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Interfacial crystallization of isotactic polypropylene molded against the copper surface with various surface roughnesses prepared by an electrochemical process

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The influence of surface topography of copper (Cu) sheet on the heterogeneous nucleation of isotactic polypropylene (iPP) at the iPP/Cu interface had been investigated mainly using polarized optical microscope with hot stage. Various textures of Cu surfaces prepared by sandpaper polishing and electrochemical anodizing had been made and they were utilized to induce interfacial nucleation of iPP upon supercooling. This process enables us to change the topological feature of the copper surface without changing their chemical compositions. The pretreated surfaces were quantitatively characterized by a surface texture instrument in terms of RMS roughness (R_a). Copper surface with higher surface roughness induced more nuclei of iPP and led to a thicker transcrystalline layer in the interfacial region upon supercooling over the temperature range $128^\circ\text{C} < T_c < 134^\circ\text{C}$. Based on the theory of heterogeneous nucleation, it was found that the induction time correlates well with the nucleation rate in determining the interfacial free energy difference function $\Delta\sigma$ of iPP. The ratio of $\Delta\sigma$ at the interface to that in the bulk matrix ($\Delta\sigma_{\text{TCL}}/\Delta\sigma_{\text{bulk}}$) for the polished surface ($R_a = 0.09\ \mu\text{m}$) is 2.89, implying the transcrystallization growth is unfavorable from a thermodynamic point of view. The ratio of $\Delta\sigma_{\text{TCL}}/\Delta\sigma_{\text{bulk}}$ becomes smaller as the current density for anodizing increases, indicating the transcrystallization growth is getting favorable. Moreover, induction times and nucleation rates were also measured to characterize quantitatively the nucleating ability of various Cu surfaces.

1. Introduction

Semicrystalline polymer surfaces may be crystallizing with different microstructures or morphologies, depending upon the cooling rate and nucleating activity of the mold surface [1, 2]. These polymers are usually reinforced with various types of organic or inorganic reinforcements to form composites with improved mechanical properties. It is well known that those reinforcements may result in changes in morphology and crystallinity of the interphase region. Some of the substrates, either organic or inorganic, may have an ability to nucleate crystallization along the interface with sufficiently high density of nuclei and result in a columnar crystalline layer, known as transcrystalline layer, with limited thickness. There have been many hypotheses proposed to account for the formation of the transcrystalline layer [3–7]. For example, Campbell and Qayyum [3] claimed that the adsorption of the highly active nucleating promoters on the substrate surface was responsible for the formation of transcrystallization. Thomason and Van Rooyen [4] reported that an application of stress at the interface between fiber and supercooled PP melt by using pulling apparatus resulted in the growth of a transcrystallization. Beck [5] reported that the chemical similarity between the crystallizing polymer and the substrate increased the possibility of transcrystallization. Hobbs [6] and Gray [7] demonstrated that the topography of the substrate surface is a major factor in transcrystallization. Suklanova and his colleagues [8] claimed that different ability of polyimide fibers to induce transcrystallization are associated with the superficial morphology of the fibers. However, the mechanism for the origin of transcrystallization is still not fully understood. We are particularly concerned the effect of surface topography of the substrate on the heterogeneous nucleation in this investigation. In our previous investigation [9], We have used hot-stage microscopy to survey the crystallization of polypropylene molded against polyimide and PTFE surfaces, respectively, with different surface complexities characterized

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by AFM. It was found that the polyimide and PTFE substrates with different surface roughnesses have different abilities to induce the nucleation of iPP at interface and found that the surface with higher complexity has tendency to induce exuberant nuclei, consequently, leading to a transcrystalline layer. The nucleating ability of aluminum, or more likely of alumina (Al_2O_3), has been demonstrated for various polymers [10, 11]. However, hot melt of crystalline polymer may also forms a transcrystalline layer acted as a reinforcement when it is molded against this oxide surface [12, 13]. A slight oxidation was reported to improve adhesion in aluminum [14], but the reasons for the observed improvement of adhesion was ambiguous. Loew and Baillie [15] utilized alumina fiber as a reinforcement material, one of the fastest growth areas in fiber technology, partly due to their excellent transcrystalline growth on mechanical shearing of the melt.

