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Research article

Flow-induced crystallization effect on polypropylene with respect to nucleating agents

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ABSTRACT

To study FIC on the laboratory scale, we used a parallel plate rheometer (PPR), which imparts shear rates of some order of magnitude. Applying shear in undercooling temperature (151 °C) conditions to induced crystallization, which was monitored by the increase in viscosity in the PPR following an established protocol that was stetted up to assess the conditions of the experiments. After annealing samples at 230 °C for 10 min to remove the melt memory effect, it was cooled to crystallization temperature (1510C) at the rate of -1.5 °C/min to undertake FIC and finally the sample was quenched by a cryo-freezer aerosol below 0 °C before being removed for characterization study. FIC involves the formation of the time and temperature-dependent relative crystallinity of a series of isotactic polypropylene (iPP) homopolymers. In this study, I selected iPP as a typical sample due to its simple formation conditions of polymorphic crystals and its unique properties of melting curves and crystalline morphology. In this research, the influence of some nucleating agents on the crystallization behavior of (iPP) Homopolymer has been investigated by OM (Optical Microscopy) and Transmission Electron Microscope (TEM) after undergoing FIC crystallization. The study of crystallization kinetics of iPP Homopolymer nucleated with (Talc, Na-Benzoate) and neat melt (Not nucleated-used as control) helped us to control the final morphologies and mechanical properties of semi-crystalline polymers. From the measured onset time of crystallization, it was possible to conclude that iPP containing Na- Benzoate as the nucleating agent was faster in crystallization.

1. Introduction

According to Emmanuelle and Rene (2002),the first simplest polyolefin is PP(polypropylene) which is obtained by polymerizing propylene. PP is PE (Polyethylene) with a methyl side group for every other carbon atom in the backbone Agrwal et al. (2003). The relative orientation of the side groups in the space (tacticity) is very important for the properties of the material. Baker and Liu (2016). Semi-crystalline polymers cover over two-thirds of the products used in our daily life. Adding a nucleating agent to a semi-crystalline polymer is a common way to control crystallization and tailor mechanical and optical properties Zhang et al. (2002).

In this research, the influence of some nucleating agents and MFR on the crystallization behavior of isotactic polypropylene (iPP) Homopolymer has been investigated by OM (Optical Microscopy) and (TEM) after undergoing FIC(Flow Induced Crystallization) crystallization by a parallel plate rheometer (PPR). For several years, the crystallization of nucleated polypropylene has been the focus of intensive investigation. As a result, some authors identified major characteristics of good nucleating agents for a polymer (Lee Wo et al., 2009). These characteristics are briefly outlined as (I) they are required to lower the interfacial surface free energies involved which is equal to saying polymer should be absorbed on its surface below the polymer melting point; (II) at and below the polymer melting point, the nucleating agent should not be soluble (III) as a rule of thumb, the nucleating agent should melt above the polymer melting point in most cases without decomposition, and (IV) they are preferably required to exhibit the following properties like non-volatile, stable and non-reactive towards its environment and manifests the same crystalline structure to that of polypropylene.

The interface between the nucleating agent and the polymer melt (Lee Wo et al., 2009) has high surface energy, which reduces the energy barrier associated with the formation of a nucleus. According to (D'Orazio et al., 1983), introducing a different type of nucleating agent and particles therefore greatly increases the nucleation density and consequently the rate of crystallization. Hence, in this study, the main focus is to see the effect of different nucleating agents on the rate of

