Pickering emulsion templated porous nanocomposites: thermal behaviour of polymer at the interface

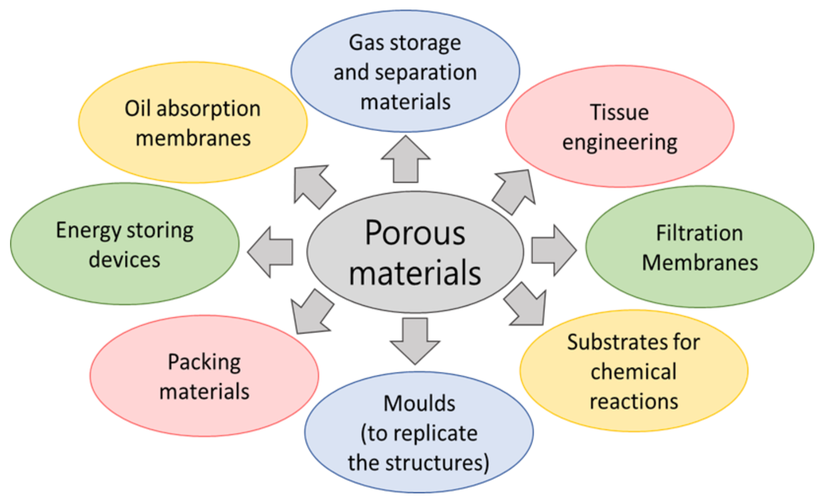
Meenal Agrawal[1] and Rajiv K. Srivastava[1*]

[1]Department of Textile and Fiber Engineering, Indian Institute of Technology Delhi, New Delhi-110016, India

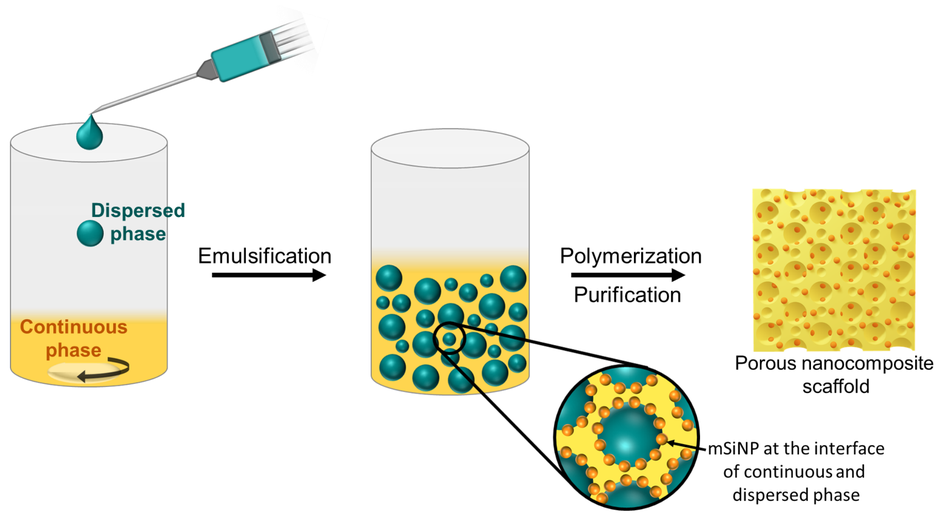
Email: meenal.bhl@gmail.com

Objective

During the past many decades, porous polymers have been used for various applications like catalysis, absorption, drug delivery, tissue engineering, etc. For these applications, thermal behaviour of a material plays a crucial role affecting the material properties. However, the effect of porosity on the thermal properties of porous polymers has scantly been reported. Addressing this, porous polymer constructs of poly(ε-caprolactone) (PCL) were developed using Pickering emulsion templating and the thermal behaviour of resulting constructs was studied under non-isothermal conditions using various models namely Jeziorny, Ozawa, and Mo model. Further changes in the crystalline structure of polymer were also observed using x-ray diffractometer (XRD).