According to the theory of heterogeneous nucleation [16], $\Delta\sigma$ is dependent upon the interfacial substance. Chatterjee and his colleagues [10] defined A as the ratio of the bulk free energy difference and the interfacial free energy difference. Exuberant nuclei will be induced at the interface if $A \geq 1$ and a columnar crystallization (i.e. transcrystalline layer) will be apt to occur. On the other hand, it's impossible to induce nuclei at the interface if $0 < A < 1$. In order to determine the values of $\Delta\sigma$ for transcrystalline layer and the buck, nucleation rates at the interface and in the bulk have to be measured. Ishida and Bussi [17] suggested a method of induction time measurement. Wang *et al.* [18] found that the induction time can be correlate well with the nucleation rate in determining $\Delta\sigma$ and reported that the ratio of $\Delta\sigma$ in the bulk matrix to that at the interface is 1.63 for the PTFE fiber/PP composites. The aim of the current study is to assess the influence of the surface topography on the formation, size and growth rate of a transcrystalline layer at the polymer/Cu interface. We had previously study the effect of aluminum substrate surface with various roughnesses but under the same chemical composition, on the heterogeneous nucleation of crystallizable polymers [19]. This work again utilized anodizing treatment on the copper surface to form copper oxide layer with various surface features and to assess the transcrystalline phenomena of iPP at the interface. The electrochemical surface treatments are used to modify the topological structure of the surface oxide layer to change its texture but without changing its chemical composition.

2. Experimental

Copper was used as the substrate and was pretreated by several procedures including mechanical grinding (sandpaper #1000), alkaline clean (3.0 g/l NaOH aqueous solution), solvent degreasing (acetone), electropolishing (70% perchloric acid, $\rho = 1.67$), neutralizing (10.0 g/l Na_2CO_3 aqueous solution), and finally anodizing in the electrolyte of 50% phosphoric acid with 5% glycol. A deionized-water rinse coped with ultrasonic cleaning was carried out between steps. The copper sheet ($5 \times 10 \times 0.6$ mm) to be anodized was attached to the anode of a d.c. supply, with stainless steel as the counter electrode. Normal faces of Al sheet was masked by 3 M Teflon tape so that the anodization was occurred merely on lateral sides which will be used to mold against iPP afterward. The voltage across the electrode was kept at 0.3 V. Various surface characteristics were prepared by varying anodizing current density. Copper surface topography was obtained by a Talysurf profilometer (Form Talysurf Series 2, Rank Taylor Hobson, USA) with a diamond probe (0.2 μm in tip radius), coupled with 3D topography software for surface texture characterization.

Isotactic polypropylene pellets were supplied by Taiwan Polypropylene Co. The isotactic structure content weights 86.52% in average. PP pellets were initially vacuum-dehydrated at 60°C for 24 hr. The dried pellets were then pre-pressed into films and were measured with a thickness about 0.5–0.7 mm. Crystallization of polypropylene on the lateral surface of the Cu sheet was observed with a polarized optical microscope (POM, Zeiss Axiolab A) equipped with a Mettler FP82 hot stage. Polymer film for crystallization study was heated using a hot stage at 210°C for 15 min for the purpose of removing all possible historical crystallizations and then cooled down at a cooling rate of -20°C/min. Isothermal crystallizations were carried out under N_2 atmosphere for the purpose of preventing from oxidation. Crystallization was carried out at different T_c and different time scales.

3. Results and discussion

3.1. Characterizations of the pretreated copper surfaces

It is well known that the oxide layer was much thicker and the whiskers longer by an acid anodizing than by a chemical etching. During the anodizing process, both formation of a new oxide and dissolution of existing oxide take place, and it leads to a barrier layer at bottom and a porous layer outward. The porous nature of the anodizing oxide is responsible for the success of this pretreatment process in promoting strong adhesive joint to copper. The sample that was polished only (referred to Sample A) and the other samples treated by the phosphoric acid anodization at different current densities (10–50 A/dm^2, respectively) (referred to Samples B–F) were made into comparison in their morphological differences. Fig. 1 shows the surface profiles from the pretreated surfaces. As can be seen, sample A has a very smooth surface while other samples exhibit different levels of rough structures due to that the high porosity of copper oxide layers were formed under the different anodizing current densities. Sample F anodized at 50 A/dm^2 has a highly porous surface with tremendous micro-pores. These surfaces were characterized by surface texture instrument and their surface characteristics were tabulated in Table I. As can be seen, sample A has a R_a value of 0.09 μm while the anodized samples show increasing surface roughness, from 0.18 μm up to 0.64 μm, as the current density for anodizing treatment increased.