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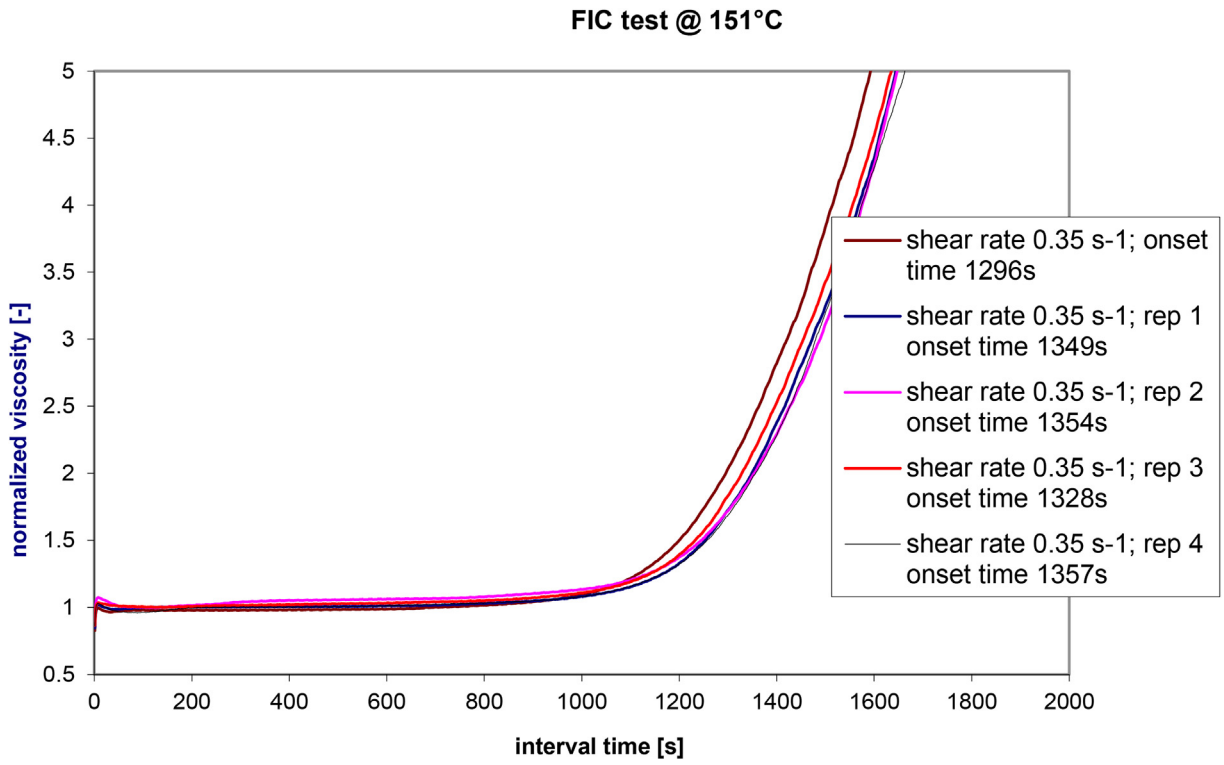

Figure 1. Normalized viscosity versus onset time of Crystallization of Talc loaded isotactic Polymer material (B_2) of HMFR (High Melt Flow Rate) at share rate of $0.35s^{-1}$.

crystallization of Homo isotactic Polypropylene samples of relatively high and low Melt Rates MFR).In general, a higher nucleation density. (Lee Wo et al., 2009) results in a higher rate of crystallization which leads to more desirable properties of polymer materials, however, the amount used in the formulation of our samples was already optimized. So our result discussion will not be based on the number or amount of nucleating agents but rather on the type of nucleating agent used.

To reiterate, the major theme of this experiment is to understand the effect of different nucleating agents and molecular parameters on the crystallization kinetics of a series of iPP samples. Generally, it is well known that the speed of polymer crystallization can be enhanced by the simultaneous application of flow and cooling, and by mixing in specific additives NA (nucleating agents) Nogales et al. (2001). Under strong shear conditions, nucleation changes from isotropic (followed by the growth of spherulites) to anisotropic (row nucleation, followed by the growth of shish–kebab structures or by the development of a trans-crystalline morphology) Nogales et al. (2001) and (D'Orazio et al., 1983). Similar effects can be induced by heterogeneities in the melt (i.e. additives) that are often used during polymer processing as an antioxidant. The presence of various nucleating agents Zuidema et al. (2001) in commodity polymers like isotactic polypropylene (iPP) is quite common but is seldom properly specified. Consequently, results from various publications on the crystallization of iPP from different commercial sources cannot be easily compared. Accordingly, the underlying mechanisms are still poorly understood despite the large amount of work over the last decades Zuidema et al. (2001).

2. Methodology

The following research methodology protocol was followed to scrutinize the effect of FIC and different nucleating agents used on the crystallization kinetics of a series of iPP Homopolymers and to examine the morphology of the materials due to these effects using different laboratory-scale instruments.

