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Application of Differential Scanning Calorimetry (DSC) and Avrami Coefficients analysis in Investigating Isothermal Crystallization Kinetics of Recycled LDPE

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Abstract

This study presents the thermal and crystallization behavior of recycled low-density polyethylene (LDPE) samples with different colors. Differential Scanning Calorimetry (DSC) was employed to analyze thermal transitions and crystallization kinetics under isothermal conditions and at multiple cooling rates. Isothermal crystallization studies were performed to assess the kinetics of phase transformation, and the Avrami model was applied to determine the exponent (n) and rate constant (k). These parameters revealed clear differences in nucleation and crystal growth mechanisms, strongly influenced by the presence of additives and filler residues. This study observed the impact of additives on the crystallinity of LDPE with different color. The results show that additive content, reflected by sample coloration, significantly affects nucleation density, crystallization rate, and crystal morphology. The variation in Avrami coefficients across samples confirms these influences, underlining the role of pigments and residual compounds in modifying the thermal response of recycled polymers. This study reinforces the value of isothermal DSC and kinetic modeling in evaluating recycled LDPE quality and highlights the need to account for additive effects in optimizing recycling processes and end-use performance.

Keywords: Low-density polyethylene (LDPE), Differential Scanning Calorimetry (DSC), additives, Avrami Coefficients, nucleation

1. INTRODUCTION

Low-density polyethylene (LDPE) is one of the most commonly used plastics, especially in packaging and everyday consumer products (Hopewell, Dvorak, and Kosior 2009; Al-Salem and Lettieri 2009). The thermal and mechanical properties of LDPE often change during recycling when compared to those of the original, or pure material. This is mainly because of the various additives, pigments, and leftover contaminants it picks up during use and the recycling process (Kale, Auras, and Singh 2007). These substances can have a big impact on how the plastic crystallizes—affecting how crystals start to form, how they grow, and ultimately how well the material performs (Thomas and Coran 2004).

Crystallization kinetics and thermal transitions in LDPE are critical determinants of its processability and end-use properties (Mucha and Królikowski 2003; Hoffman 1983). Differential Scanning Calorimetry (DSC) has been extensively utilized to characterize melting and crystallization phenomena in polymers (Avalos, Lopez-Manchado, and Arroyo 1996). However, there is still limited understanding of how differences in additive content often associated with color variations, influence the isothermal crystallization kinetics of recycled LDPE (Jia, Wang, and Xu 2014). Isothermal crystallization studies, combined with kinetic modeling such as the Avrami equation, which is essential for optimizing processing conditions (Avrami 1939; Jeziorny 1978). This study focuses on the thermal and crystallization behavior of recycled LDPE samples with different pigmentation levels. Using DSC was analyzed the influence of additives on crystallization kinetics under controlled isothermal conditions and multiple cooling rates. The application of the Avrami model allowed for quantitative assessment of crystallization mechanisms across differently colored samples, revealing how residual compounds affect thermal stability and crystallinity. These findings contribute to a better understanding of the structure-property relationships in recycled LDPE and support efforts to enhance material quality through improved recycling and processing strategies (Kreiger et al. 2014).

2. MATHERIAL AND METHODS

2.1 Thermal Analysis

Our sample analysis were performed at the Laboratory of Polymer's Material Transport Phenomena at the Nanoscience and Nanotechnology Institute in the National Centre for Scientific Research "DEMOKRITOS", Athens, Greece. The apparatus used is a TMDSC of TA Instruments (MDSC 2920). All experiments are performed at constant nitrogen flow. The baseline of TMDSC apparatus is being determined using the measurements protocol with empty capsules. At all measurements were used pure aluminum capsules, and the heating rate it was held at10°C / min with oscillation of ±1.59°C every 60 sec. The mass of the samples varies at 9-12 µg. As it is balanced for 2 min at 25.00°C, the sample is heated at rate 10°C/min up to 140 °C and maintained under isothermal conditions for 5 min, to continuing cooling up to 25 ° C. The same cycle is repeated for the second time. ΔH_{M0} = 290.0 J/g for 100% crystalline LDPE [10, 11]. By integrating the melting peak surface at 115°C-135°C limits it is determined for each sample the respective value for entalpi of melting ΔH_M (J/g). Likewise, by integrating the crystallization peak surface at 100-120°C limits it is determined for each sample the respective value for enthalpy of crystallization ΔH_C (J/g). By the ratio of respectively $\Delta H_C / \Delta H_{M0}$ it is calculated the percentage of crystallinity.