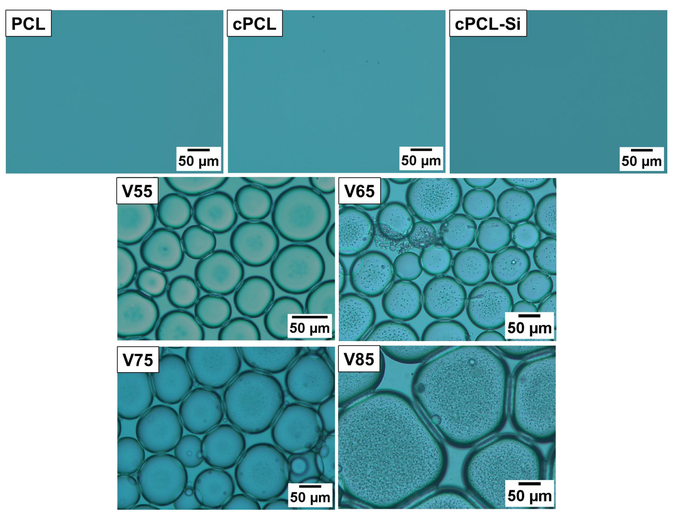


Fabrication of porous construct

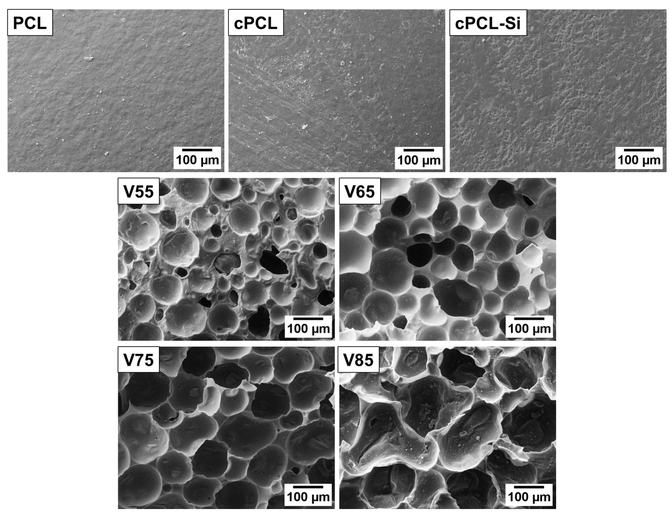


Results

Optical microscopy

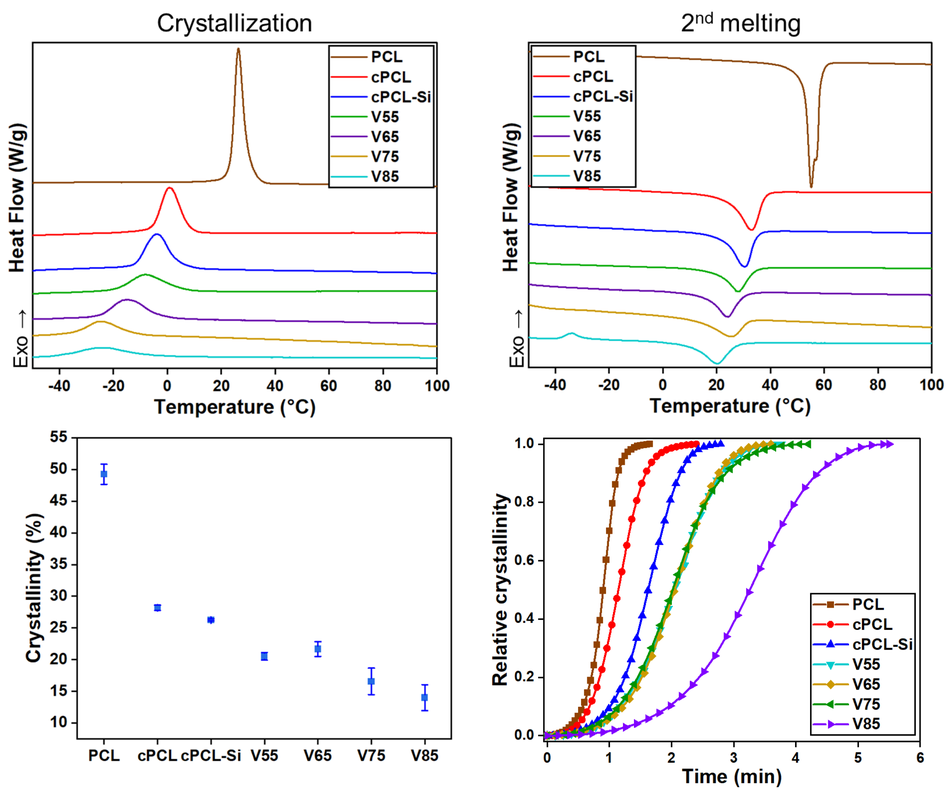


Scanning electron microscopy



Thermal characterization of PCL constructs

DSC thermograms recorded at 10 °C/min



Jeziorny model

$$X_t = 1 - e^{-k_t t^n}$$

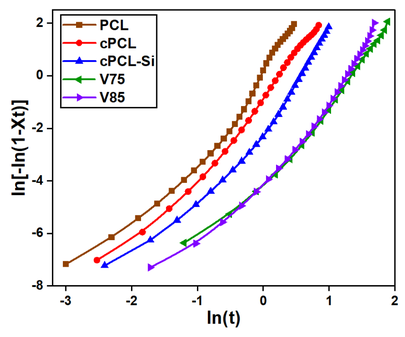
X_t is relative crystallinity at time t, k_t is rate constant, and n is Avrami exponent.

Double logarithmic form of equation:

$$ln[-ln(1 - X_t)] = n\,ln(t) + ln(k_t)$$