Disc-shaped 25 mm diameter with 1.5 mm thickness samples were prepared from iPP Homopolymer pellets by compression molding at a temperature of 200 °C and pressure of 50 bar by compressing for 3 min and then followed by compressing and releasing at 500 bars for 1 min to remove entrapped gas using a CARVER Laminating press. Finally, the product was put under a cold metal plate to cool and carefully cut out disc-shaped samples for final use,

After initializing MCR 301 Rheometer (PPR) by making force normal and Gap width zero adjusted, then the sample was put between plates,and it was heated at 230 °C for 5 min to melt and then trimmed by a special knife to remove an excess melt from parallel plates of rheometer outer edge, then heating chamber was closed-back, heated again for 5 min to melt the polymer sample which was at open-air and cooled while trimming. Then the sample was heated for 10 min (first soaking time) at a constant temperature of 230 °C to remove any thermo-mechanical history before the start of the test and to be sure that it is free from any memory effects associated with the cluster, crystal aggregates, and molecular formation, then we applied simultaneously Small Amplitude Oscillatory Shear (SAOS),

Subsequently, the sample was cooled to the desired common crystallization temperature with a controlled cooling rate of -1.5 °C/min (ramp time) to avoid any undershoots to reach the common temperature selected after a series of tests conducted. The gap between the plates was fixed at 1 mm for all measurements undertaken,

Once the final temperature has been reached, the sample is kept at common crystallization temperature for 10 min, during which second annealing time, dynamic viscosity was monitored. At this point experiments continued either maintaining dynamic regime (0 shears), or applying continuous shear at preselected values to make Steady state shear flow-induced crystallization isothermal measurements.

Finally the sample is quenched with 1, 1, 1, 2-Tertrafluroethane until it is frozen below zero degrees centigrade at the rate of 500 °C/min, then removed from plates and kept for morphology study. This quenching was used in consideration that all samples were treated in the same way so that different cooling rates usually experienced by our polymer melt

