Available online at www.sciencedirect.com
ScienceDirect
Materials Letters 62 (2008) 2084–2087
materials letters
www.elsevier.com/locate/matlet

Temperature anomalies of DEA–$CuCl_4$ and TEA–$CoCl_2Br_2$/PMMA nanocomposites

M. Piasecki [a], P. Bragiel [a], S. Tkaczyk [a], I.V. Kityk [a,*], J. Ebothe [b], V. Kapustianyk [c], M. Partyka [c], V. Rudyk [c], K. Nouneh [d], A.H. Reshak [e]

[a] *Institute of Physics, J.Dlugosz University Czestochowa, Poland*
[b] *Laboratoire LTME, Universite de Reims, France*
[c] *Low Temperature Physics Department, Lviv University, Ukraine*
[d] *Technological Center of Kyoto University, Japan*
[e] *Institute of Physical Biology-South Bohemia University, Institute of System Biology and Ecology-Academy of Sciences – Nove Hrady 37333, Czech Republic*

Received 18 September 2007; accepted 8 November 2007
Available online 17 November 2007

Abstract

Phase transitions were studied for the new synthesized ferroic $(NH_2(C_2H_5)_2CuCl_4$ (DEA–$CuCl_4$) and $(NH_2(C_2H_5)_4CoCl_2Br_2$ (TEA–$CoCl_2Br_2$) nanocrystallites (NC) incorporated into polymer matrices. Comparison with the bulk crystals is performed. A giant temperature shift (from 305.1°C to 360.3°C) of onset temperature for TEA–$CoCl_2Br_2$ nanoparticles after their incorporation into the PMMA matrix was found and is substantially larger compared to the DEA–$CuCl_4$. The DSC analysis shows that the temperature of phase transition is crucially dependent on the thermocycling and temperature rate. The principal role of the nano-sized effects is shown.

Keywords: Ferrolectrics; Phase transitions

The single crystals of diethylammonium tetrachlorcuprtate $(NH_2(C_2H_5)_2CuCl_4$ (DEA-$CuCl_4$) (space group $P2_1/n$ $a = 7.36$A; $b = 15.025$A; $c = 45.193$A) cause substantial interest due to the high sensitivity of the $CuCl_4$ clusters to the surrounding environmental background. It was established that the phase transitions observed at 311–330K are dependent on the local environment of crystallites. We have observed substantial shift of the phase transition temperature for the 10nm DEA–$CuCl_4$ NC in the polymer PMMA matrices compared to the bulk materials. This is related to manifestation of the nano-sized effects in the investigated nanocomposites. The origin of the phenomenon is discussed within a framework of existed nano-confined models. Different regime of cooling-heating cause different features of the phase transitions. Got comparison we will give the same temperature measurements for the $(NH_2(C_2H_5)_4CoCl_2Br_2$ (TEA–$CoCl_2Br_2$) nanocrystallites (NC) incorporated into PMMA matrices.

Following the Figs. 1, 2, 3 and 4 one can see substantial shift of the DSC maxima after incorporation the investigated NC into the PMMA matrix. A giant temperature shift (from 305.1°C to 360.3°C) of onset temperature for the TEA–$CoCl_2Br_2$ nanoparticles after their incorporation into the PMMA matrix was found. The observed shift is substantially larger compared to the DEA–$CuCl_4$ composites compare the Fig. 4 and Figs. 1, 2 and 3. The onset temperature for DEA–$CuCl_4$ compound is shifted from 47.2°C for the pure crystallites up to the 53.6°C for the composites. The obtained results unambiguously show that principal role here play the interface borders separating the nanoparticles and the polymers. Because the temperature heating rate is the same these results may indicate on principal role of the nanointerfaces NC-polymer on the observed features of the DSC. It is crucial to emphasize that due to the incorporation of the nanocrystallites into the polymer matrices the

* Corresponding author.
E-mail address: i.kityk@ajd.czest.pl (I.V. Kityk).

