

Integration methods for thermosensitive gel systems in garments

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Abstract. Humans live and work under severe thermophysiological conditions, which are characterized by extreme temperatures and humidities. Furthermore, additional burdens can arise from physical activities of the human body or the work conditions (resulting in psychological stress) [1]. The thermoregulation of the human body compensates such situations and maintains the core body temperature at 37°C (98,6 °F). The currently used systems for supporting human thermoregulation, such as PCM-equipped surface structures or mobile water-based cooling units have the disadvantage that the running cooling process is neither switchable nor reversible. Another promising possibility for a personal cooling is the use of temperature-dependent superabsorbers (so-called LCST and UCST) in garments, which absorb the human sweat and transmit it to the environment by evaporation. Cooling during evaporation results in heat transfer from the human body.

1. Introduction

Under extreme environmental conditions (cold store or fires) or high humidity (jungles) the body's own thermal regulation mechanisms are only partially able to compensate the performance-reducing effects of the environment. The comfort zone of humans is between 17°C - 25°C (62,6°F – 77°F) with a relative humidity between 32% - 70% (for naked bodies) (see Figure 1). In addition to these environmental situations, the physical activities under these conditions causes further burdens on the thermoregulation process.

The possibilities of insuring the safety of people, who must work under these conditions are based on the circumstance that the temporal thermal impact of extreme condition are limited. In some cases, however, it is possible that these time limits may be exceeded or that these cannot be met due to the circumstances. Such conditions are often found by firefighters, police or athletes. Another way of protecting people under these adverse environmental conditions is the active cooling / heating of their immediate environment. These systems, such as air conditioning, heaters or phase change materials, are able to absorb thermal energy from bodies over a longer period of time. However, these options cannot be used by individuals as they can be very large, heavy and mostly non-reversible. In order to support groups of people working under extreme thermal conditions, thermoregulatory support is necessary, which can regulate the body temperature in a reversible and switchable manner. In addition to that, it is important that the thermal support system does not further influence its wearer, meaning for him it is comfortable.

In order to meet these requirements, the physical approach of evaporation was followed. By means of temperature-dependent superabsorbers, so-called LCST (Low Critical Solution Temperature) and UCST (Upper Critical Solution Temperature), which are incorporated into various textile surface structures, the thermoregulation of the human body can be supported. These LCST and UCST (see Figure 2) absorbers can absorb water at a set switching temperature. At this switching temperature, they change from a hydrophobic to a hydrophilic behavior (or vice versa). The LCST-gels always absorb water below their switching temperature and store it in their internal structure (hydrophilic behavior).



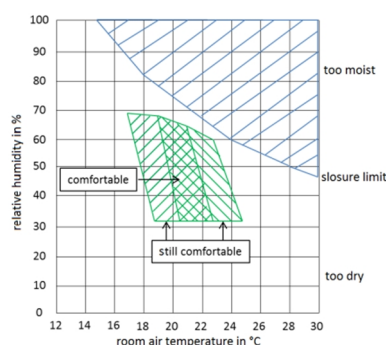


Figure 1. Comfort zone for the human body [2]

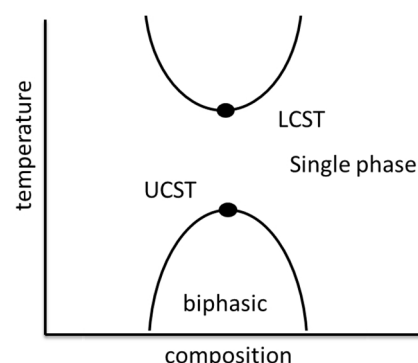


Figure 2. Phase diagrams with LCST and UCST [3]

Above the switching temperature, the LCST-gels release the stored water again and assume a hydrophobic behavior. The behavior towards water is different by the UCST-gels. It is the exact opposite of the LCST-gels, that's why the UCST-gels absorb water over their switching temperature and release it below it.