TABLE I Surface characteristics of the copper sheets

Sample	Current density, (A/dm^2)	Roughness, R_a (μm)	Max height, R_t(μm)	TCL thickness (μm)
A	Polished	0.09	0.69	—
B	10	0.18	2.17	37
C	20	0.31	2.29	44
D	30	0.44	3.53	50
E	40	0.53	3.75	54
F	50	0.64	4.19	58

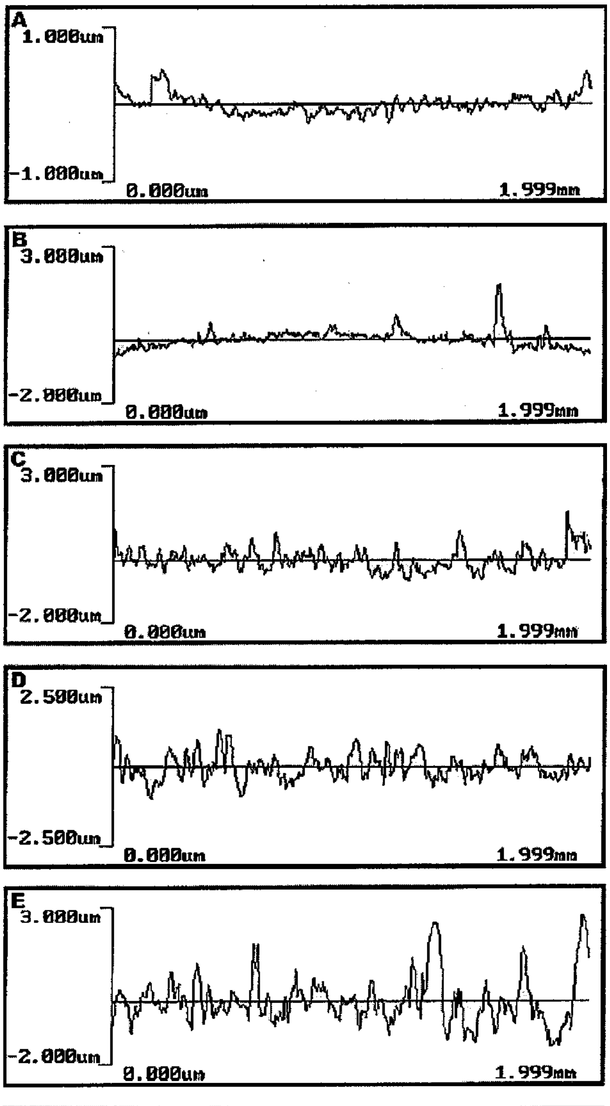

Figure 1 Surface profiles of polished and anodized Cu sheets at various current densities.

3.2. Observation of transcrystallinity on Cu surfaces

When iPP was melt against copper surface, it was realized that nucleation of iPP takes place at the surface sites of substrate surface after a certain induction time. As the substrate surface is filled with nuclei, a transcrystalline layer forms and the growth of crystal will be restricted to the direction normal to the interface. The POM photographs for the crystallizing behaviors of polymer at the interface with various Cu surfaces are shown in Fig. 2, under the supercooling conditions of $T_c = 134°C$ and $t = 60$ min. The polished Cu surface exhibited sparse polymer crystalls without significant nucleating activities at the interface. On the other hand, dense crystallizations were observed on the anodized surfaces such as sample C–F. The thickness of transcrystalline layer becomes greater as the anodizing level (i.e. current density for oxidation) gets higher. A thick transcrystalline layer with a thickness of approximate 58 μm had been developed on sample F. As reported earlier [9], higher surface complexity has better nucleating ability than smoother surface and consequently is capable of inducing a well transcrystalline layer. We obtain similar results in this investigation. It is therefore drawn a conclusion that surface topography is a significant factor influencing the heterogeneous nucleation of polymer at interface.