2.2 Isothermal Crystallization of Recycled LDPE

It is made the characterization of thermal properties for all recycled LDPE samples and it is selected the red and black one. The samples are balanced for 2 min at 25 ° C to remove air from the DSC cell, then heated up to 160 ° C where are held for 5 min at isothermal conditions in order to destroy their thermal history , in the following are cooled and held to the predetermined temperature for 30 min. The last stage is the reheating of the samples until 170 °C and is performed two types of experiments:

i. with free cooling rate until the predetermined temperature
ii. with 10°C/min cooling rate until the predetermined temperature

The temperatures predetermined for isothermal measurements are 111°C, 115°C 118°C 120°C 122°C, in order to occupy the entire temperature range of polymer crystallization peak.

Figure 1. Recycled LDPE granules (EVERETST I.E.)

3. RESULTS AND DICUSSIONS

3.1 Thermal analysis

In the figure 2 are presented separately, thermograms of ΔH dependence vs. temperature, of heating-cooling cycle for red recycled LDPE. A TMDSC thermogram is divided into:

Total Signal
Signal of reversible processes
Signal of irreversible processes

By integration the surface of crystallization peak area at 100°C-120°C temperature limits it is determined respective value of crystallization enthalpy ΔH_C (J/g). By the ratio of this value with ΔH_0, it is calculate the percentage of crystallinity by the formula:

$$X_{CC} = \frac{\Delta H_C}{\Delta H_O} \times 100\%$$

The literature value of melting enthalpy for 100% crystalline LDPE is $\Delta H_0 = 290.0$ J/g.

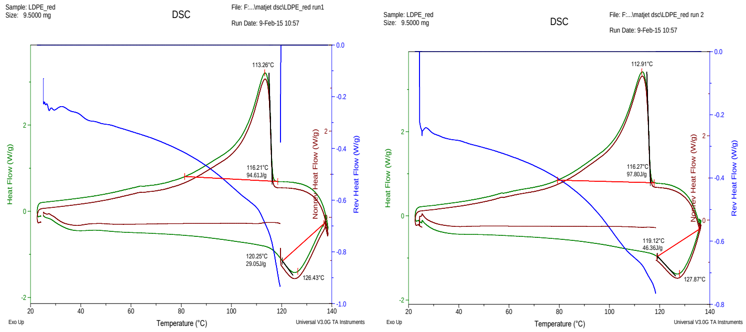

Figure 2 Thermogram of ΔH dependence vs. temperature for red recycled LDPE for first and second run

The figure 2 clearly shows that the thermogram patterns are consistent, with similar melting and crystallization peaks. We can see the same trend in the Tm and Tc values listed in Table 1 for the first run and Table 2 for the second, for all the samples we're studying. Repeatability of thermograms is an indicator of sustainability of recycled LDPE structure, regardless of the additives.

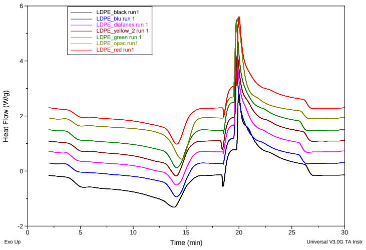

Figure 3 Thermograms of all LDPE samples (first run)

Melting and crystallization peak seen in figure.3 have different shape and size due to variable amounts of additives the samples have. From the table 1 results that they have small Xc changes due to the thermal history of the samples, an expected result as LDPE is a thermoplastic material. Theoretically, the shape of the peak provides information about the quantity and quality of the material's crystallinity (Papajani. B, et al 2018). Specifically, a sharp peak indicates good crystal quality in polymers. From a quantitative perspective, the degree of crystallinity depends on the total area under the peak (Kreiger et al.2014) Therefore, a high and sharp peak is a sign of well-structured material, whereas a broad and smooth peak indicates poorer structural organization (Schultz, J.M., 2001).