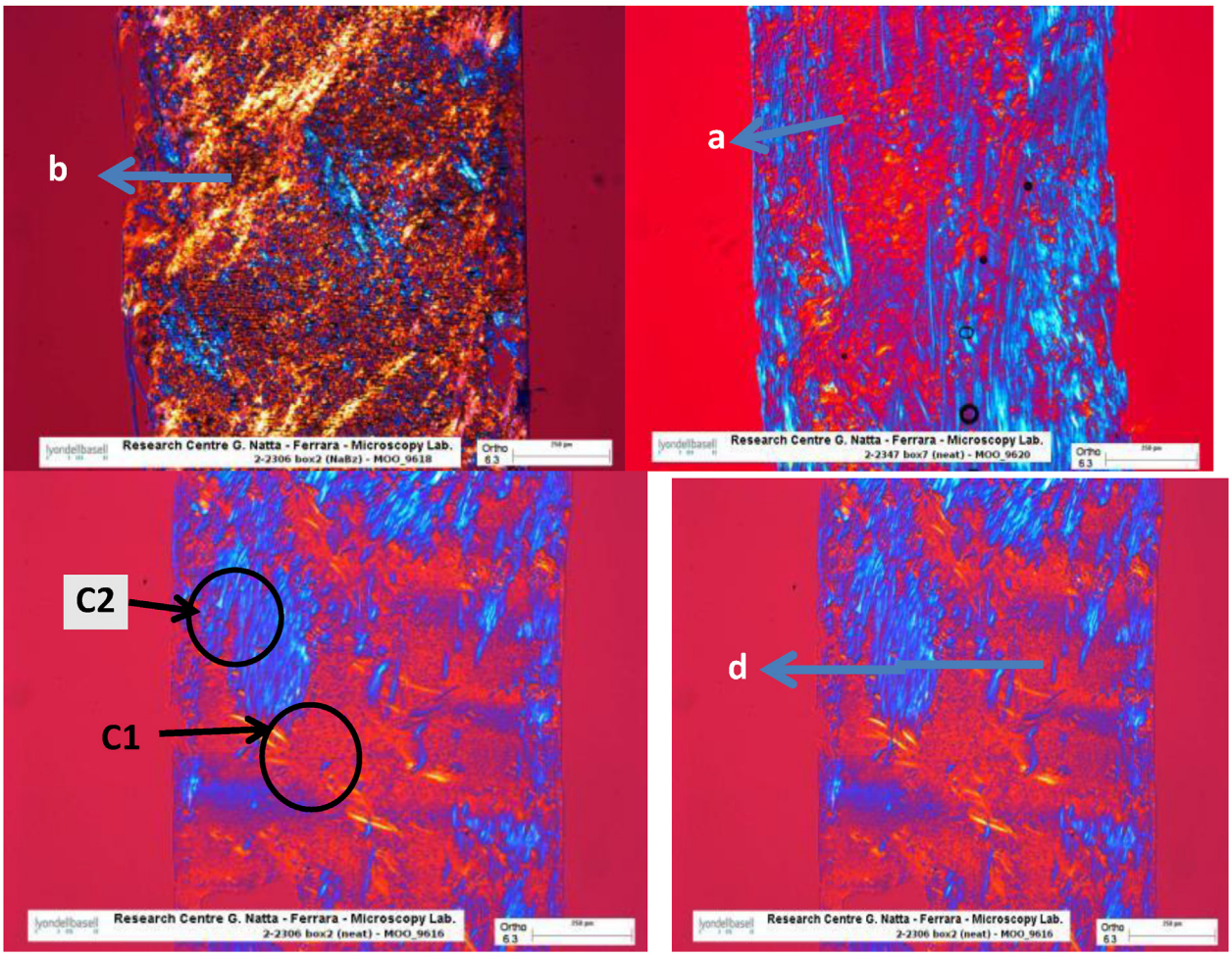

Figure 2. Optical Microscopy (OM) observed microstructure. a) (A_o) Non-Nucleated Neat iPP homopolymer (LMFR)Low Melt Flow Rate; b) (A_1) Sodium_Benzoate nucleated iPP Homo-peculiar morphology because of slow crystallization kinetics, we can see quite clear orientation of macro structure for this materials; c1) Bo(HMFR) Neat iPP Homopolymer sphurulit; C_2) B_2 (HMFR) Talc loaded iPP Homopolymer,); Because of high under cooling and crystallization kinetics, we can't see well-structured morphology d) Bo(HMFR) Neat iPP sssHomopolymer.

sample after flow-induced crystallization under a steady shear process by open atmospheric condition was avoided.

3. Results and discussion

In this paper, we reported the results of Parallel plate Rheometer studies of the crystallization of well-characterized Homo iPP materials loaded with selected nucleating agents, both under steady shear and flow conditions (Figure 3). Here normalized viscosity indicates there is crystallinity due to cooling and flow resulting in clear morphology change (Figures 1, 2, 3).

The OM analysis in polarized light also shows (Figure 2 c1) peculiar crystallization morphology with the presence of macro islands containing oriented "objects" for both high and low MFR neat samples (Table 2). On the other hand, the Na-Benzoate sample gets the observed crystallinity orientation as compared to its neat counterpart. It was confirmed that the nucleating agent effect of the added Sodium- Benzoate and Tlac materials, and this was simply because the microstructures were very fine and strong.

As we have seen from Figure 2, crystallizing iPP homopolymer develops large scale spherulite and thick threads, large enough for direct observation of growth structures by optical microscopy, and shows undergoing a liquid-to-solid transition as an expression of increasing microstructure development (Figure 2 c1 and c2).

As we have observed in series of experiments we conducted, during the shear treatment of the polymer melt at temperatures well above the equilibrium melting point, Tom, no crystallization occurs (Figure 3). However, after cooling the pretreated polymer melt to temperatures well below Tm, the typical lamellar texture and shear zone are obtained in the samples due to shear-induced crystallization as observed by OM (Figure 2 a, b, c1 and d). As also observed, on the other hand, if the pretreated melt is allowed to remain at the temperature below Tm without further shearing (without both steady and dynamic shearing) for a prolonged period and then quenched, a typical-certain texture or increased crystallinity in the sample could appear. When observed by OM due to only the thermal history of the samples (Figure 2 d, c2), however, further experimental studies should be done to make clear the observed phenomena.

(A_0) Net isotactic Polymer material sample without Nucleating Agent(N.A)

(B_2)Talc loaded isotactic Polymer material sample with N.A.