3.3. Effect of surface roughness on the crystal growth rate

Fig. 3 is a plot of crystal size against time for Sample F, in which a linear relationship was found for crystal growing in TCL and in bulk, respectively. The slope of the straight line representing the crystal growth rate. As can be seen, the growth rates are almost equal for transcrystals in TCL and spherulites in buck. From the kinetic theories [20], the nucleation-controlled polymer crystal growth with chain folds leads to the expression

$$G = G_0 \exp[-U^*/R(T_c - T_\infty)] \exp[-K_g/T_c(\Delta T)f]$$

for the growth rate G, where G_0 is a constant and T_c is the crystallization temperature. The parameter K_g for regime II can be expressed by

$$K_g(\mathrm{II}) = 2b_0\sigma\,\sigma_e\,T_m^0\big/k\Delta h_f,$$

and

$$K_g(\mathrm{III}) = 4b_0\sigma\,\sigma_e\,T_m^0\big/k\Delta h_f$$

in regime III, where b_0 is the layer thickness. The theoretical ratio of K_g (III)/K_g (II) is therefore 2.0, according to Hoffman *et al.* [20]. Fig. 4 shows the growth of transcrystalline layer at the interface with sample F as a function of time at various temperatures. As can be seen, the growth rate of TCL is largely dependent upon T_c and is increasing with lowering T_c. Similar result was also found on the other surfaces. Meanwhile, as discussed in previous section, the thickness of TCL at the same time scale was observed to be greater as T_c was reduced. Fig. 5 is a plot of the dependence of crystal growth rate upon T_c, in which the growth rate dramatically increases at about 132°C, a transition temperature from regime II to regime III. These data can be further analyzed by plotting $\log G + U^*/2.303R(T_c - T_\infty)$ against $1/2.303T_c\Delta T_f$. Fig. 6 shows such a plot. The slopes for both regimes were determined to be $-285912K^2$ and $-138364K^2$, respectively, and the ratio of K_g (III)/K_g (II) is therefore equal to 2.07, reasonably close to the theoretical value.

