Theoretical Investigation of Thermal Dependence of Linear **Amorphous and Semicrystalline Polymers**

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Abstract

The temperature dependence of the thermal diffusivity (α) of linear amorphous and semicrystalline polymers can be stated as $\alpha = \alpha 0 \exp (kTc / kT)$. Based on the Spring Dashpot Model. Elasticity and flexibility of the polymeric chains are measured respectively by 0 and kTc. The respective contributions of polymeric chains' recoverable and irrecoverable motions to thermal diffusivity are 0 and exp (kTc / kT). Calculated values of α of twenty-two polymers are in excellent agreement with the measured values, throughout a wide range of temperatures including glassy, leathery, and rubbery areas, with maximum variance being 6%. Further, the examined glass transition temperatures Tg are similarly in close agreement with the published values, with the maximum variance being less than 4% for all the polymeric samples except P4MP1.

Keywords: Thermal diffusivity, Glass transition temperature, Spring-Dashpot model, Linear polymers, Semicrystalline polymers, Heat transfer, Polymer flexibility

Introduction

The thermal diffusivity (α) is a significant thermophysical property when temperature fluctuations are rapid. Precise estimates of thermal diffusivity are essential for heat flow calculations and material selection and comparison. Therefore, the heat diffusivity of polymers is of tremendous practical importance to the designers of processing equipment such as extruding and injection molding machines. It provides insight into structure-property connections for the material considered.

Although several attempts (Choy et al., 1981; Chen et al., 1977; Zhang and Fujii, 2003; Hattori, 1964; Steere, 1966; Santos et al., 2005; Morikawa et al., 1995; Agari et al., 1995) have been made to measure the thermal diffusivity of polymeric materials, yet a few efforts have been made to explain the observed thermal diffusivities theoretically. Any theoretical development of thermal diffusivity of polymers is a tough task as it depends on many elements such as the strength of primary and secondary bonding, existence of polar side pendants, length of side groups, constituents of the main chain, crystallinity, pressure, etc. Usually, information about these issues is not available. Generally, it is not possible to compute α from relation $\lambda = \alpha \rho$ Cp as it is very difficult to collect literature value of the thermal conductivity (λ), density (ρ) and specific heat (Cp) for the same polymeric sample. The most remarkable feature of the thermal properties of linear amorphous and semicrystalline polymers is that different materials show considerable diversities in trends of λ with temperature whereas

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there is a common pattern about the dependence of α on temperature. Regarding trends of λ , broadly these polymers can be grouped in three groups: (i) those that exhibit a marked conductivity maximum in the region of the glass transition temperature Tg. (ii) those that show a broad plateau around Tg with very small negative or positive slope (iii) those that show an almost linear increase in glassy and rubbery zones, with a change in slope at Tg . In contrast, for thermal diffusivity, these materials show a general trend of exponential decrease with rise in temperature, in both glassy and rubbery state with a notable change in pre-exponent and exponent factor at Tg. The specific heat shows complex temperature dependence although it increases with temperature in both the zones below and above Tg.

The varying patterns of λ with temperature have been explained successfully through a formalism created lately by Dashora and Gupta (Dashora and Gupta, 1996), considering structural properties and the effect of temperature on the structural units in a phenomenological manner. Motivated by this, in the present work, a simple relation for variation of thermal diffusivity α with temperature based on the Spring-Dashpot model (Hayden et al., 1968; Cowie, 2004; Young and Lovell, 2004) has been developed. It is fascinating to see that the simple mathematical relation obtained successfully explains the observed temperature dependence of thermal diffusivity of twenty-two samples of fourteen different polymers viz. Polypropylene (PP), Polyvinylidene fluoride (PVDF), Polychlorotrifluoroethylene (PCTFE), PolyButene1 (PB-1), Poly4methylpentane1 (P4MP1), Polyvinylchloride (PVC), Polymethylmethacrylate (PMMA), Polystyrene (PS), Polyethylene oxide (PEO), Polyoxymethylene (POM), Nylon, Polyethylene terephthalate (PET), Polybutylene terephthalate (PBT) and Polycarbonate (PC). It is rather promising that theoretically assessed Tg are likewise quite similar to the reported ones for all linear polymers.

