fig. 12, the linear volume contraction for the amorphous rubber continues to much lower temperatures and the melting curve is not retraced in the reverse direction simply because, measurable recrystallization fails to occur in the time – span of the experiment. For the highly crystallizable polymer, polyethylene, however, the melting and crystallization / recrystallization processes are by and large reversible in a practical sense and the recrystallization curve is mostly a retrace of the melting curve, fig. 13 from the opposite direction.

For the amorphous polymer, natural rubber, whereas melting occurs over an extended range of temperature, the beginning of melting and the temperature range over which the melting process is accomplished and completed are also largely dependent on the temperature at which the preceding crystallization was done. Usually, melting begins at a temperature that is 4–6⁰C higher than the temperature at which the preceding crystallization was accomplished, fig. 14.

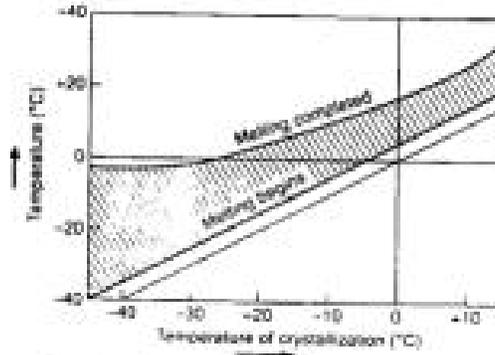


Fig. 14: Plot indicating dependence of melting range of natural rubber on temperature of crystallization, the diagonal line below the melting range (shaded zone) indicating temperature of crystallization. (Courtesy: Tata McGraw –Hill, New Delhi)

It is the common experience that in a polymer crystallizing from the melt, a crystallite domain being formed and increasing in size does not remain in equilibrium with the amorphous phase as because the segments of the chain molecules in the liquid or the amorphous phase are physically locked into the crystallites and also because the same molecule may pass from one crystallite to another via the intervening amorphous zones. This position of lack of true equilibrium between the solid (crystalline) and liquid (amorphous) phases in the rubber chain molecular system leads to some unique but interesting effects, as revealed by features in fig. 14. For rubber crystallized at very low temperatures, say, - 40⁰C, melting is complete at a temperature close to but < 0⁰C. If after completion of melting, the temperature is not allowed to rise any further and the rubber sample is held at the upper melting temperature for a long period, a second crystallization process would set in. Thus, it is possible to have simultaneous or consecutive melting and recrystallization in a given piece of rubber as it is slowly heated over the melting range (shaded area in fig. 14) after initial crystallization and then held at a specific temperature within that (melting) temperature range.

Polymer Single Crystals

Single crystals of different readily crystallizable polymers can be grown by slow cooling and precipitation from very dilute solutions. They appear in the form of very thin plates or *lamellae*, usually diamond shaped with spiral growth pattern and showing step – like formation on the surface.

The single crystals are very small in size and can not be examined by x-ray diffraction. However, they can be readily and conveniently studied by electron microscopy. Electron diffraction pattern and electron micrographs reveal certain interesting features about polymer single crystals. The thickness of the lamellae is very small (100 – 200 Å)

compared to the usual polymer chain length. The diffraction pattern reveals with no uncertainty that the chain axis is directed perpendicular to the plane of the lamellae. The structural pattern of the single crystal is thus understood well on the basis of the well known *folded chain theory*. This theory envisages that a single molecule of the polymer must bend or fold forwards and backwards many numbers of times across the thickness of the lamellae. Such folded chains are readily stacked in the crystal lattice with ease. It is widely believed that the single crystal comprises an array of folded chains packed individually and successively between the top and bottom surfaces or planes and on the growing edges of the lamellae as schematically shown in fig. 15.