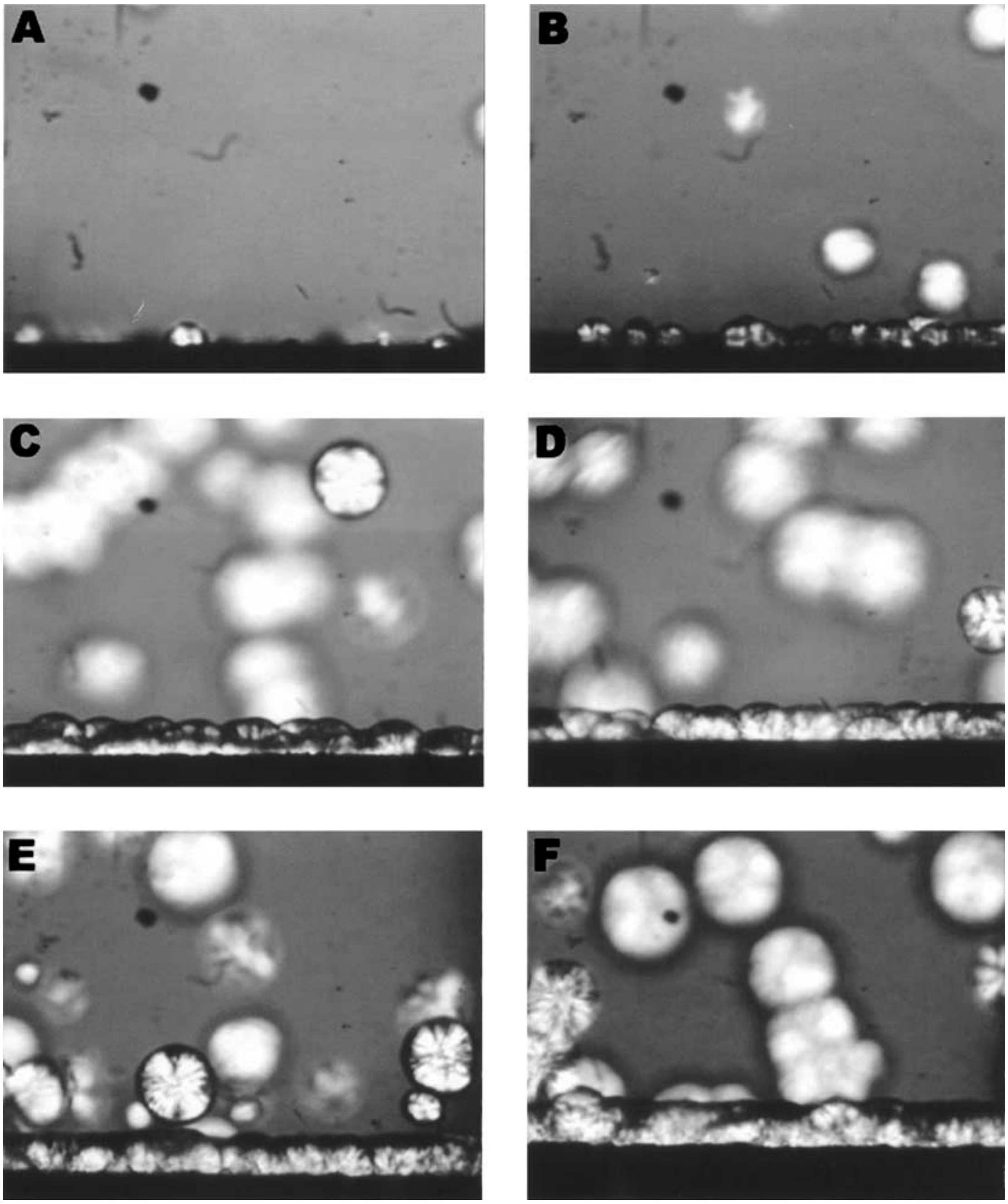

Figure 2 Isothermal crystallization of molten iPP contact with various Cu surfaces.

TABLE II Nucleation rates (min^{-1}) and induction times (min) for iPP under different supercoolings on different substrates

	Nucleation rate (min^{-1})				Induction time (min)			
Sample	128°C	130°C	132°C	134°C	128°C	130°C	132°C	134°C
A	3.32	2.28	1.49	0.98	3.0	7.0	24.0	58.0
B	3.85	2.87	1.70	1.14	2.0	5.5	13.0	22.5
C	4.31	2.45	1.35	0.88	2.0	4.5	8.0	15.0
D	4.42	2.62	1.42	0.92	2.0	3.0	6.0	9.5
E	4.67	2,53	1.81	1.13	1.5	2.0	3.5	6.0
F	4.53	2.59	1.59	1.04	1.0	1.5	2.0	3.0

3.4. Effect of surface roughness on the nucleation rate

The nucleation rates and induction times were determined from the intercepts and the initial linear slopes, respectively, of the plots (not shown here) of nuclei number against time at various temperatures. Their results were tabulated in Table II. As expected, the induction time increases and nucleation rate decreases with increasing T_c. The dependence of nucleating rate and induction time on the surface roughness seems not so prominent. However, the nucleation rate of the anodized surface is usually greater than that of the polished

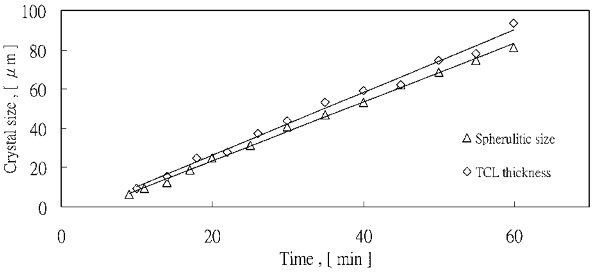

Figure 3 Spherulitic size and TCL thickness plotted against time at $T_c = 132°C$.

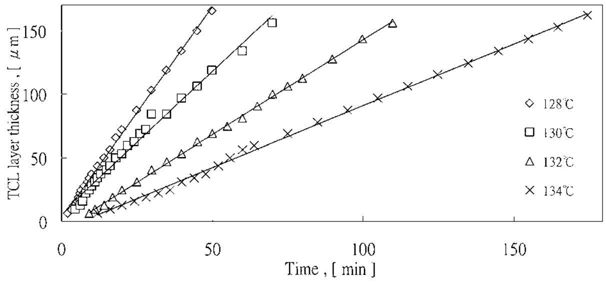

Figure 4 TCL thickness of sample E plotted against time at various temperatures.