Development of formalism

Theoretical concerns

In the case of linear polymers, there are strong covalent bonds along the chain axis whereas the interchain interactions are weak van der Waals type or are strongly polar, depending on the chemical composition of the material. Depending on the structure type, different forms of movements of structural units become possible in different temperature areas. So, the essential component of the present technique is the precise identification of the dominant movements of the structural units in different temperature regions, which has been done here using the Spring Dashpot model (Hayden et al., 1968; Cowie, 2004; Young and Lovell, 2004). According to this hypothesis, in the glassy state at relatively low temperatures, the little atomic vibrations and small angle rotations i.e. recoverable movements are dominating.

The polymer in this state behaves like a stiff spring with high modulus. At high temperatures, in the melt state, the irrecoverable motions like large angle rotations; skeleton vibrations of chains as a whole, and cooperative movements of small chains become dominant creating the system dashpot-like behavior. At intermediate temperatures, while the transition from the glassy to rubbery via

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leathery state takes place, the system exhibits a mixture of both spring-like and dashpot-like characteristics. Initially, the system is more spring and when irrecoverable motions start ramping up progressively, with an increase in temperature, it becomes more dashpot-like. The transition from a glassy state to a rubbery state can be understood as the transformation of a stiff spring to a weak spring. For glassy, leathery, and rubbery areas the significant structural change happens in the glass transition zone, hence in the suggested approach, the temperature range has to be separated into two distinct sections: below Tg and above Tg.

Temperature relation of thermal diffusivity

The thermal diffusivity is defined as the flux of energy, across any segment, per unit enthalpy gradient, under unstable state heat transfer conditions. It may be defined by Fourier's law for heat conduction through a medium, for the unsteady state, i.e.

$$Jq = -\alpha dx/d (p Cp T)$$

Where Jq is the flux of heat and ρ CpT represents enthalpy per unit volume. Equation (1) demonstrates that the state of the system, which regulates permissible movements of the constituent units as well as the enthalpy per unit volume are the major elements in deciding the flux of energy across a section. As the system transitions from the glassy to rubbery through the leathery state, heat transmission by both recoverable and irrecoverable movements contributes to thermal diffusivity.

Contribution of recoverable movements to the thermal diffusivity

According to the Spring Dashpot model, for all linear amorphous and semi-crystalline polymers, in the glassy state recoverable movements i.e. the small atomic vibrations and short angle rotations are prominent. So, the major percentage of heat transfer is placed through the coupling of the recoverable movements. Besides the allowed small angle rotations, permissible conformations chain separations, etc., the recoverable movements principally depend on the chemical composition of the polymeric chains through the primary and secondary bond strengths. Consequently, the contribution of recoverable motions or chain elasticity in a given physical state is almost independent of temperature and changes solely upon change of state. Here it is represented by $\alpha 0$. Since below Tg these polymers behave as a stiff spring a large value of $\alpha 0$ is expected below Tg and a decrease in $\alpha 0$ across the glass transition is reflective of the transition of the system from the stiff spring-like to weak spring-like region. According to the proposed model polymers which have symmetrical chains or reasonably strong bonding, polar bonding through the side pendants, and which have a greater possibility of chain entanglement should have a high value of $\alpha 0$.

Contribution of irrecoverable movements to the thermal diffusivity

The heat transfer through irrecoverable movements depends on both the chain flexibility as well as the thermal condition of the system. The irrecoverable movements like the big angle rotations,

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skeletal vibrations of the chain as a whole, sliding of chain segments, chain straightening, etc. depend on chain flexibility. It is hypothesized here that a quantitative measure of the chain flexibility can be written as the characteristic energy kTc. Where k is the Boltzmann constant and Tc is the characteristics temperature. kTc is a constant in a given physical state which besides inter and intrachain interactions, mostly depends on the available free volume and degree of polymerization. It also indicates the energy transfer capability through irrecoverable movements in a given system or the dashpot-like character of the system. Therefore, as per the proposed model, its value must increase across glass transition for all linear amorphous and semicrystalline polymers. The presence of a longer sequence of aliphatic groups in the backbone chain limits the chain flexibility resulting in a decrease in the value of Tc for such polymers.



Fig 1. Variation of thermal diffusivity (α) with temperature (T). () Calcd. and (♦) exptl. data of POM; (−−) Calcd. and (Δ) exptl. data of PEO.



Fig 2. Variation of thermal diffusivity () with temperature (T). () Calcd. And (\square) exptl. data of PVC; () Calcd. and (\triangle) exptl. data of PMMA; () Calcd. and (\blacklozenge) exptl. data of PSd; (--) Calcd. and (+) exptl. data of PSh.