2. Research method and result

2.1. Development of gel systems with switching behaviour

The requirements of the LCST-gels and UCST-gels for their use in supporting the human thermoregulation are different. Important for subsequent use is the switching temperature, which should be between 35°C - 38°C (95°F – 100,4°F). They should include a relatively small range so that the phase transition can take place more specifically, so the gels achieve the desired effects. For the characterization of the microgels it is important to note the following feature: In the common literature, the phase transition of thermosensitive microgels is usually described with the volume phase transition temperature (VPTT). Thus, the temperature at which a significant volume change of the particles occurs is described. However, this does not clearly define whether the microgels shrink above a defined temperature, as would be the case for LCST-polymers, or swell as it happens with UCST-polymers. The switch between the various hydrostatic states must be reversible in order to ensure the functionality.

Furthermore, the degree of swelling should be large enough so that the microgels can absorb adequate amount of water (see Figure 3 and Figure 4), but small enough to minimize the tendency to agglomerate. The desired particle size of the non-swollen microgels should be as low as possible, this means less than 50 µm, since the diffusion rate during swelling and de-swelling depends considerably on the radius of the non-swollen microgels. The decisive factor for the investigations was the development of a robust manufacturing process, whereby two factors are particularly important. Firstly, the process must guarantee the reproducible synthesis of microgels with a stable switching temperature and secondly the production of sufficient sample quantities must be guaranteed.

For this purpose, two methods have been studied. The major part of literature uses precipitation polymerization to prepare LCST-microgels. The primary polymer poly-N-isopropylacrylamide (PNIPAM) used during research has a VPTT of 32°C (89,6°F) (see Figure 5). By mixing with other polymers such as poly-N,N dimethylacrylamide (PDMAAm), the VPTT could be increased to 37°C (98,6°F) and particle sizes of less than 1 µm could be produced (see Figure 6). The thermosensitive properties of these microgels can thus be determined by means of dynamic light scattering (DLS, see Figure 6). Ultimately, the preparation methodology had to be discarded by precipitation since insufficient amounts of LCST-microgel could be generated. In addition to precipitation polymerization, microgels can also be synthesized by means of inverse emulsion polymerization. In synthetic principle, microgels are produced from dispersed water droplets which contain monomer, cross-linker and initiator.

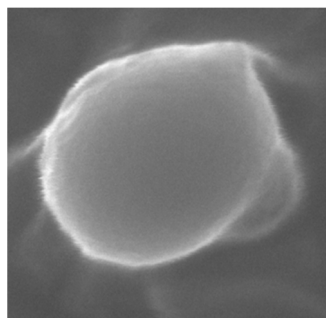


Figure 3. Initial state of the microgel

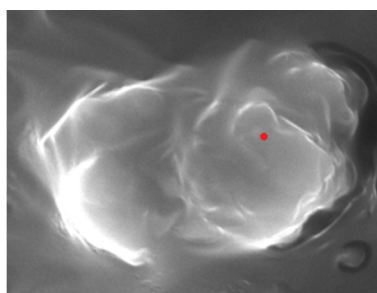


Figure 4. Microgel with absorbed water, the red mark symbols the size of the initial state of the microgel

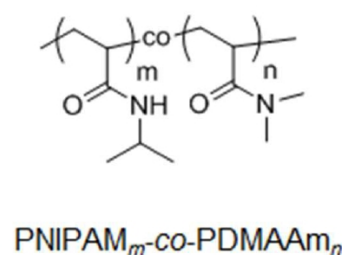


Figure 5. Chemical structure of the synthesized microgels PNIPAM_m-co-PDMAAm_n, where *m* and *n* are the molar proportions of PNIPAM and PDMAAm.

The aqueous phase is thereby dispersed in a hydrophobic solvent (e.g. cyclohexane, dodecane, paraffin), a mixture of emulsifiers (e.g. Span, Tween) being added for stabilization. This usually leads to particle sizes > 1 μm, therefore the polymerization temperature has to be chosen below the VPTT, since otherwise a precipitation polymerization takes place in the water droplets. If the polymerization is then initiated, the water droplets completely crosslink and form microgels.