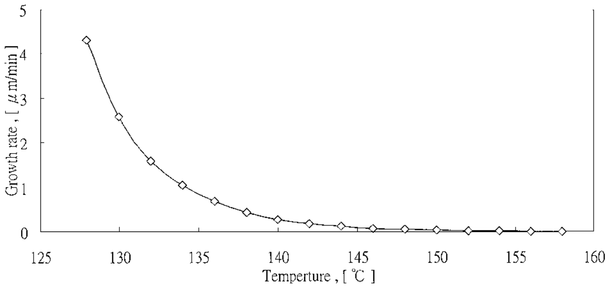

Figure 5 Dependence of crystal growth rate upon crystallization temperature.

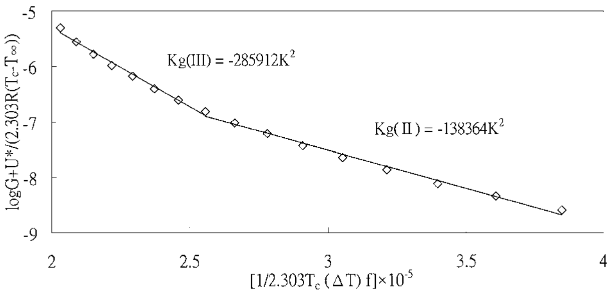

Figure 6 Determination of K_g from the kinetic theory by plotting $\log G + U^*/2.303R(T_c - T_\infty)$ against $1/2.303T_c\Delta T_f$.

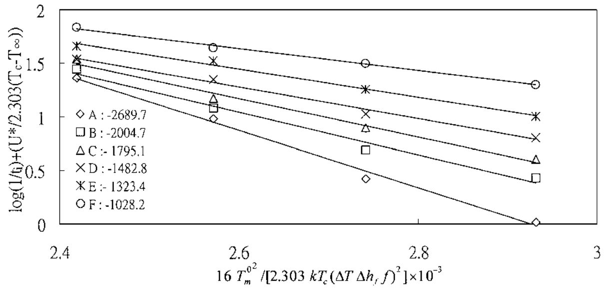

Figure 7 Determination of $\sigma\,\sigma_e\Delta\sigma_{TCL}$ from the slope by plotting $\log(1/t_i) + U^*/2.303R(T_c - T_\infty)$ versus $[1/T_c(\Delta T)f]^2$.

surface. For example, the nucleating rate for sample F (i.e. 4.53 min^{-1}) is greater than that of polished sample (i.e. 3.32 min^{-1}) and the induction time for the former (1 min) is much shorter than the later (3 min) at $T_c = 128°C$.

According to the theory of nucleation, the rate of heterogeneous nucleation is given by [16],

$$\log I = \log I_0 - U^*/2.303R(T_c - T_\infty) - 16\sigma\,\sigma_e\Delta\sigma T_m^{0\,2}\big/2.303kT_c(\Delta T\,\Delta h_f f)^2$$

where I_0 is a constant, U^* is the activation energy related to molecules to transport across the phase boundary, R is the gas constant, T_c is crystallization temperature, T_∞ is the temperature below which crystallization ceases, T_m^0 is the equilibrium melting temperature of the polymer, ΔT is the degree of supercooling ($=T_m^0 - T_c$), Δh_f is the heat of fusion per unit volume of the polymer and f is a correcting factor, being equal to $2T_c/(T_c + T_m^0)$. Further details regarding these definitions are given in the references [16, 21]. Values of U^*, T_∞, and Δh_f taken from literature [21] are 6.28 kJ/mole, 223 K, and 1.96×10^9 erg/cm^3, respectively. σ and σ_e are the lateral and fold surface energies, respectively.

Consequently, the surface energy parameter $\sigma\sigma_e\Delta\sigma_{TCL}$ is determined from the slope by plotting of $\log I + U^*/2.303R(T_c - T_\infty)$ versus $[1/T_c(\Delta T)f]^2$ as shown in Fig. 7. TCL is used to denote the interfacial free energy difference for nucleation taking place in the interfacial region. Similarly, the surface energy parameter $\sigma\sigma_e\Delta\sigma_{bulk}$ can be determined from the slope by plotting $\log\ (1/t_i) + U^*/2.303R(T_c - T_\infty)$ versus $[1/T_c(\Delta T)f]^2$ as our previous report [19], where t_i is the induction time. The slope is equal to 1408 K^3 for the method of nucleation rate for iPP melt in the bulk.