$$lnk_c = \frac{lnk_t}{\beta}$$

β is cooling rate, *i.e.* 10 °C/min

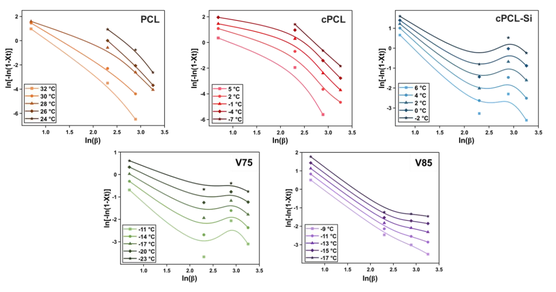


Sample Id	Regime 1			Regime 2			Regime 3		
	n_1	k_{c1}	R^2_1	n_2	k_{c2}	R^2_2	n_3	k_{c3}	R^2_3
PCL	2.17	0.87	0.993	5.05	1.02	0.997	3.11	1.04	0.996
cPCL	2.36	0.85	0.996	3.58	0.91	0.998	2.75	0.96	0.993
cPCL-Si	2.13	0.76	0.996	4.25	0.79	0.999	-	-	-
V75	1.96	0.73	0.999	3.36	0.76	0.998	3.00	0.79	0.993
V85	2.32	0.67	0.995	4.10	0.59	0.999	-	-	-

Ozawa model

Double logarithmic form of equation:

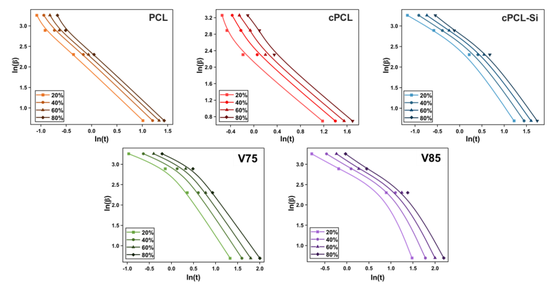
$$ln[-ln(1 - X_T)] = m\,ln(\beta) + lnK[(T)]$$