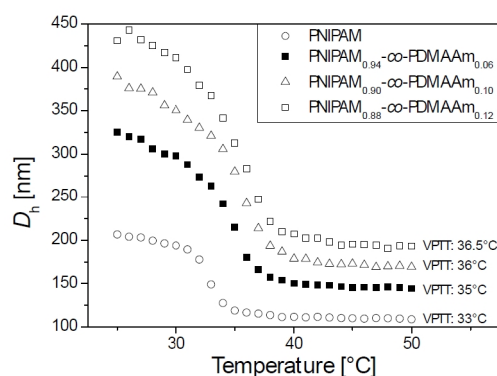


Figure 6. Representative results of dynamic light scattering for PNIPAM and a series of PNIPAM_m-co-PDMAAm_n microgels with 6, 10 and 12 mol% PDMAAm. The hydrodynamic diameter is applied D_h as a function of the temperature.

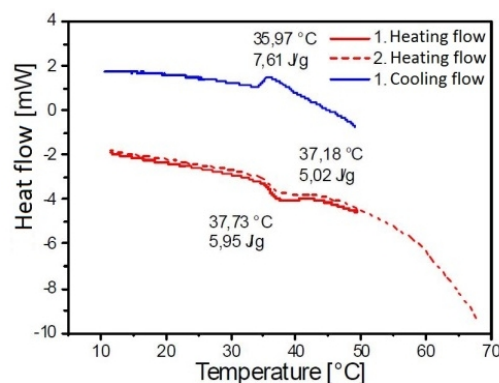


Figure 7. Representative results of the DSC measurement for PNIPAM_{0.86}-Co-PDMAAm_{0.14} (0.25% BIS).

In contrast to the microgels produced by the precipitation polymerization and having particle sizes between 200 nm - 400 nm, the microgels obtained by the inverse emulsion polymerization are significantly larger and broader. By increasing the experimental reactor, 250 g of LCST-microgels could finally be produced per production. However, this led to process-typical problems such as increased production times and process uncertainties. Irrespective of the production method, the developed LCST-microgels showed a pronounced switching behavior at a temperature of 37°C (98.6°F) and a small particle size, so they are suitable in the use as a thermoregulation system in garments.

In addition to the development of LCST-microgels exhibiting water-releasing properties, another objective was to produce microgels exhibiting water-absorbing properties at temperature elevation, the UCST-microgels. The observed pathways showed that the UCST-microgels are difficult to analyze than the LCST-microgels. Two manufacturing methods have also been tested to produce reliably switchable UCST-microgels in large quantities.

The first manufacturing test for UCST-microgels was carried out by the generation of interpenetrating networks (IPN) based on polyacrylamide and polyacrylic acid. The networks are generated by a two-step inverse emulsion polymerization. The composition of the networks were tested with several variations in production. The thermosensitive properties of the IPN particles were characterized by DSC (differential scanning calorimetry) and rheological methods. The summary results show that the IPN-microgels swell continuously over a wide temperature range. This means that no clearly defined switching temperature could be detected, which is inappropriate.

The second preparation approach was based on the development of microgels based on sulfobetaines. These investigations were initiated because homo- and copolymers of this monomer class are known to have thermosensitive properties which can be systematically influenced. The experiments and subsequent investigations showed that the UCST-microgels have a reversible switching behavior with a switching temperature between 36°C and 37°C (96,8°F and 98,6°F). However, the swelling behavior is very difficult to describe and determine. For the further investigation only the produced LCST-gels are considered for functional thermoregulation material in garments.

2.2 Characterization of textile functional materials

For the textile functional material it is necessary that their thermoregulation behavior is also provided under stress conditions. The textile materials should have sufficient strength and extensibility so that they can be used in garment systems. Furthermore, the textile materials must be open-pored, so that water vapor can permeate the microstructure and fill them. Furthermore, the materials must be a porous structure so that the microgels can also store sufficient water. Unfortunately such a porous structure can lead to a noticeable release of microgels during stress conditions, which is hardly to prevent. Foam foils based on polyurethane and polyvinylchloride are suitable for the thermosensitive microgels as a carrier material because of their chemical adjustable inner volume.