Table 1. Summary results for all samples of recycled LDPE to the first heat run

Samples LDPE	**T_m (°C)**	**T_{mp} (°C)**	**ΔH_m (J/g)**	**T_c (°C)**	**T_{cp} (°C)**	**ΔH_c (J/g)**	**X_{cc} (%)**
pure	97.73±0.2	108.16±0.3	34.78±0.24	98.77±0.4	94.92±0.4	82.13±.0.31	28.3±1.1
opaque	119.8±0.6	130.1±0.5	72.5±0.46	116.6±0.7	110.3±0.3	129.9±0.26	44.8±1.8
blue	120.0±0.7	126.8±0.6	26.4±0.32	116.4±0.5	113.4±0.5	93.61±0.45	32.3±0.4
Tech pure	119.0±0.4	126.5±0.5	33.6±0.53	116.0±0.3	113.0±0.4	95.35±0.23	32.9±0.8
green	119.2±0.7	126.4±0.9	38.3±0.35	116.6±0.4	114.0±0.5	95.39±0.41	32.8±1.2
red	120.3±0.1	126.4±0.7	29.1±0.24	116.2±0.6	113.3±0.7	94.61±0.26	35.4±1.3
black	120.1±0.3	125.4±0.5	15.0±0.55	115.0±0.4	112.3±0.7	87.45±0.32	30.2±0.9
yellow	119.3±0.3	127.4±0.4	40.5±0.67	115.8±0.3	112.6±0.2	96.21±0.26	31.9±1.0

Table 2. Summary results for all samples of recycled LDPE to the second heat run

Samples LDPE	**T_m (°C)**	**T_{mp} (°C)**	**ΔH_m (J/g)**	**T_c (°C)**	**T_{cp} (°C)**	**ΔH_c (J/g)**	**X_{cc} (%)**
pure	98.59±0.4	108.56±0.5	24.54±023	98.49±0.4	94.84±0.5	81.24±0.43	28±0.8
opaque	120±0.3	130.1±0.3	85.4±0.32	116.7±0.5	110.6±0.3	127.1±0.64	43.8 ±1.7
blue	120.0±0.3	128.1±0.5	43.0±0.03	116.6±0.6	113.6±0.5	90.4±0.025	31.2±1.1
Tech pure	119.1±0.4	128.4±0.2	40.4±0.17	116.2±0.5	113.1±0.4	89.6±0.36	30.9±0.9
green	119.6±0.8	128.7±0.5	47.7±0.34	116.6±0.3	113.9±0.5	94.6±0.34	32.6±1.2
red	119.1±0.9	127.9±0.7	46.4±0.48	116.3±0.5	112.9±0.4	97.8±0.40	35.8±0.7
black	120.0±0.1	126.0±0.6	22±0.18	114.9±0.7	111.8±0.6	85.4±0.27	29.5±0.8
yellow	118.9±0.7	128.2±0.5	45.7±0.26	115.7±0.3	112.4±0.24	98.14±0.12	32.5±1.0

In the figure 4. is made the comparison of red recycled LDPE sample with the black one.

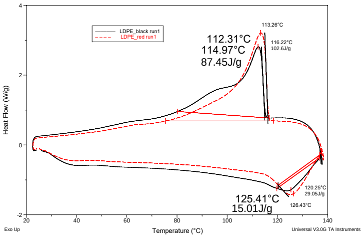

Figure 4. Thermograms of red [— —] and black [—–] recycled LDPE of ΔH dependence vs. temperature

As demonstrated figure 4, the recycling process does not induce significant structural changes, and the thermoplastic properties of the material are preserved. Furthermore, table 1 and table 2 demonstrate that the degree of crystallinity in the red recycled LDPE is observed to be higher than that of the black recycled LDPE (Durmus A., Yalcinyuva T. 2009).