(A_1)Sodium Benzoate(Na-Benzoate) loaded isotactic Polymer Material sample with N.A (Nucleating Agent).

4. Discussion

Generally, the microstructure formed by monitoring Flow-Induced Crystallization at different share rates (Figures 2 and 3) during the

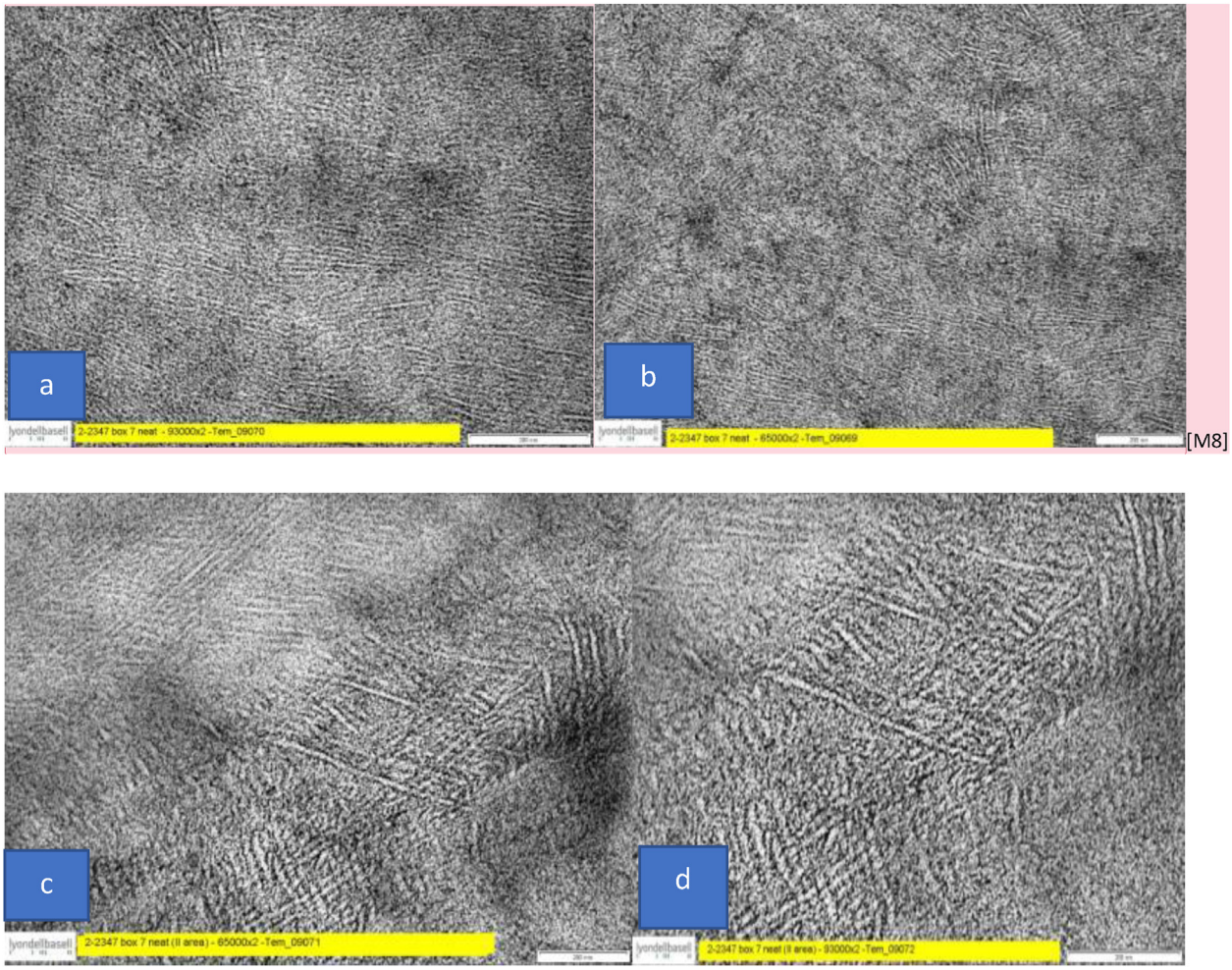

Figure 3. Transmission Electron Microscopy (TEM) observed microstructure. 1) (a, b) were undergone share rate of the order of 0.35s–1 whereas (c, d) were undergone a share of the order of 0.5s–1. 2) (B_0) Net Material without N.A (HMFR)Low Melt Flow Rate iPP Homopolymer:In this case,we could see packed lemella (like finger print) after undergone steady share at undercooling temperature 151^{0}C (FET Tecnai 10 TEM).