The disadvantage of the foam foils are that the tensile strength and elongation is too low (see Figure 8 and Figure 9) for the apply in clothing. Due to this behavior the equipped foam foils have been joint with classical textile materials to reduce the mechanical stress on the foam foils. Furthermore, the foam foils must have a certain thickness so that the microgels can have sufficient volume for swelling. However, as the thickness increases, flexural stiffness rise considerably, which doesn't match normal requirements of sportswear. In addition, the use and combination of the foam foils with the equipped microgels resulted in a very pronounced behavior towards water (see Figure 9).

Since the foam foils were equipped with only LCST-microgels with a switching temperature of 37°C (98,6°F), they swelled continuously until they were fully filled. It should be noted that the amount of absorbed water in the microgels depend on the available moisture in the room and the local surface texture of the carrier material. The absorbed water in the microgels influences the mechanical properties of the foam foils considerably. Swollen foam foils show a significant higher elongation and a different tensile strength behavior than unfilled foam foils.

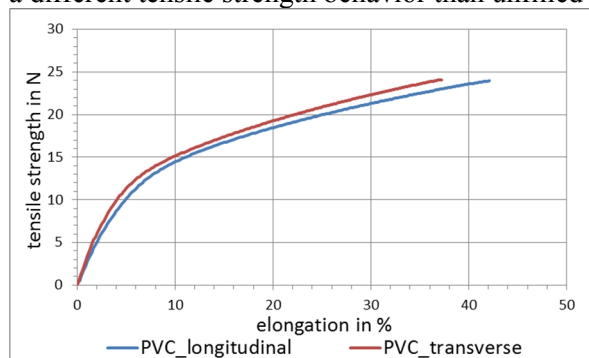


Figure 8. Tensile strength behavior of PVC-based foam foils in longitudinal and transverse direction

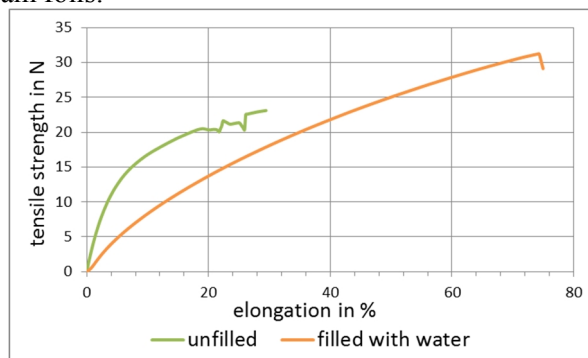


Figure 9. Tensile strength behavior of water filled and unfilled foam foils

2.3 Structure and function of the thermocouples

The first design of the thermocouple (see Figure 10) for the application of the LCST- and UCST-microgels was a multilayer structure of porous textiles (e.g. non-woven fabrics) equipped with LCST- and UCST-microgels. The design ensures theoretically an efficient cooling as well as it prevents the subject of undercooling. However, this design could not be further pursued because the swelling behavior of the microgels could not be sufficiently controlled.

The swelling microgels formed gelatinous structures in which swollen and non-swollen microgel-particles coexisted. Furthermore the swelling is differently pronounced and took place in diverse parts of the textile carrier material. Further challenges occur due to the discharging of water. Since the water is not evenly distributed and stored equally in the microgels, it diffuses with different rates to the surrounding. The direct result of this process is an odor development and a mold growing in the affected areas. It was shown by the fact that it is necessary to design a connection and a separation of the microgels. This has been realized by foam foils.