3.2 Isothermal crystallization of LDPE

The thermal analysis revealed that.Red recycled LDPE presents the best quality and black recycled LDPE presents the worse one. For a more in-depth investigation of the crystallization kinetics of these samples it is done: a) isothermal study of the crystallization kinetics, b) definition of the Avrami coefficients.

The crystallization at different cooling rates

In the figure 5 is presented the thermograms of black recycled LDPE at 115°C crystallization temperature at free cooling rate and 10°C/min controlled cooling rate. By the peak's shape it is apparent that there are significant differences in the crystallization ways.

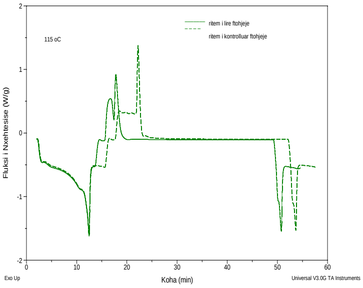

Figure 5. Thermograms of ΔH dependence vs.time for black recycled LDPE at 115°C crystallization temperature of free cooling rate [—–] and 10°C/min controlled cooling rate [- - -].

In the case of free cooling, the crystallization curve appears broad and begins immediately with the onset of cooling. This behavior suggests that, alongside the solidification of the material, an irregular and poorly structured crystallization process also begins. The peak that appears at the expected temperature is not sharp, which suggests poor crystallization quality. At free cooling rate, the volume decreases rapidly and barriers of other molecules neutralizes the ability of molecules to achieve this condition. The system is locked in a metastable state; however, limited molecular movement via diffusion may still occur, depending on the degree of polymerization (Hurnik, H. 2001). In the case of controlled cooling rate the change of ΔH to time is constant until temperature is close to the predetermined crystallization temperature, when it is displayed a sharp peak that is an indicator of good crystallization quality. In the case of free cooling rate the shape of crystallization peak is irregular and loses the possibility of measuring the linearity.

Isothermal crystallization kinetics

To study the crystallization kinetics of the polymer, isothermal DSC measurements were performed at predetermined temperatures of 111 °C, 115 °C, 118 °C, 120 °C, and 122 °C, carefully selected to span the range around the crystallization peak temperature.

The thermograms of five predetermined crystallized temperatures are presented overlapped in the figure 6 and figure 7. As the temperature approaches the melting point, the material tends to favor the amorphous state over the crystalline one. This behavior is observed in both red and black recycled LDPE samples.

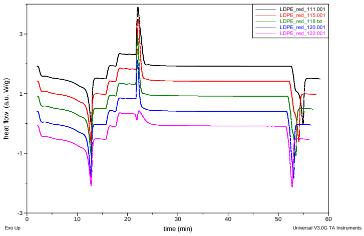

Figure 6. Thermograms of ΔH dependence vs. time for red recycled LDPE at all predetermined crystallization temperatures Tc.

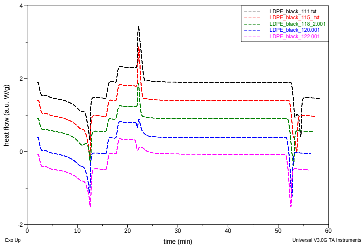

Figure 7. Thermograms of ΔH dependence vs. time for black recycled LDPE at all predetermined crystallization temperatures Tc

A comparison between red and black recycled LDPE reveals that the black sample exhibits poorer crystal quality, as indicated by the shape of the crystallization peak, and a lower degree of crystallinity, as reported in Table 3, compared to the red sample.

Table 3. Experimental data of thermograms and the percentage of crystallinity for red and black recycled LDPE

	LDPE red					LDPE black				
Temp °C	ΔH J/g	X_{cc} %	T_{cf} °C	T_{cc} °C	Time of cryst. (min)	ΔH J/g	X_{cc} %	T_{cf} °C	T_{cc} °C	Time of cryst. (min)
111	79.48	27.4±0.8	120.44	118.03	22.05	54.77	18.9±0.7	119.09	116.81	22.15
115	64.13	22.1±0.9	119.97	117.58	22.13	36.64	12.6±0.4	118.82	116.60	22.2
118	53.83	18.6±1.1	120.67	119.04	21.98	19.72	6.8±0.5	118.89	118.04	22.13
120	40.03	13.8±0. 6	120.60	120.30	21.97	7.69	2.7±0.3	-	119.76	22.25
122	36.86	12.7±0.8	120.58	120.32	21.95	7.49	2.6±0.6	-	121.94	22.63

