IOCC 2024 Conference

The 4th International Online Conference on Crystals

18–20 September 2024 | Online

Study of structure and filler crystallinity index of polymer composite with silica nanofibrous filler

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INTRODUCTION & AIM

In modern composite materials science, the application of track membranes for creating nanostructured replicas by the template method is of considerable interest. This method, in addition to obtaining nanostructured replicas, can also be used to create composite materials. In this case, no removal of the template occurs after the replica is obtained. Most often the process of creating such composites consists in metal particles electrodeposition in the pores of a polyimide track membrane, as a matrix with relatively high thermal and chemical resistance parameters [1-3]. Obtaining of such composites is of high importance for technologically demanding areas of industry, as deposition of some known and, what is more importantly, controlled amount of filler in polymer matrix allows to control different properties of such composites.

One of the important parameters for the filler of composite track polyimide membrane is the degree of its crystallinity, which is defined as the mass ratio of crystalline phase to sample weight. This parameter strongly correlates with the crystallinity parameter defined as the ratio of the area under crystalline peaks to the total geometric area under the XRD pattern, which in turn allows indirectly analyze the degree of crystallinity using XRD.

METHOD

When assessing the degree of crystallinity of amorphous-crystalline silica filler, a hypothesis was put forward about the existence of a relationship between the parameters of the actual crystallinity index (CI_{real}), calculated by formula 1, and the estimated crystallinity index ($CI_{XRD\ est.}$), calculated by formula 2. Within the scope of the work, the ratio of the mass of crystalline additive to the mass of amorphous additive was taken as the numerical value of the actual crystallinity index:

$$CI_{real} = \frac{m_{cryst.}}{(m_{cryst.}+m_{am.})} \cdot 100\%, \qquad (1)$$

where $m_{cryst.}$ is the mass of the crystalline phase/component (for calibration mixtures), $m_{am.}$ is the mass of the amorphous phase/component (for calibration mixtures). Based on this ratio, it can be noted that complete absence of amorphous additive (CI_{real}=100%) is considered as complete crystallization, the opposite of which is complete absence of crystalline additive (CI_{real}=0%). The ratio of the area of crystalline peaks in the diffraction pattern to the total area was taken as the numerical value of the crystallinity evaluation index ($CI_{XRD\ est.}$).

$$CI_{real} = \frac{S_{cryst.}}{S_{total}} \cdot 100\%, \qquad (2)$$

where $S_{cryst.}$ is the sum of the areas of crystalline peaks, S_{total} is the total area under the XRD pattern.

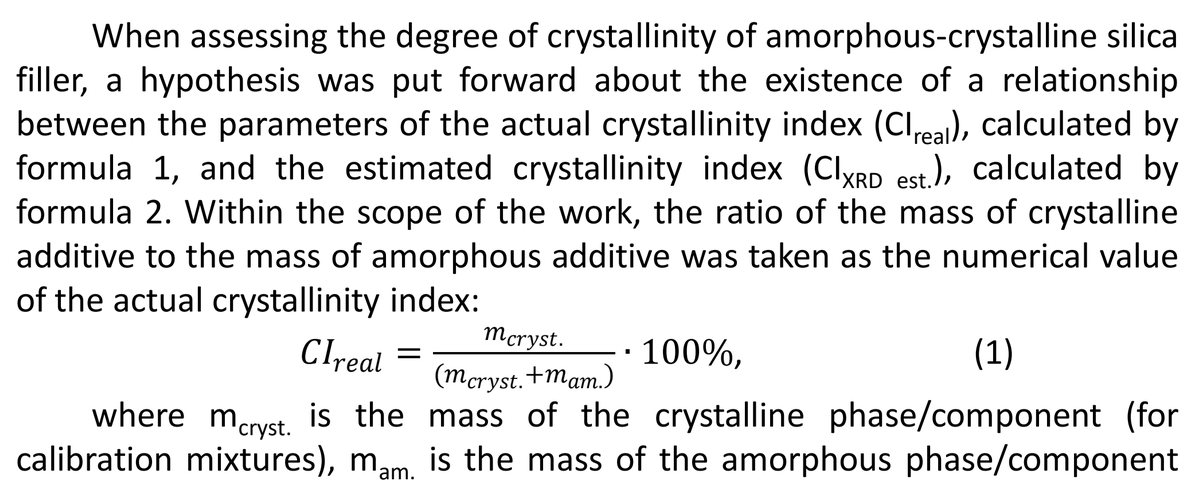

Fig. 1. $S_{cryst.}$ and S_{total} visualization

RESULTS & DISCUSSION

Numerical integration was performed in the program Origin Pro 2021 using the tools "Peak analyzer" (to calculate the total area of crystalline peaks) and "Integrate" (to calculate the total area under the diffraction pattern). The integration results are presented in Table 1 (columns $S_{cryst.}$ and S_{total}).