0167-577X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2007.11.024

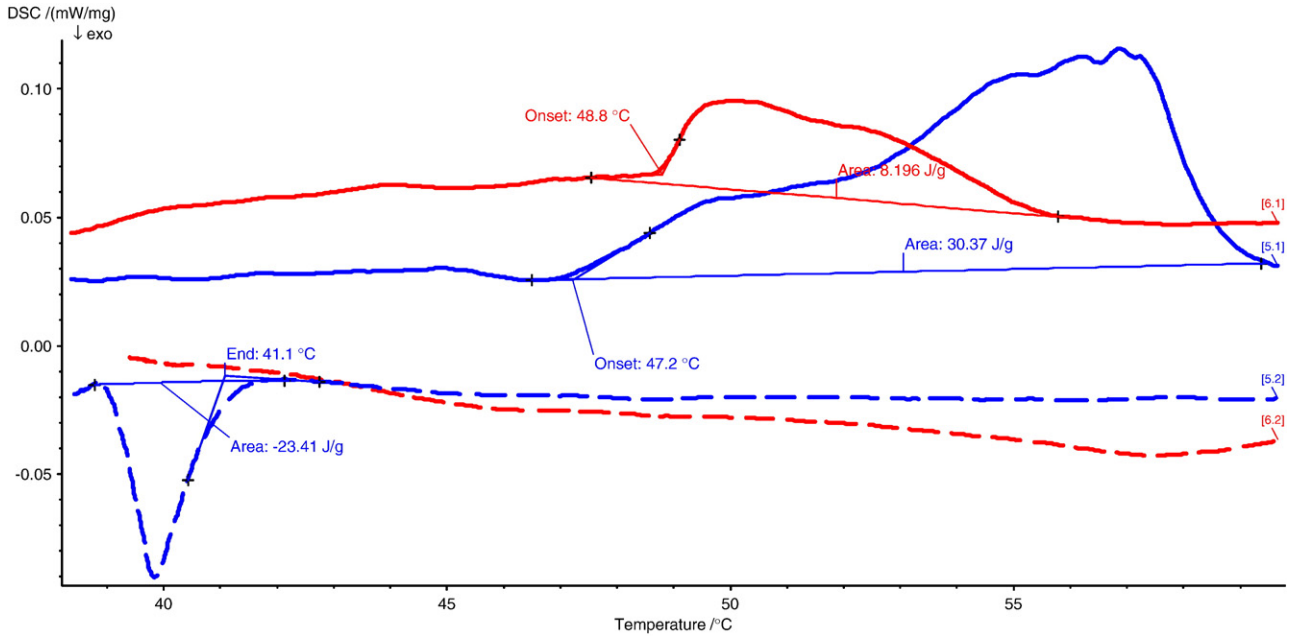

Fig. 1. Temperature dependence of the DSC for bulk DEA–$CuCl_4$: red line — first cycle of the heating–cooling (dotted), blue line — second cycle. Temperature rate 0.3 K/min. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

principal bonds on the borders separating the nanocrystallites and the polymer matrices will be in different external electric field, which leads to the observed temperature shift of the phase transformations [1]. Moreover, the temperature range of the phase transformation is decreased. At lower NC content the temperature shift is lower which confirms principal role of the chemical bonds in the observed phase transitions. Particular role belongs here to the near-the surface state dipole moments which may change both temperature of the phase transformations as well as the transition dipole moments [2]. One can not exclude

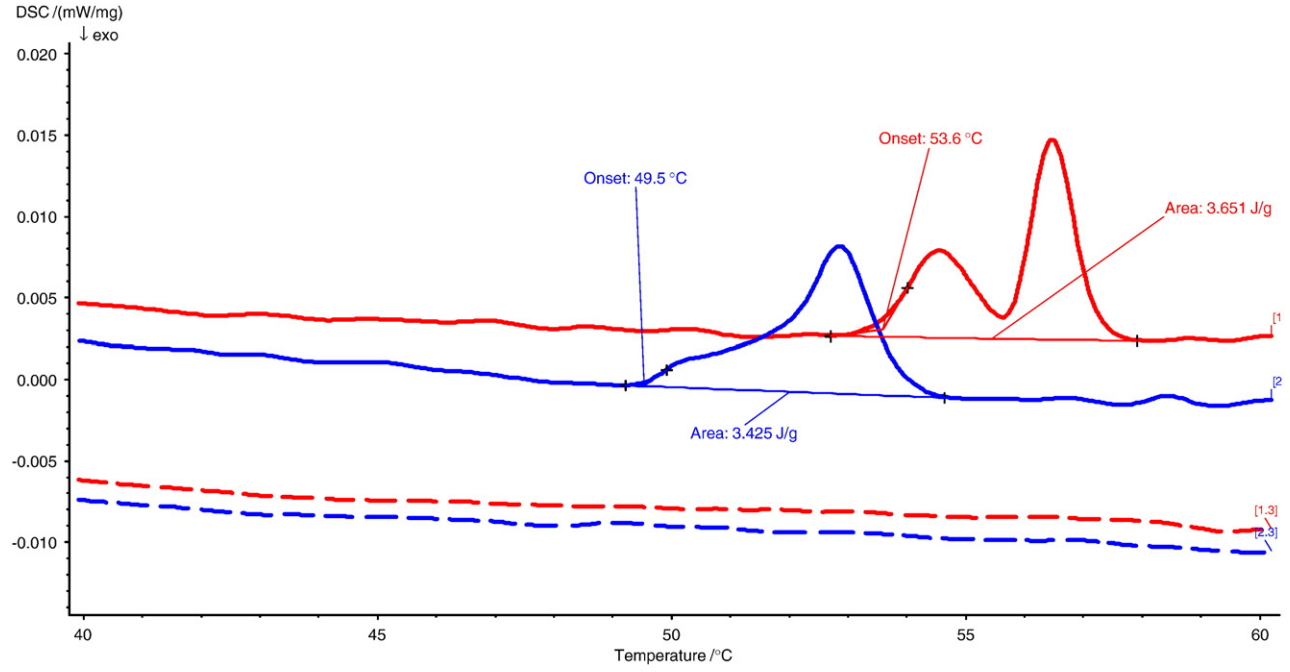

Fig. 2. Temperature dependence of the DSC for 20% DEA–$CuCl_4$/PMMA composites: red line — first cycle heating-cooling (dotted), blue line — second cycle. Temperature rate 0.3 K/min. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)