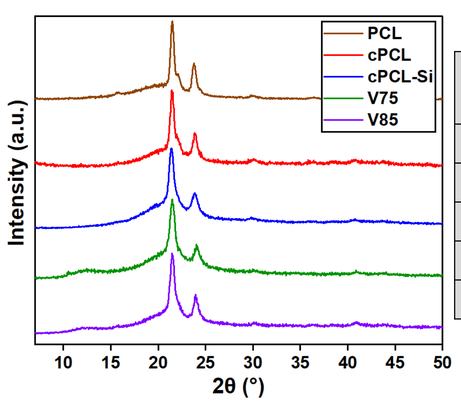
Mo model

Double logarithmic form of equation:

$$nlnt + ln(k_t) = ln[K(T)] - mln(\beta)$$

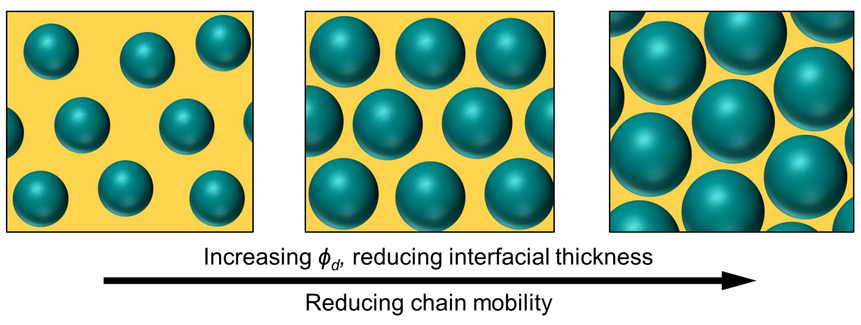


XRD results



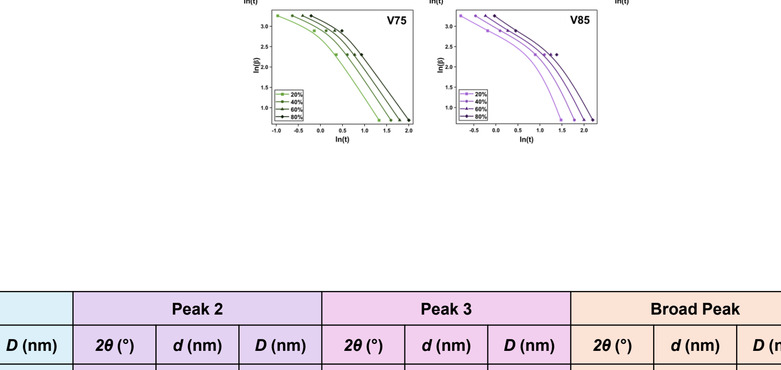
Sample Id	Peak 1			Peak 2			Peak 3			Broad Peak		
	2θ (°)	d (nm)	D (nm)	2θ (°)	d (nm)	D (nm)	2θ (°)	d (nm)	D (nm)	2θ (°)	d (nm)	D (nm)
PCL	21.5	0.4	23.2	22.1	0.4	23.2	23.8	0.4	18.0	-	-	-
cPCL	21.5	0.4	20.7	21.7	0.4	7.2	23.9	0.4	14.4	-	-	-
cPCL-Si	21.4	0.4	17.1	21.5	0.4	7.0	23.9	0.4	11.3	-	-	-
V75	21.5	0.4	12.7	-	-	-	24.1	0.4	12.8	12.9	0.7	1.7
V85	21.5	0.4	13.6	-	-	-	24.0	0.4	15.2	13.2	0.7	1.6

Hypothesis



Conclusions

- Pickering emulsion templating successfully led to the formation of porous constructs with different porosity by varying dispersed phase volume fraction.
- The resulting porous constructs demonstrated significantly diminished crystallization temperature and crystallinity percentage.
- Jeziorny model indicated a 3 regime crystallization along with 3D crystal growth stating the absence of confined crystallization.
- Significant deviation from linearity in Ozawa and Mo models concluded complex crystallization which couldn't be explained from currently used models.
- Absence of (111) crystal plane along with a new broad peak at 12.23° confirmed significant changes in crystal structure of porous constructs at higher porosity.



References

1. Agrawal M., et al. (2024). Langmuir, 40(9), 4893-4903.
2. Agrawal M., et al. (2023). Int. J. Pharm., 633(2), 122611.
3. Agrawal M., et al. (2020). Chem. Comm., 56(83), 12604-12607.

Acknowledgement

1. Central Research Facility, IIT Delhi
2. Industrial Research and Development Unit, IIT Delhi