Regime Kinetics of Poly Ethylene Terephthalate/ Thermotropic Liquid Crystalline Polymer PET/TLCP Polycomposites

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Abstract

The crystallization behavior of polyethylene terephthalate (PET) and PET/Thermotropic liquid crystalline polymer (TLCP) composites was analyzed under isothermal conditions using calorimetric kinetic data, with thermodynamic parameters derived from the Lauritzen–Hoffman (L-H) model. The crystal growth process, dominated by secondary nucleation, deviates from simple spherulitic radial growth, instead reflecting a complex interplay of nucleation and lamellar growth phenomena. The temperature dependence of the linear crystal growth rate (G) follows a biexponential form as per the L-H relation, integrating both segmental transport and thermodynamic driving forces. Through kinetic modelling, values of nucleation constants (Kg), pre-exponential growth factors (G$_0$), and surface free energies (σ and σ$_e$) were obtained. The analysis confirmed crystallization in Regime II across all compositions and temperatures studied (195–210°C), characterized by a chain-folding mechanism where growth occurs on pre-existing crystalline substrates. The substrate length (L), estimated via the Lauritzen Z test, increases with TLCP content and crystallization temperature, indicating enhanced nucleation and hindered chain folding in composites. PET/TLCP blends exhibited higher fold surface energy and work of chain folding compared to neat PET, revealing the inhibitory effect of TLCP on PET crystallization kinetics. These findings offer a comprehensive understanding of the crystallization regime transitions and underlying thermodynamics in PET/TLCP systems.

Mathematical models

Interfacial free energy and regime kinetics based on Hoffman and

Lauritzen :

$$G = G_0 \exp\left(\frac{-U^*}{R((T_0 - \alpha t) - T_\infty)}\right) \exp\left(\frac{-K_g}{(T_0 - \alpha t)(T_m^0 - T_c)f}\right)$$