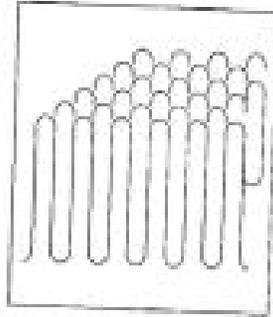


Fig. 15: Chain folding to yield polymer single crystal (schematic)

This kind of oriented structure or crystal formation involving whole individual polymer molecules discretely without interference or interposition of other molecules is apparently made possible due to large distances that exist to ideally separate the individual molecules in very dilute solutions, fig. 16. The wide – distance separation ensures practical elimination of chain entanglements. Hence, when one segment of a polymer molecule gets attached to one of the thin edges of the growing crystal, it faces practically no competition from other far away molecules for occupation of the close by, adjacent lattice site. There will be little hindrance to the successive occupation of immediately adjacent sites by segments of the same molecule by a chain folding mechanism that would continue till the whole molecule is drawn and arranged and oriented into the folds.

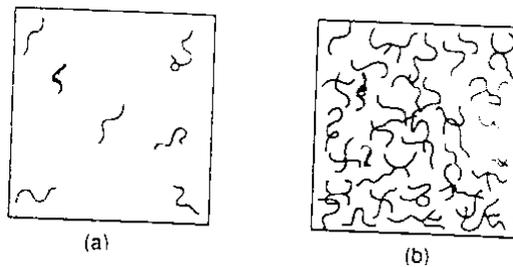


Fig. 16: Separation between polymer chain molecules in (a) very dilute solution and (b) concentrated solution (schematic). (Courtesy: Tata McGraw –Hill, New Delhi)

Structure of Bulk Polymers

Crystalline polymers obtained on cooling of their melts likewise produce electron micrographs showing the lamellae structure for the crystallites and providing little direct evidence for the presence of major amorphous regions. An idealized model of the lamellae structure as in fig. 17(a) is probably far from the real state of affairs and it may not be applicable to all types of polymers. Most polymers other than the polyethylenes

(HDPE and LDPE) contain amorphous regions to the extent of 20 – 50% or even more, distributed in the material along with the crystalline domains. In the structural model for a real system, a provision has to be made to accommodate the amorphous material. In a *fringed – micelle* or *fringed – crystallite model*, fig. 17 (b), the disoriented, amorphous material fractions are shown interspaced between the randomly distributed and positioned crystallites. This model explains and reveals the morphological features in such materials as rubbers and some cellulosic or other non-crystalline or semi-crystalline polymers with isotropic property pattern. For different polymers of intermediate orders of crystallinity, random mix of fringed micelle model and regularly stacked lamellae model may represent the overall structural pattern. These structural concepts make allowances for imperfections commonly encountered, such as the interlamellar entanglements, molecular loops of diverse dimensions, irregular fold lengths and interconnecting chains passing through different lamellae.

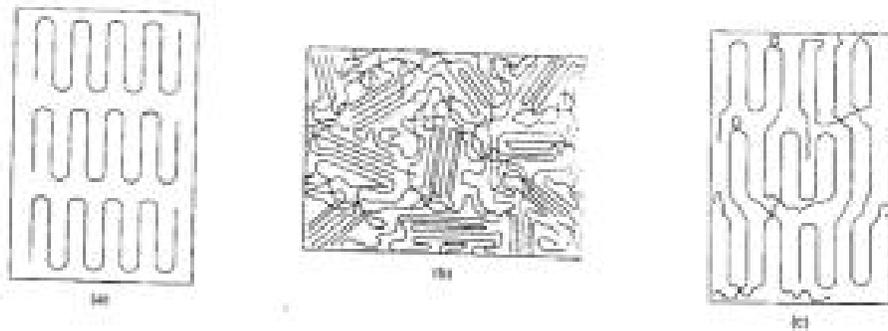


Fig. 17: Schematic representation of (a) ideal stacking of lamellar crystals (discrete folded chains), (b) fringed – micelle model showing randomly distributed amorphous and crystalline zones, and (c) interlamellar amorphous model. (Courtesy: Tata McGraw –Hill, New Delhi)

A model consisting of stacks of lamellae interspaced with and connected by amorphous regions may be referred to as the *interlamellar amorphous model*, fig. 17(c). This unique model provides the most useful approach to the understanding of the mechanical property profile of bulk crystallized polymers of moderate to high degrees of crystallinity. The different degrees of ductility and cohesive character are direct consequences of the existence of interlamellar ties. Somewhat like stacks of bricks without clay or sand – cement interlayers as the mortar, stacks of lamellae (crystals) without the existence of interlamellar tie molecules such as those obtained by slow cooling of a very dilute solution, would prove relatively fragile and brittle. The tie molecules reduce brittleness and infuse ductility and stability.