3.5. Comparison of nucleating ability of Cu surfaces

The energy barrier for nucleation is used to characterize the tendency for iPP to crystallize on the heterogeneous phase, from a thermodynamic point of view. $\Delta\sigma$, termed interfacial free energy difference, is the energy change caused by the creation of new surface on the top of foreign substrates. The values of $\Delta\sigma$, as can be seen in Table III, for different substrates were deduced by obtaining the $\Delta\sigma\sigma_e$ value from crystal growth studies. Most of the samples have higher values of $\Delta\sigma$ than that of the bulk, i.e. $\Delta\sigma_{bulk} = 1.38$ erg cm^{-2} (determined

TABLE III Values of $\Delta\sigma\ \sigma_e\Delta\sigma_{TCL}$, $\Delta\sigma_{TCL}$ and $\Delta\sigma_{TCL}/\Delta\sigma_B$ for various substrates

Sample	$\Delta\sigma\ \sigma_e\Delta\sigma_{TCL}$ (erg^3/cm^6)	$\Delta\sigma_{TCL}$ (erg/cm^2)	$\Delta\sigma_{TCL}/\Delta\sigma_B$
A	2690	3.99	2.89
B	2005	2.97	2.15
C	1795	2.66	1.93
D	1483	2.20	1.59
E	1323	1.96	1.42
F	1028	1.52	1.10

$\Delta\sigma\ \sigma_e = 674.6$ erg^2/cm^4.
$\Delta\sigma_B = 1.38$ erg/cm^2.

from the slope $\sigma\ \sigma_e \Delta\sigma_{\text{bulk}} = 1408\ K^3$ [19], indicating that copper is a material hard to induce transcrystallization. This is somewhat unexpected since the surface energy of anodized copper, like most of metal oxide, is rather high (typically greater than about 500 mJ m^{-2}). Sample A has the highest value of $\Delta\sigma_{\text{TCL}}$, i.e. 3.99 erg cm^{-2}, which indicates that a polished copper surface (i.e. smooth surface) possesses the poorest nucleating ability among the substrates investigated. In other words, transcrystallization of iPP is hardly to take place on the polished surface with the ratio of $\Delta\sigma_{\text{TCL}}/\Delta\sigma_{\text{bulk}} = 2.89$. This is consistance with the observations by POM, in which there is no transcrystalline layer observed on sample A under any supercooling. It is also noticed in Table IV that the value of $\Delta\sigma_{\text{TCL}}/\Delta\sigma_{\text{bulk}}$ decreases with the increasing current density, from 2.15 down to 1.10, showing that transcrystallization becomes favorable as the anodization level gets higher. $\Delta\sigma_{\text{TCL}}/\Delta\sigma_{\text{bulk}}$ ratio is equal to 1.10 for the sample F, indicating the tendency of nucleating is still favorable in the bulk than at the interface, from a thermodynamic point of view. We draw a conclusion that the nucleation ability of the substrate can be varied by changing its surface micro-roughness, no matter what its chemical nature is. This finding agree well with the result from PTFE (i.e., $\Delta\sigma_{\text{TCL}}/\Delta\sigma_{\text{bulk}} = 0.61$) [18] which has been reported frequently to be a prominent material to induce transcrystals although it is a material with very low surface energy. However, its nucleating ability is also largely dependent upon its surface topography [9]. Similarly, although copper oxide has a relatively high surface energy, its nucleation ability seems to be a function of micro-roughness of its oxide layer. However, the authors support the view that the surface roughness in inducing nucleation of the polymer at the interfaces with most substrates is paramount and the highly porous structure produced by anodizing process is an ideal method without changing the chemical compositions of the substrate to prove this argument.

4. Conclusions

A method of anodizing through an electrochemical process was applied on the surface oxidation of copper for the purpose of investigating the topological effect of the substrate upon the interfacial crystallization of polymer. This approach assures that the change of surface structure is merely physical change without variation of chemical composition. The phosphoric acid-anodized copper surface characterized by a surface texture instrument in terms of RMS roughness has higher values of R_a as the applied current density increases. Copper oxide with a higher surface roughness has better nucleating ability and consequently is capable of inducing a thicker transcrystalline layer, no matter from a thermodynamic concern or from a direct observation by POM. This result is consistent with the previous investigation on PTFE, polyimide, aluminum surfaces [9, 19] that the surface roughness, instead of chemical factors or surface energy, playing an important role in heterogeneous nucleating, consequently determing whether a transcrystalline layer can be formed at the interface or not.

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