By the comparison between the red and black sample, it is obvious seen that for the same crystallization temperature Tc, black recycled LDPE has lower percentage of crystallinity and thus has bad quality of crystal than the red one

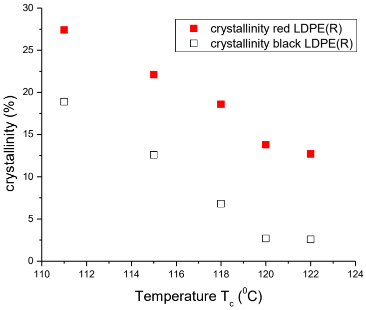

Figure 8. The crystallinity dependence vs. isothermal crystallization temperature for red recycled LDPE [■] and black recycled LDPE [□].

Determination of Avrami coefficients

In this part of the study, the crystallization behavior of red and black LDPE samples was analyzed within the temperature range of 111°C to 122°C, using the Avrami model. The experimental data were fitted to the Avrami equation, and the values of the kinetic coefficients were determined using the following equations:

$$X_c(t) = 1 - \exp\left(-Kt^n\right)$$

$$Log\left[-\ln\left(1 - \mathrm{Xc}(\mathrm{t})\right)\right] = \log(K) + n\log(t)$$

For the linearization of the curves, the analysis focuses on the experimental data from the onset of crystallization up to the peak crystallization point for each material, across all predetermined crystallization temperatures.

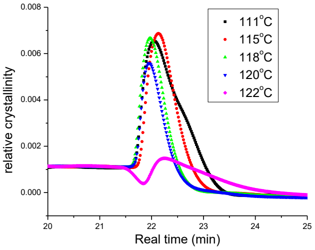

Figure 9. Relative crystallinity vs. real time of TMDSC measurements for red recycled LDPE.

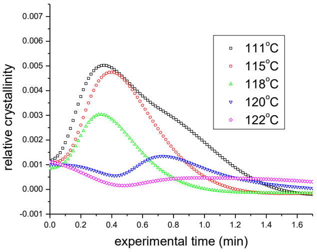

Figure 10. Relative crystallinity vs. experimental time of TMDSC measurements for black recycled LDPE.

As it seen from the figures relative crystallinity varies with the crystallization temperature.

The linearization of the experimental data from the onset of the crystallization process follows the Avrami equation, preserving the physical meaning of the coefficients. The coefficient "K" is obtained from the intercept of the linearized curve with the y-axis, while the coefficient "n" corresponds to the slope of the curve at different crystallization temperature (Callister W. D. and Davi.G. Rethwisch, 2012)

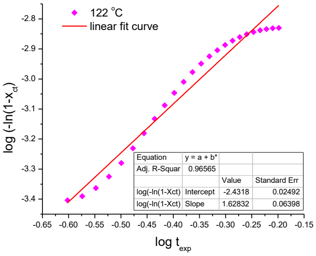

Figure 11. Linearization of log (-ln (1-x_{ct})) vs. log t_{exp} at T=122°C for red recycled LDPE.

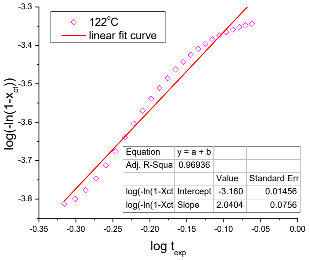

Figure 12. Linearization of log (-ln (1-x_{ct})) vs. log t_{exp} at T=122°C for black recycled LDPE.

The figures present the linearization for only one temperature for both red and black recycled LDPE. For both materials at all crystallization temperatures Tc, the first parts of the curves are almost linear and the curves lose their linearity as crystallization time increases, thus lose the physical meaning of the Avrami parameters.