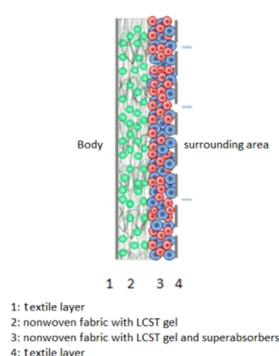


Figure 10. First design of the layer for the thermocouples

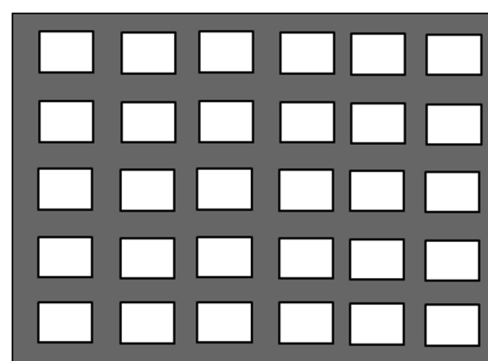


Figure 11. Structural principles for the application of the LCST-equipped PVC foam foils (white) in the non-woven fabric (grey)

For an improved water distribution the available surface of foam foils was increased by subdividing the foam foils into 10mm x 10mm pieces (schematic illustration, see Figure 11, real representation, see Figure 12). A polyester-based nonwoven fabric has been selected as a textile carrier material. The joining between the gel-equipped foam foils and the non-woven fabric has been realized by suitable adhesives. The produced non-woven inserts have been integrated into various sportswear garments, e.g. on the chest of a functional shirt (see Figure 13). The function tests were carried out by test persons on the treadmill, with a running time of 30 min and a subsequent regeneration time of 10 min. The cooling effect of the microgels was confirmed by the subjects.

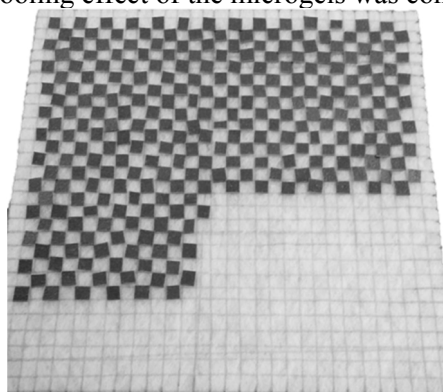


Figure 12. Patterns of microgel-equipped foam foils for use in sport shirt



Figure 13. Functional shirt made of PES with equipped foam foils on the chest

To assure this subjective evaluation, the material combinations were examined thermodynamically by the Hohenstein Institutes, whereby the cooling effect could be confirmed as well.

3. Conclusion

It was demonstrated that the thermosensitive microgel-equipped foam foils applied in sportswear can support the human thermoregulation. The used LCST-microgels can be synthesized on a large scale and have a swellable behavior even above a relative humidity of 90% (in powder form). The investigations have been carried out with pure water, but the assumption is that the experiment with electrolytic water must lead to the same results. The change from hydrophilic to hydrophobic behavior (or vice versa) of the microgels is precisely adjustable with a variable definable switching temperature.

The production and testing of UCST microgels occurs as a great challenge and requires further intensive investigations. The challenge is the detection of the temperature-dependent swelling behavior of the UCST-microgels. The used detection methods were not reliable, therefore new methods have to be developed especially for UCST-gels.

The developed temperature-dependent microgels has be integrated into a carrier system in order to ensure an optimal swelling behavior without clumping and additionally to improve the durability against external influences. As a carrier system, non-woven fabrics are less suitable since they can't prevent the formation of clumps. The integration of the LCST-gels in foam foils is more encouraging and can be used in combination with textile carrier systems. The foam foils have a sufficient accessible surface so that the water can permeate and is porous enough not to hinder the swelling capacities of the LCST-microgels. A filling degree of 60 percent by mass was achieved. The combination with a textile carrier system also increases the resilience to mechanical influences. However, the use of small foam foil patches integrated in a chamber structure is preferable, because the strength of the compound and the available surface area increases.

Despite the difficulties, a garment for sport applications was made with a mixture of 30% LCST-microgel and 30 percent superabsorber to study the effect of thermoregulatory support. The cooling effect of the absorber mixtures was confirmed by subjective evaluation of test persons and thermodynamic simulations.

Acknowledgment

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