Numerical integration was performed in the area of diffraction pattern from the top bounded by intensity data line and from the bottom by constant baseline defined as a minimum of the intensity value (integration mode "To base line", baseline setting mode "Baseline mode - constant"). The fluctuations of the baseline parameter are reflected in Table 1, column "Baseline". The values presented in it were used in the numerical integration of the diffraction pattern in the "To base line" mode.

Sample		Baseline	$m_{cryst.}$, g	$m_{am.}$, g	CI_{real},%	$S_{cryst.}$	S_{total}	$CI_{XRD\ est.}$,%
0%	1	22	0	1,5	0,00	232,20	3780,86	6,14
	2	30	0	1,5	0,00	348,58	3846,51	9,06
	3	20	0	1,5	0,00	274,20	3316,23	8,27
	4	18	0	1,5	0,00	201,28	2284,78	8,81
	5	20	0	1,5	0,00	259,58	2857,36	9,08
	6	17	0	1,5	0,00	248,73	2755,87	9,03
20%	1	18	0,3	1,2	20,00	636,28	3052,43	20,84
	2	22	0,3	1,2	20,00	664,25	3203,96	20,73
	3	18	0,3	1,2	20,00	578,93	3046,58	19,00
	4	13	0,3	1,2	20,00	465,00	2453,88	18,95
40%	1	26	0,606	0,912	39,92	1209,30	3989,97	30,31
	2	12	0,607	0,902	40,23	989,05	3133,94	31,56
	3	12	0,604	0,905	40,03	721,63	2306,96	31,28
	4	14	0,602	0,901	40,05	975,30	3204,21	30,44
60%	1	26	0,905	0,604	59,97	1911,05	5161,92	37,02
	2	26	0,906	0,6	60,16	2022,00	4828,39	41,88
	3	24	0,907	0,601	60,15	2065,08	4557,12	45,32
	4	18	0,904	0,604	59,95	2077,10	5010,94	41,45
80%	1	24	1,201	0,3	80,01	2328,63	4537,43	51,32
	2	25	1,205	0,302	79,96	2390,50	5128,37	46,61
	3	24	1,207	0,303	79,93	2388,15	4645,27	51,41
	4	28	1,201	0,304	79,80	2499,50	5058,94	49,41
100%	1	8	1,5	0	100,00	2109,83	3089,45	68,29
	2	22	1,5	0	100,00	2658,95	4594,34	57,87

Table 1. Analysis results

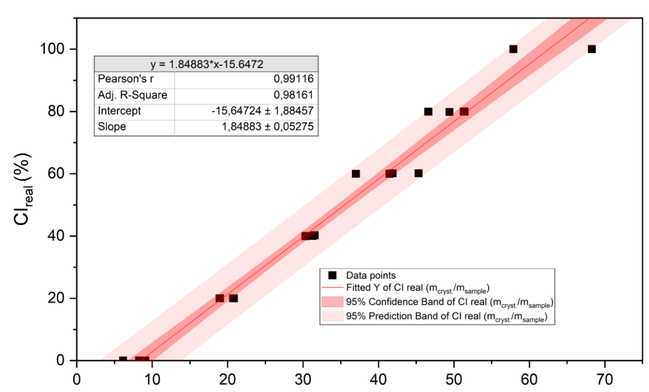

Fig. 2. Calibration curve

CONCLUSION

The determination of the real degree of crystallinity of a substance from a powder diffractogram is a powerful analytical tool for analyzing a substance. Due to the existence of a linear relationship between the imaginary ($CI_{XRD.\ est.}$) and real degree of crystallinity (CI_{real}) parameter, the calibration curve can be plotted using only two points corresponding to the absolutely amorphous and absolutely crystalline states of the substance

FUTURE WORK / REFERENCES

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2.Zhu, X. R., Wang, C. M., Fu, Q. B., Jiao, Z., Wang, W. D., Qin, G. Y., & Xue, J. M. (2015). Preparation of Ag/Cu Janus nanowires: electrodeposition in track-etched polymer templates. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 356, 57-61.

3.Cherkashina, N. I., Pavlenko, V. I., Domarev, S. N., & Kashibadze, N. V. (2023). Effect of a Tetraethoxysilane Hydrolysis Reaction Catalyst on the Precipitation of Hydrolysis Products in the Pores of a Polyimide Track Membrane. ChemEngineering, 7(2), 32.