Spherulites

The most distinctive, prominent and common feature of bulk crystallized (melt cooled) polymers is the development of *spherulites*, i.e. spherical crystallites. A spherulite is characterized by a symmetrical structure build – up arising as a consequence of the cooperative growth of oriented chain segments called crystallites radially outward from a core or nucleus in three dimensions, fig. 18. Bulk crystallized polymers are, in fact, not merely a series of stacked lamellae separated and interconnected by amorphous regions; the lamellae units are intricately organized in a radial fashion within the spherulites. The crystallization process through which the spherulites are formed follows sequential steps beginning with nucleation. The nucleation process may be aided by intentional addition

of a foreign substance, called the nucleating agent. The nucleating agents by their presence reduce the size of the spherulites by increasing the number of nuclei. Growth of large spherulites contributes to enhanced brittleness.

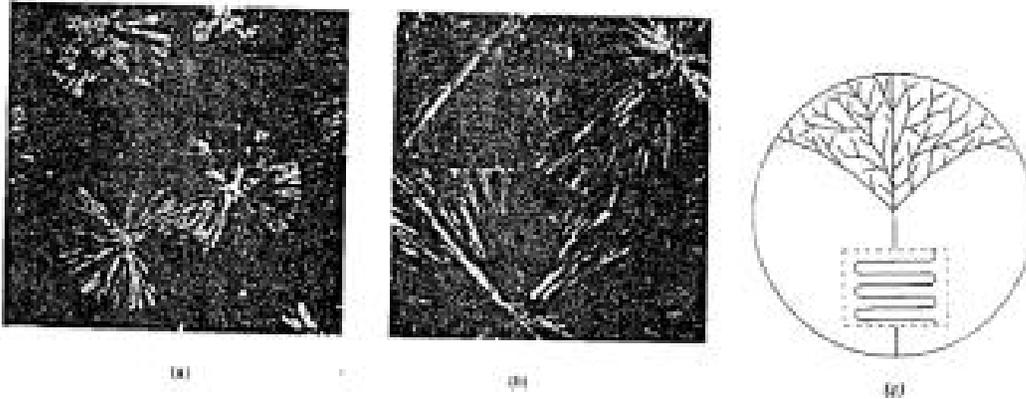


Fig. 18: State of spherulite growth for polypropylene [(a) and (b)] and (c) schematic structure of a spherulite (radial growth and branching of the lamellae with an enlarged portion showing chain folding perpendicular to the spherulitic radius). (Courtesy: Tata McGraw –Hill, New Delhi)

It is generally observable that most polymers continue to slowly *densify* long after spherulite growth is complete. The *post – primary crystallization* densification occurs both in the interspherulitic regions and intraspherulitic regions. The densification due to *secondary crystallization* slowly taking place after the primary process of spherulite growth leads to thickening of the lamellae, as chain segments are gradually pulled in from the amorphous zones. One more consequence of the secondary crystallization is the trend toward increase in brittleness. The whole after-effects on mechanical and related properties of the polymer are recognized to be complex and they depend largely on many factors including the rate and span of cooling, annealing, cold – drawing or stretch – cooling.