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Fig 3. Variation of thermal diffusivity (α) with temperature (T). () Calcd. and (\square) exptl. data of PCg; () Calcd. and (Δ) exptl. data of PCc; (—) Calcd. and (\square) exptl. data of PC



Fig 4. Variation of thermal diffusivity (α) with temperature (T). () Calcd. and (+) exptl. data of Nylon; () Calcd. and (2) exptl. data of PET(X=0.3); (--)Calcd. and (2) exptl. data of PET (X=0)

As the polymer enters its glass transition region, the available free volume increases and chain straightening takes place. This procedure may greatly diminish the inter-chain interactions and also the chain entanglements present below Tg, resulting in an increase in the value of Tc above Tg. Moreover, the thermal state of the system represented by kT is a measure of the enthalpy of the constituent units. Hence it is the ratio (Tc / T), which governs the temperature dependence of the thermal diffusivity. Further, it is argued here that the approach from an ideal spring-like to ideal dashpot-like behavior will follow an exponential route i.e. the irrecoverable movements are projected to take up exponentially with temperature rise. Consequently, an exponential dependence on (Tc / T) is envisaged for the contribution of irrecoverable movements to the thermal diffusivity.

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Combining both the contributions, the variation of the thermal diffusivity with temperature for linear amorphous and semi-crystalline polymers may be written as e polymers may be expressed as:

$\alpha = \alpha 0 \exp(Tc / T)$

According to the spring dashpot model, the contribution of the recoverable movements in the region below the glass transition must be higher than the contribution of the irrecoverable movements and vice versa in the region above Tg.

RESULTS AND DISCUSSION

In the present work, computations have been done for the thermal diffusivity of twenty-two samples of fourteen various linear polymers throughout a wide range of temperatures encompassing glassy, leathery, and rubbery regions. The computed and published experimental (Choy et al., 1981; Chen et al., 1977; Zhang and Fujii, 2003; Hattori, 1964; Steere, 1966; Santos et al., 2005; Morikawa et al., 1995; Agari et al., 1995) values of α of these twenty-two polymeric samples are presented in Figures (1-8). The largest variation in values of calculated thermal diffusivities and the reported ones is less than 6% which is well within the experimental errors.

The maximum percentage deviations for these polymers are: POMa (2.28%), PEOa (1.4%), Nylon (0.39%), P4MP1a (2.01%), PB-1 a (4.25%), PPe (3.1%), PPa (1.4%), PVCd (5.3%), PMMAf (1.2%), PSh (2.4%), PSd (3.4%), PCh (1.4%), PCg (5.9%), PCc (5.85%), PET(Amorphous)b (4.87%), PET(X=0.3)b (0.76%), PBT(X = 0.12)a (2.53%), PBT(X=0.34)a (5.76%), PVDFa (3.9%), PCTFEd (3.7%), PCTFEd (1.9%) and PCTFEd (1.7%).



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A comprehensive inspection of Figures (1-8) reveals that in glassy, leathery, and rubbery regions with the rise in temperature thermal diffusivity of all linear amorphous and semi-crystalline polymers demonstrate a common trend of exponential reduction. As expected according to the proposed description there is a marked change in both pre-exponent and exponent factors at the glass transition. The computed values of characteristic constants α 0 and Tc affording the best fit with the reported experimental values of diffusivity [1-8], both in the region below and above Tg, have been shown in Table 1. This table also includes the stated crystallinity (X) of the polymeric samples. For all the polymers investigated here the value of pre-exponent factor α 0 declines on glass transition representing the marked decrease in spring-like behaviour while Tc increases on glass transition representing the increase in the dashpot-like behaviour.

For all polymers in the region below the glass transition the value of $\alpha 0$ is higher than exp (Tc / T) and vice versa in the region above Tg which indicates that below Tg most of the heat is diffused through the recoverable movements while above Tg irrecoverable movements play dominant role. It is also exciting to note that the values of constants $\alpha 0$ and Tc for these polymers match well with their structural properties. Following are some of the intriguing observations: the strictly linear polymers POM and PEO have symmetrical chains bearing polar backbone bonds that encourage strong intermolecular interaction; both these polymers have highly stiff chains and hence substantially greater $\alpha 0$ in the region below and above Tg. The carbonate molecule also has a symmetrical structure and is more polar than the ester group hence for amorphous PC the value of $\alpha 0$ is higher and the value of Tc is lower than that of amorphous PET. Comparison of the semi-crystalline samples of PBT and PET of the same crystallinity shows that $\alpha 0$ is larger and Tc is less for PBT because the presence of a longer sequence of methyl groups in the repeating units of PBT provides the chains reduced flexibility and makes PBT more polar than PET. A close inspection for PPe, PB-1, and P4MP1 demonstrates that an increase in side chain length, in the region below Tg will stiffen the chain so that $\alpha 0$ increases as side chain length increases.