Table 1. Onset time of crystalization versus Normalized viscosity at share rate 0.0s^{-1}.

Variable	Obs	Mean	Std. Dev.	Min	Max
ynormalize ~ y	5	.0272	.0105688	.01	.036
xinseconds	5	49394	3430.214	44600	52392

Table 2. Onset time of crystalization Versus Normalized viscosity at share rate 0.35s^{-1}.

Variable	Obs	Mean	Std. Dev.	Min	Max
ynormalize ~ y	5	1.268	.1548225	1.1	1.48
xinseconds	5	1322.2	43.44192	1258	1354

processing of polymer products determines the final characterization properties the materials under investigation. Some characterization properties shown (Table 4) such as modulus, which is the strength of the material and its crystallinity,heat of Enthalpy and percentage index isotacticity of iPP sample materials, helped us to reveal the effect of nucleating agents.

Table 3. Onset time of crystallization versus Normalized viscosity at share rate of 0.65s^{-1}.

Variable	Obs	Mean	Std. Dev.	Min	Max
ynormalize ~ y	5	1.476	.1217785	1.3	1.61
xinseconds	5	612.6	40.5931	570	670

Therefore, according to (Tables 2 and 3), it is possible to see that there is a great correlation between the microstructure of polymer products formed according to the thermo-mechanical history and FIC (Figure 1) of the polymer melt and the mechanical property of the material under investigation. Furthermore, it is possible to see the effect of share rate (Figures 3a, 3b, 3c and 3d) on the microstructure formed during FIC. During sample preparation, our samples developed thermo-mechanical history by compression molding; however, the effect on the microstructure was negligible. In addition, the microstructure developed in this process was observed when the material has undergone different Characterization involving TEM, and OM (Figures 2 and 3). From the onset of crystallization shown in (Tables 1, 2, and 3) and characterization results indicated during OM and TEM, it is possible to see iPP material nucleated with Sodium Benzoate has shown high crystallinity and good strength.

Table 4. Characterization of isotactic Homo Polyproplyene samples (iPP).

iPP homo polymer samples	Nucleating Agent (N.A) was used and amounted added to the polymer Sample	MFR (Melt Flow Rate) [g/10min]	Elastic modulus at 23 °C [Mpa]	Crystallinity WAXD [%]	ΔHm 1st run in DSC [J/g]	Isotacticity Index [%] from NMR
Ao	Without N.A	45	1957	47	116.1	98.2
A1	Sodium Benzoate [900ppm]	45	2515	49	118.9	98.2
A2	Talc [8500ppm]	47	2088	61	119.3	98.2
Bo		77	1956	48	117.4	98.7
B1	Sodium Benzoate [900ppm]	77	2365	49	123.3	98.7
B2	Talc [8500ppm]	71	2260	59	120.4	98.7

Melt Flow Rate in gram per 10 min (MFR-g/10 mint) isotactic Homo Polypropylene(iPP): Elastic modulus in Mega Pascal(MP) at 23°C measured using DMA 800:Percentage crystallinity by WAXD; Enthalpy of melting in Jule per gram(J/g) the 1st run by DSC; and isotacticity Percentage index of series of isotactic Polypropylene (iPP) materials.

5. Conclusion

It is rather difficult to establish the relationship between the observed microstructure and rheological properties at this level. However, extensive studies on more relevant kinetics properties governing the Induced Flow Crystallization (FIC) experiments are needed to establish the relationship between morphology and rheological properties. Therefore, this extensive study should be induced by high pressure and cooling from crystallization temperature during the evolution of viscosity or solidification of the polymer melt, and that should be carried out accurately in order to optimize the process simulation of the injection molding.

Declarations

Author contribution statement

Mulugeta Goa Sellelo, M.Sc: Conceivd and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

The authors do not have permission to share data.

Declaration of interest's statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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