As it is seen from the figure 13, for the first three crystallization temperatures Avrami coefficients values of black LDPE are a bit smaller compared to red LDPE. This relates to the fact that crystallinity of black recycled LDPE is lower than the red one. The absolute value of log K decreases (i.e., log K becomes less negative) as the crystallization temperature increases; consequently, the coefficient K decreases with increasing crystallization temperature. The coefficient K is related to both the crystal growth rate and the nucleation mechanism (Callister W. D. and Davi.G. Rethwisch, 2012).

It can be concluded that, for our samples, the crystal growth rate decreases with increasing crystallization temperature

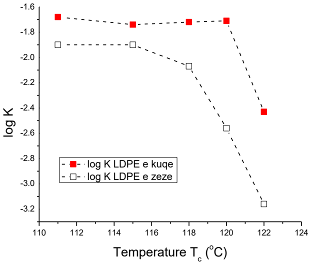

Figure 13. Log K vs. predetermined crystallization temperature T_c, for red recycled LDPE [■] and for black recycled LDPE [□].

LogK values are lower at black recycled LDPE sample, compared with the red one, so the crystal growth rate to black LDPE is smaller compared to the red sample. This relates to the different persentage of crystallinity and to different quantities of additives they have. The result is consistent with the literature (Avrami, M. 1939, and Mucha, M., and Z. Królikowski. 2003). On the other hand, "K" coefficient indicates the nucleation mode. Referring to the literature for our "K" values it results that for our samples nucleation mode is heterogeneous. Heterogeneous nucleation occurs on the surface of impurities within the system, therefore occurs to the limits of additive's molecules.

Table 4: Summary table of Avrami coefficients

Sample	Red LDPE					Black LDPE				
Temp	111°C	115°C	118°C	120°C	122°C	111°C	115°C	118°C	120°C	122°C
n	1.11	0.95	0.94	1.08	1.63	0.78	0.96	0.86	1.94	2.04
log K	-1.68	-1.74	-1.72	-1.71	-2.43	-1.90	-1.90	-2.07	-2.56	-3.16
K	0.0208	0.018	0.0190	0.019	0.0037	0.0125	0.0125	0.0085	0.0027	6.91831E

The values of "n" coefficient vary between to n = 1.11 to n = 1.63≈2 for red sample and between n = 0.78 to n = 2, 04 for black sample. So the crystal growth is one and two-dimensional at the first crystallization stage. The crystals grow as fibrile and disc shape. For this crystallization's phase, because of our samples are recycled, it is not possible to obtain the value of coefficient "n" = 2.5 ~ 3, three-dimensional spherical growth indicator. This change is attributed to the presence of additives in the samples. The linear section of Avrami approximation loses after the peak of crystallization. By changing the slope of the curve, Avrami model cannot predict the rate and mode of nucleation after the crystallization peak.

CONCLUSIONS

The recycling process does not induce structural changes in the material, which retains its thermoplastic properties. The degree of crystallinity varies between samples of different colors and depends on the amount of additives used during recycling. The measured crystallinity values (30–40%) are consistent with those reported in the literature. Comparing thermograms obtained under free cooling and controlled cooling conditions reveals distinct behaviors: under free cooling, the crystallization rate is high, which leads to an irregular crystallization peak that compromises the linearity necessary for kinetic analysis. In contrast, controlled cooling produces a sharp crystallization peak that maintains linearity during the initial phase of crystallization. Thermograms obtained from thermal analysis of isothermal kinetic of red and black recycled LDPE color we detect repetition in the thermogrames shape and displacement of the melting peak vs. time of two samples at different crystallization temperature.There are Xc changes as a result of various quality of both materials. Red and black recycled LDPE have higher and lower percentage of crystallinity respectively. The isothermal crystallization kinetics of red and black recycled LDPE, analyzed using the Avrami model for bulk crystallization, show that at the onset of crystallization, the model fits the experimental data well for both samples. According to literature, the "K" values imply that nucleation in both samples is heterogeneous, occurring on impurity surfaces such as additive molecules. During the initial crystallization stage, crystal growth is predominantly one- or two-dimensional.