$$\ln G + \left(\frac{-U^*}{R((T_0 - \alpha t) - T_\infty)}\right) = \ln G_0 - \frac{K_g}{(T_0 - \alpha t)(T_m^0 - (T_0 - \alpha t))f}$$
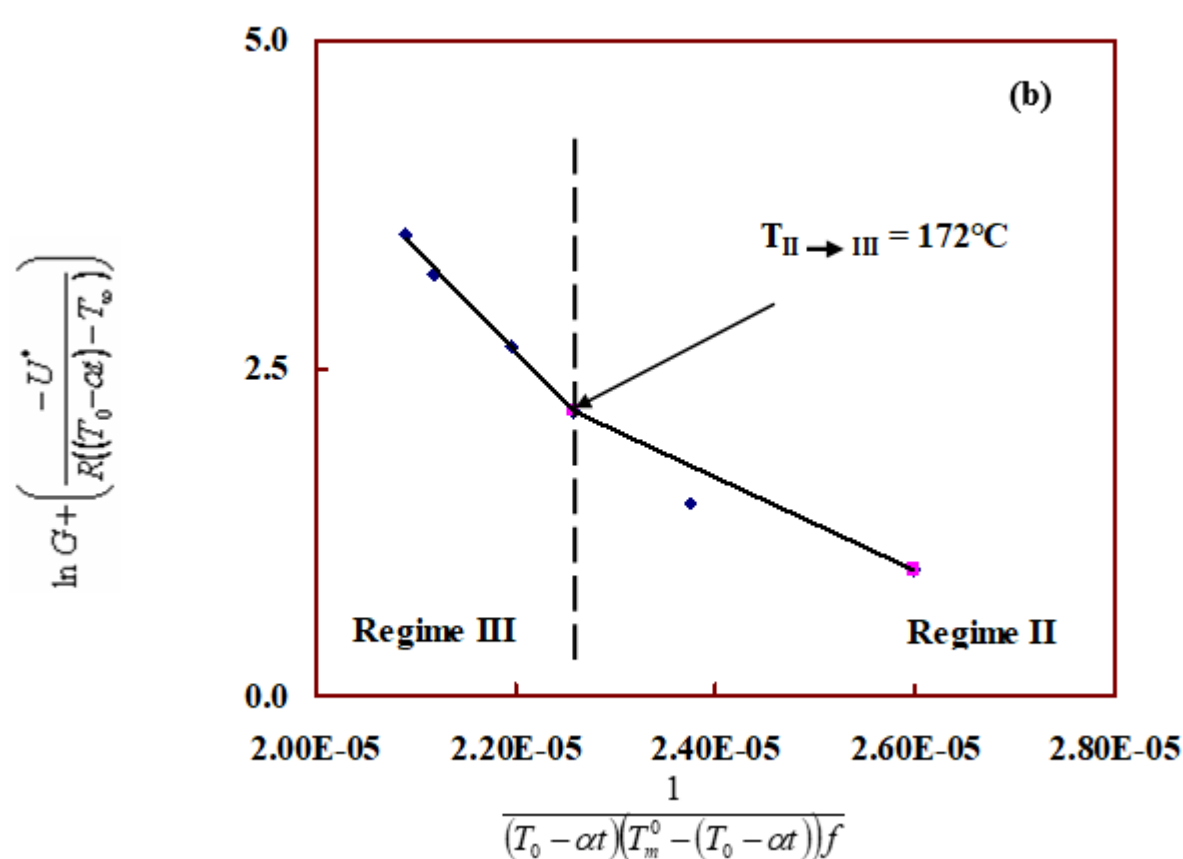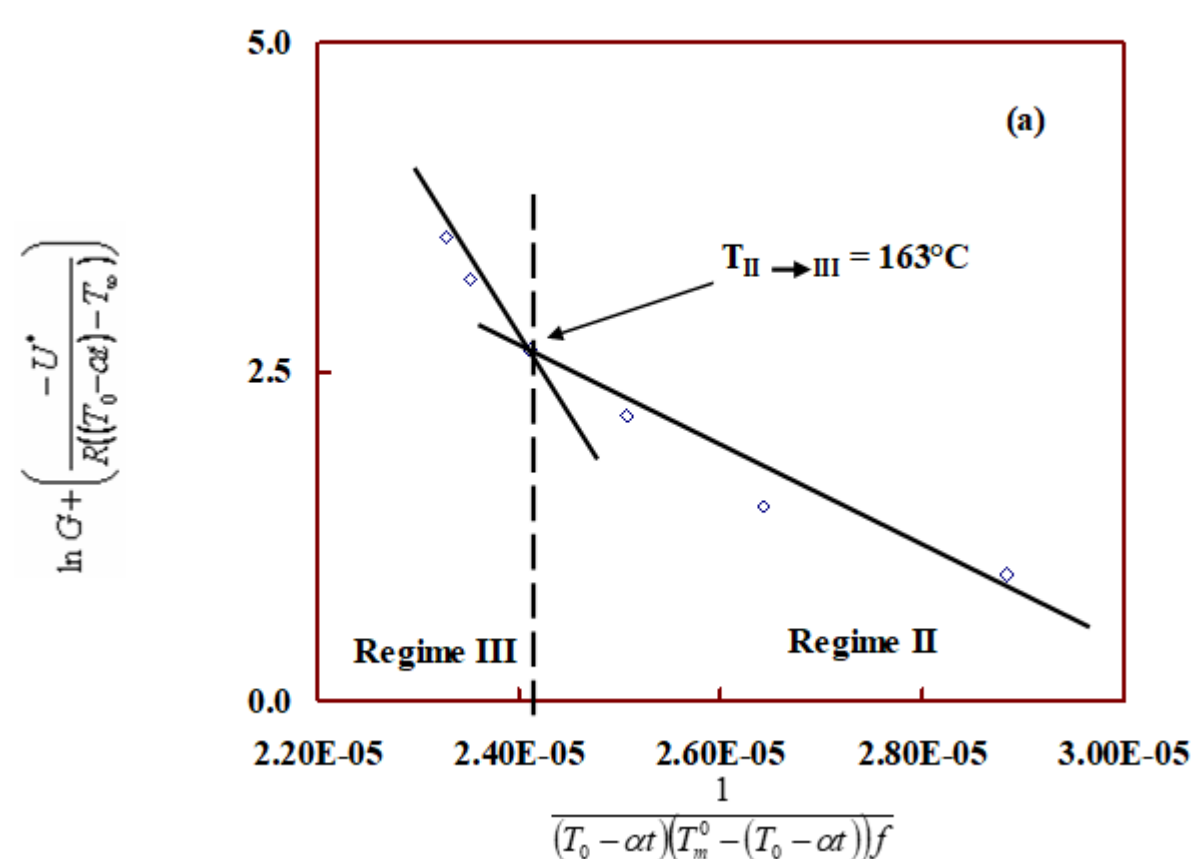
PET/ TLCP	T_m^0 (C)	Regime transition temp. (°C)	Nucleation constant K$_g$ x 10^5 (K^2)		K$_g$(III) / K$_g$ (II)	Fold surface free energy σ$_e$ (ergs/cm^2)		Work of chain folding q (kcal/mol)	
			II	III		II	III	II	III
100/00	271	163	5.2	13.5	2.6	208.2	272.3	15.1	19.8
90/10	284	172	3.6	7.8	2.2	141.3	154.7	10.3	11.2
80/20	289	171	5.1	9.8	1.9	198.4	191.1	14.4	13.9
70/30	287	165	4.7	10.4	2.2	200.2	204.9	14.5	14.9
60/40	275	154	4.4	11.6	2.6	177.2	233.4	12.9	17.0
50/50	264	153	4.5	11.6	2.6	183.7	238.5	13.3	17.3

The regime parameters (for regime II and regime III) of nonisothermal crystallization kinetics of PET/TLCP composites based on the Hoffman- Lauritzen theory

Results

Conclusions

- The modified Lauritzen and Hoffman regime nonisothermal crystallization analysis exhibited a significant regime transition for both resins.
- It is believed that the transition that is observed is the regime II to III transition.
- The ratios of the regime III to regime II slopes were roughly 2.2, 1.9 and 2.2 for 10, 20 and 30 wt/wt% of TLCP into PET, respectively.
- For loading of TLCP ≤ 30 % in PET, regime transition temperature is higher as compared to neat PET.

References:

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