Thermal Analysis

The thermal properties of polymers are conveniently studied by employing such techniques as differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The DTA technique usually allows detection of thermal response and effects that

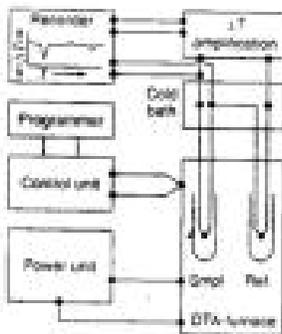


Fig.19: A block diagram for a DTA apparatus

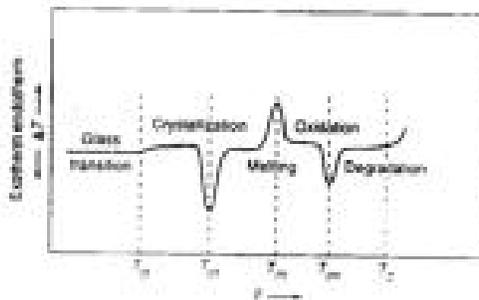


Fig. 20: A typical DTA thermogram indicating thermal changes of a crystallizable polymer (schematic)

(Courtesy: Tata McGraw –Hill, New Delhi)

accompany chemical or physical changes in a material system when it is heated or cooled in a programmed manner through a zone of transition, phase change, chemical transformation or decomposition. It allows location and measurement of glass transition temperature, T_g , the crystallization temperature (T_c), the (crystalline) melting point (T_m), and the temperatures of thermal / oxidative degradation, cross linking and other types of reactions. Figures 19 and 20 show respectively a block diagram of a DTA equipment and schematic representation of a DTA thermogram.

In practice, the material sample and a thermally inert reference material placed in the respective holders of the DTA cell are heated in a programmed manner. Any physical or chemical change in the test material at a specific temperature, which is the characteristic feature of the material under study, is usually associated with thermal change leading to a notable difference in temperature (ΔT), between the test and reference materials held in the furnace temperature. ΔT is recorded as a function of temperature, T . For no thermal change / transition, in the test sample, ΔT remains nearly unchanged (constant). In DTA, the correlation between ΔT and energy changes over a specific transition or transformation (reaction) is uncertain and unknown, thereby making the conversion of the endotherm or exotherm peak areas to energies also uncertain. However, the DTA technique is applicable to virtually all polymers and many other material systems, revealing in most cases qualitative information about the thermal effects giving clear indications of the transition (endothermic or exothermic) temperatures, fig. 20. The technique is commonly unsuitable for quantitative measurements of parameters such as heat capacity, heat of fusion or heat of crystallization (for crystallizable polymers) or change in specific heat associated with glass transition for amorphous polymers; quantitative measurements are, however, readily done employing differential scanning calorimetry (DSC). In DSC, the test sample and the reference material are heated separately by individually controlled units. The power or electrical energy inputs to those heaters are controlled and continuously adjusted consequent to any thermal effect in the test sample in such a manner as to maintain the two at identical temperatures. The differential power or heat energy needed to achieve this state of affairs is recorded against the programmed temperature of the system. For transition involving latent heat such as for fusion, the heat of the transition (fusion) is determined by integrating the (heat) energy input over the time interval covering the transition in question.

Different polymers decompose over different ranges of temperature releasing some volatiles and leaving some residues. Thermogravimetric analysis (TGA) is a useful analytical technique for recording weight loss or weight retained of a test sample as a function of temperature, which may then be used for an understanding of the chemical nature of the polymer. Along with the analysis of the released volatiles and the residue left behind, TGA provides information about thermal stability, and decomposition of the material in an inert atmosphere or in air or oxygen and about moisture content and other volatiles or plasticizer content, ash content and extent of cure for cross linked polymer. The test sample is placed in a furnace while it remains suspended from one arm of a precision balance. The TGA thermograms are obtained by recording change in the weight of the test sample as it is held at a fixed temperature or as it is dynamically heated

in a programmed manner. TGA thermograms of some selected polymers are shown in fig.21.

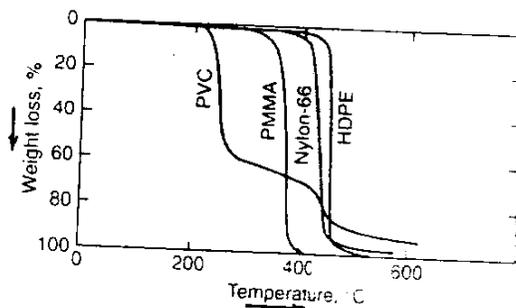


Fig. 21:TGA thermograms of some selected polymers
(Courtesy: Tata McGraw –Hill, New Delhi)

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