REFERENCES

1. Al-Salem, S. M., and P. Lettieri. 2009. "Recycling and Recovery Routes of Plastic Solid Waste (PSW): A Review." *Waste Management* 29 (10): 2625–2643. https://doi.org/10.1016/j.wasman.2009.06.004.
2. Avalos, F., M. A. Lopez-Manchado, and M. Arroyo. 1996. "Crystallization Kinetics of Polyethylene and Polypropylene." *Polymer* 37 (25): 5681–5688. https://doi.org/10.1016/S0032-3861 (96)00429-6.
3. Avrami, M. 1939. "Kinetics of Phase Change. I General Theory." *The Journal of Chemical Physics* 7 (12): 1103–1112. https://doi.org/10.1063/1.1750380.
4. Callister W. D. and Davi.G. Rethwisch,2012: *Fundamentals of Material Science and Engineering,* 4th Ed) Published by John Wiley &Sons; ISBN 978-1-118-06160-;325-339
5. Durmus A., Yalcinyuva T. 2009. "Effects of additives on non-isothermal crystallization kinetics and morphology of isotactic polypropylene",. *Journal of polymer research, http://doi.org/10.1007/ s10965-008-9252-9, 16(5), 489-498*
6. Hoffman, John D. 1983. "Kinetics of Crystallization from the Melt and Chain Folding in Polyethylene Fractions Revisited: Theory and Experiment." *Polymer* 24 (1): 3–26. https://doi.org/10.1016/0032-3861 (83)90074-5.
7. Hopewell, J., R. Dvorak, and E. Kosior. 2009. "Plastics Recycling: Challenges and Opportunities." *Philosophical Transactions of the Royal Society B: Biological Sciences* 364 (1526): 2115–2126. https://doi.org/10.1098/ rstb.2008.0311.
8. Hurnik, H. 2001, *Plastics Additives Handbook*, 5th ed; publisher Carl Hanser Verlag, Munich, p. 699; ISBN: 978-3-446-40801-2
9. Jeziorny, A. 1978. "Parameters Characterizing the Kinetics of the Non-Isothermal Crystallization of Polymers." *Polymer* 19 (10): 1142–1144. https://doi.org/10.1016/0032-3861 (78)90066-7.
10. Jia, H., Y. Wang, and Y. Xu. 2014. "Effect of Impurities on Crystallization Behavior of Recycled Polyethylene." *Polymer Testing* 39: 117–123. https://doi.org/10.1016/ j.polymertesting.2014.05.008.
11. Kale, G., R. Auras, and S. P. Singh. 2007. "Biodegradability of Polylactide Bottles in Real and Simulated Composting Conditions." *Polymer Testing* 26 (8): 1049–1061. https://doi.org/10.1016/ j.polymertesting.2007.07.006.
12. Kreiger, M. A., M. L. Mulder, A. G. Glover, and J. M. Pearce. 2014. "Life Cycle Analysis of Distributed Recycling of Post-Consumer High Density Polyethylene for 3-D Printing Filament." *Journal of Cleaner Production* 70: 90–96. https://doi.org/10.1016/ j.jclepro.2014.02.009.
13. Mucha, M., and Z. Królikowski. 2003. "Application of DSC to Study Crystallization Kinetics of Polypropylene Containing Fillers." *Journal of Thermal Analysis and Calorimetry* 74: 549–557. https://doi.org/10.1023/ B: JTAN.0000008070.47294.2e.
14. Papajani. B, et al 2018. "The study of the influence of additives in the crystallinity of recycled LDPE by IR and XRD analysis" *RAD Conference Proceedings,* vol. 3; 236–240, ISSN 2466-4626 (online) | DOI: 10.21175/ RadProc.2018-49, www.rad-proceedings.org.
15. Hiemenz, P.C., and Lodge.P.Timothy, 2007. *Polymer Chemistry*; CRC press New York, , 510-562.
16. Schultz, J.M., 2001. *Polymer Crystallization*, Oxford University Press, New York, 288, **ISBN-10**: 0841236690