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Polymer	XX	TgT_g (K)	TgT_g (K)	% dev	α(0)×108\alpha(0) \times 10^8 (m2s-1m^2s^{-1})	TcT_c (K)	TcT_c (K)
		exp.	Calc.		Below TgT_g	Above TgT_g	Below TgT_g
РОМ	0.63	202	210	3.96	25	4.46	84
PEO	0.8	210	218	3.81	18	8.88	88
NYLON	Crystalline	328	327	0.3	10.22	3.06	107
P4MP1	0.23	323	319	1.17	11.31	2.97	90
PB-1	0.55	256	259	1.17	11.31	2.97	93
РР	0.6	295	290	1.47	11.03	2.49	95
PVC	Amorphous	333	332	0.3	5.02	4.11	98
РММА	Amorphous	378	380	0.53	5.64	4.39	100
PS	Amorphous	373	366	1.95	3.4	5.93	100
PS*	Amorphous	373	366	1.95	4.18	7.22	100
РС	Amorphous	426	427	0.23	7.68	6.48	100
PC*	Amorphous	426	427	0.23	8.81	6	100
PC**	Amorphous	436	436	0	5.58	5.58	100
PET	0.3	346	346	0	3.61	3.06	105
PET*	0.12	326	326	0	5.56	5	105
PBT	0.34	340	340	0	5.18	2.97	106
PVDF	0.36	338	330	2.36	5.08	2.56	106
PCTFE	0.82	325	322	0.92	2.56	2.79	176
PCTFE*	0.84	330	330	0	2.79	1.96	176
Note:-The experimental data for thermal diffusivity of the polymer has been taken from aRef.1, bRef.2 , cRef.3, dRef.4, eRef.5, fRef.6, gRef.7, hRef.8.							

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The Tc value below Tg for P4MP1 is the least among these three suggesting that the chains in this polymer below Tg may be significantly entangled limiting the chain flexibility in the region below Tg. It seems that above Tg chain straightening occurs and there is a rise in the intermolecular distance so that Tc increases and $\alpha 0$ decreases with the increase in side chain length representing the greater chain flexibility. Inspecting the fluoro polymers PVDF and PCTFE one discovers that the introduction of a chlorine atom in PCTFE, which is larger than the fluorine atom, diminishes the close chain packing. This improvement in the chain flexibility is evident in the values of Tc of PCTFE and PVDF.

The study finds that the semi-crystalline polymers have higher values of α than the amorphous polymers and the latter shows more reduction in value when it crosses the glass transition region. PMMA being helical does not show much change in constants across glass transition as the other amorphous polymers are showing. Helical polymers like PMMA, PCTFE, and Nylon show a smoother variation throughout the glass transition. As expected, the value of $\alpha 0$ is bigger and Tc is less, in regions both below and above Tg, for the samples having higher crystallinity in the case of samples of PCTFE, PBT, PET, and PP. The glass transition temperatures Tg computed from the intersection of trends below Tg and that above Tg, are also in close accord with published experimental values of Tg as shown in Table 1. The highest variation in values of estimated glass transition temperature and the reported (experimental) one is less than 4 % except for P4MP1 which is 7.3%.

CONCLUSIONS

In this study, a simple connection for fluctuation of thermal diffusivity α with temperature based on the Spring Dashpot model has been proposed. According to this model, in the glassy state, the recoverable movements, and in the rubbery state the irrecoverable movements of the polymeric chains are prominent. The study indicates that the irrecoverable movements are predicted to grow exponentially with temperature rise. The allowed movements of the constituent units of the polymeric chain as well as the enthalpy per unit volume are the predominant elements in determining the thermal diffusivity of the polymer. Remarkably, the so-called mathematical connection describes satisfactorily the observed temperature dependency of thermal diffusivity of twenty-two samples of fourteen distinct polymers. The proposed constants correlate the trends of diffusivity with the structural features of the polymers besides providing the values of thermal diffusivities as a function of temperature for linear amorphous and semi-crystalline polymers which can be used in the absence of available experimental data.

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